

SYNTHESIS, CHARACTERIZATION AND  
CATALYTIC APPLICATIONS OF TANTALUM AND  
NIOBIUM ALKYL, ALKYLIDENE AND OLEFIN COMPLEXES

by

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CATALYTIC APPLICATIONS OF TANTALUM AND  
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ABSTRACT

Chapter 1

Compounds of the type  $Ta(CH_2R)_4X$  where  $X = Cl, OMe_3$ , alkyl decompose by  $\alpha$ -hydrogen abstraction to give the corresponding alkylidene complex,  $Ta(CHR)(CH_2R)_2X$ . Details of the  $\alpha$ -hydrogen abstraction mechanism are reported for some alkylidene complexes of this type. Reactions of electrophiles with these species show similarities to those found for phosphorous ylides, i.e. the alkylidene  $\alpha$ -carbon atom is nucleophilic.

Chapter 2

The preparation and characterization of octahedral alkylidenes, olefin complexes, and their substituted analogues of the type  $M(R)X_3L_2$  (where  $M = Nb$  or  $Ta$ ,  $X =$  halide, alkyl, or alkoxide and  $L =$  alkyl or aryl phosphine) are described. Structural assignments, based upon spectroscopic data, are also reported for these species. Substitution of one ethyl group for a halide ligand in  $Ta(CHCMe_3)Cl_3(PMe_3)_2$  yields a mixture of the two equilibrating species,  $Ta(CHCMe_3)(C_2H_5)Cl_2(PMe_3)_2$  and  $Ta(CH_2CMe_3)(C_2H_4)Cl_2(PMe_3)_2$ . A reversible  $\beta$ - and  $\alpha$ -hydrogen transfer via the intermediate,  $Ta(CHCMe_3)(C_2H_4)(H)Cl_2(PMe_3)_x$ , is suggested as a mechanism for this process. Stoichiometric reactions of phenyl-substituted olefins with *t*-butoxide neopentylidene complexes yields a new benzylidene species, by olefin metathesis. These stoichiometric reactions indicate that an alkylidene complex functions as the chain carrier in the olefin metathesis reaction.

### Chapter 3

Attempts to trap the product formed in the decomposition of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  with  $\text{PMe}_3$  gave  $\text{Ta}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$ . Reaction of this product with alkyl lithium reagents gives the analogous alkyl-bisneopentylidene complex. A single crystal X-ray structure of  $\text{Ta}(\text{CHCMe}_3)_2(\text{mesityl})(\text{PMe}_3)_2$ , performed by Churchill, shows it to be a trigonal bipyramid containing axial  $\text{PMe}_3$  ligands and two planar equatorial neopentylidene ligands pointing in the same direction. Structurally analogous ethylene compounds of the type  $\text{Ta}(\text{L})(\text{C}_2\text{H}_4)\text{R}(\text{PMe}_3)_2$  (where  $\text{L} = \text{CHCMe}_3, \text{C}_2\text{H}_4$ ;  $\text{R} = \text{CH}_2\text{CMe}_3, \text{C}_2\text{H}_5$ ) were also prepared. NMR studies show that the ethylene ligand(s) is(are) bonded in the equatorial plane aligned parallel to the  $\text{PMe}_3\text{-Ta-PMe}_3$  axis. In most cases analogous niobium complexes also could be prepared and are believed to be of similar structure as their tantalum counterpart.

### Chapter 4

$\text{Ta}(\text{III})$  neopentyl complexes rearrange to form  $\text{Ta}(\text{V})$  neopentylidene-hydrides. The stability of Ta in the +5 oxidation state is believed to be the driving force for this reaction. Several novel species are obtained from the two electron reduction of  $\text{Ta}(\text{V})$  neopentyl compounds. These include;  $\text{Ta}(\text{CHCMe}_3)(\text{H})\text{Cl}_2(\text{PMe}_3)_3$  and  $[\text{Ta}(\text{CHCMe}_3)\text{Cl}(\text{PMe}_3)_2]_2(\text{N}_2)$ . In the  $\alpha$ -hydrogen elimination reaction in which  $\text{Ta}(\text{CHCMe}_3)(\text{H})\text{Cl}_2(\text{PMe}_3)_3$  is formed, labeling studies show that the hydride bonded to the metal arises from the  $\alpha$ -carbon atom of the neopentyl ligand in the starting complex (i.e.  $\text{Ta}(\text{CH}_2\text{CMe}_3)\text{Cl}_4$ ). In addition, the synthesis and characterization of  $\text{Ta}(\text{III})$  halide complexes are also discussed.

### Chapter 5

$\text{Ta}(\text{C}_2\text{H}_4)_2\text{Bu}^n(\text{PMe}_3)_2$  selectively catalyzes the dimerization of ethylene to 1-butene. It is the end product obtained from the reaction of ethylene with bisneopentylidene complexes of the type  $\text{Ta}(\text{CHCMe}_3)_2\text{R}(\text{PMe}_3)_2$ , only if R is neopentyl or ethyl. If R is Cl then  $\text{Ta}(\eta\text{-C}_4\text{H}_6)(\text{C}_2\text{H}_4)\text{Cl}(\text{PMe}_3)_2$  is formed instead, which is not an active catalyst. Ultimately, the resultant products are believed to form via a metallacyclopentane intermediate. The reactions of ethylene with  $\text{Ta}(\text{CHCMe}_3)_2\text{R}(\text{PMe}_3)_2$  are believed to proceed by a stepwise loss and replacement of the neopentylidene ligand with ethylene.  $\text{Nb}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$  reacts with ethylene to give  $\text{Nb}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  which is not a dimerization catalyst since it cannot form a metallacyclopentane complex.  $\text{Nb}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  reacts with ethylene to give  $[\text{Nb}(\text{C}_2\text{H}_4)\text{Cl}(\text{PMe}_3)_3]_x(\text{N}_2)$ , the first dinitrogen complex of niobium. The analogous tantalum complex can be prepared by the two electron reduction of  $\text{trans,mer-Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  under  $\text{N}_2$ .

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ABBREVIATIONS USED IN TEXT

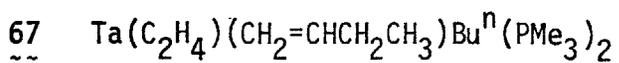
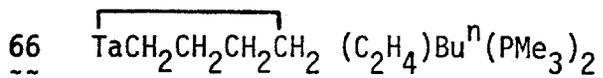
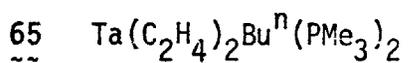
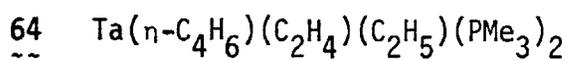
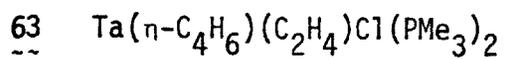
Bu <sup>n</sup>	n-butyl
t-Bu	tertiary-butyl
C <sub>α</sub>	alpha carbon, directly bonded to metal
C <sub>β</sub>	beta carbon, directly bonded to C <sub>α</sub>
Cp	C <sub>5</sub> H <sub>5</sub>
d	doublet
dd	double doublet
diox	1,4-dioxane
EPR	electron paramagnetic resonance
Et	ethyl
GLC	gas-liquid chromatography
HMDS	hexamethyldisiloxane
IR	infrared
L	ancillary ligands (usually PMe <sub>3</sub> )
Me	methyl
NMR	nuclear magnetic resonance
Np	neopentyl
Ph	phenyl
Pr <sup>n</sup>	n-propyl
q	quartet
s	singlet
t	triplet
THF	tetrahydrofuran
THT	tetrahydrothiophene
TMS	tetramethylsilane
{ <sup>1</sup> H}	proton-decoupled

List of Compounds

- 1 Ta(CHCMe<sub>3</sub>)(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>
- 2 Nb(CHCMe<sub>3</sub>)(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>
- 3 Ta(CH<sub>2</sub>Ph)<sub>5</sub>
- 4a Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>Cl[O(Me)C=CHCMe<sub>3</sub>]
- 4b Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>Cl[O(Ph)C=CHCMe<sub>3</sub>]
- 5 Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>(OPh)[O(Ph)C=CHCMe<sub>3</sub>]
- 6a Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>[N(Me)C=CHCMe<sub>3</sub>]
- 6b Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>[N(Ph)C=CHCMe<sub>3</sub>]
- 7 Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>4</sub>Cl
- 8 Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>
- 9 "Ta(CHCMe<sub>3</sub>)(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>Cl"
- 10 Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>Cl[N(Me)C=CHCMe<sub>3</sub>]
- 11 TaCp(CHCMe<sub>3</sub>)(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>
- 12 Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>Cl[N=C(Me)CH<sub>2</sub>CMe<sub>3</sub>]
- 13 Nb(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub> [N(Me)C=CHCMe<sub>3</sub>]
- 14 Nb(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>Cl[O(Me)C=CHCMe<sub>3</sub>]
- 15 Ta(CH<sub>2</sub>Ph)<sub>3</sub>[N(Me)C=CHPh]
- 16 Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>(OCMe<sub>3</sub>)<sub>2</sub>
- 17 Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>Cl(OCMe<sub>3</sub>)
- 18 Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>(OCMe<sub>3</sub>)
- 19 Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>4</sub>(OCMe<sub>3</sub>)
- 20 Ta(CHCMe<sub>3</sub>)(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>(OCMe<sub>3</sub>)
- 21 Ta(O)(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>(OCMe<sub>3</sub>)
- 22 Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub>
- 23 Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub>(PMe<sub>3</sub>)
- 24 Ta(CHCMe<sub>3</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>
- 25 [Ta(CHCMe<sub>3</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)]<sub>2</sub>

- 26 Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>
- 27 [Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>L]<sub>x</sub>; L = PMe<sub>3</sub>; PPr<sub>3</sub><sup>n</sup>
- 28 Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>(PMe<sub>2</sub>Ph)L; L = PMe<sub>3</sub>; PPr<sub>3</sub><sup>n</sup>
- 29 Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>
- 30 [NbCl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>
- 31 Ta(C<sub>2</sub>H<sub>4</sub>)(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub>
- 32 Ta(C<sub>2</sub>H<sub>4</sub>)(C<sub>2</sub>H<sub>5</sub>)Cl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>
- 33 [Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>(THF)<sub>2</sub>]<sub>x</sub>
- 34 Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)Cl<sub>2</sub>
- 35a Ta(CHCMe<sub>3</sub>)(C<sub>2</sub>H<sub>5</sub>)Cl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>
- 35b Ta(CH<sub>2</sub>CMe<sub>3</sub>)(C<sub>2</sub>H<sub>4</sub>)Cl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>
- 36 Ta(CHCMe<sub>3</sub>)(C<sub>2</sub>H<sub>4</sub>)(H)Cl<sub>2</sub>(PMe<sub>3</sub>)<sub>x</sub>
- 37a Ta(CHCMe<sub>3</sub>)(C<sub>2</sub>H<sub>5</sub>)Cl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>
- 37b Ta(CH<sub>2</sub>CMe<sub>3</sub>)(C<sub>2</sub>H<sub>4</sub>)Cl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>
- 38a Ta(CHCMe<sub>3</sub>)(C<sub>2</sub>H<sub>5</sub>)Br<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>
- 38b Ta(CH<sub>2</sub>CMe<sub>3</sub>)(C<sub>2</sub>H<sub>4</sub>)Br<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>
- 39 Ta(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)Cl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>
- 40 Ta(C<sub>2</sub>H<sub>4</sub>)(OCMe<sub>3</sub>)Cl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>
- 41a Ta(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)
- 41b Nb(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)
- 42a Ta(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub>
- 42b Nb(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub>
- 43 Nb(C<sub>2</sub>H<sub>4</sub>)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub>
- 44a Ta(CHPh)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)
- 44b Ta(CHPh)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub>
- 45a Nb(CHPh)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)
- 45b Nb(CHPh)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub>

- 46a  $\text{Ta}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$   
 46b  $\text{Nb}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$   
 47a  $\text{Ta}(\text{CHCMe}_3)_2\text{Me}(\text{PMe}_3)_2$   
 47b  $\text{Ta}(\text{CHCMe}_3)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$   
 47c  $\text{Ta}(\text{CHCMe}_3)_2\text{Bu}^n(\text{PMe}_3)_2$   
 47d  $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$   
 47e  $\text{Ta}(\text{CHCMe}_3)_2(\text{mesityl})(\text{PMe}_3)_2$   
 48  $\text{Ta}(\text{C}_5\text{H}_5)(\text{CHCMe}_3)_2(\text{PMe}_3)$   
 49  $\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_4)(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$   
 50a  $\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$   
 50b  $\text{Nb}(\text{CHCMe}_3)(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$   
 51a  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$   
 51b  $\text{Nb}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$   
 52  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{C}_2\text{H}_5)_3$   
 53  $\text{TaCl}_3(\text{PMe}_3)_3$   
 54  $[\text{TaCl}_3(\text{PMe}_3)_2]_2$   
 55  $[\text{Ta}(\text{CHCMe}_3)\text{Cl}(\text{PMe}_3)_2]_2(\text{N}_2)$   
 56a  $[\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2]_2(\text{N}_2)$   
 56b  $[\text{Ta}(\text{CHCMe}_3)\text{Me}(\text{PMe}_3)_2]_2(\text{N}_2)$   
 57a  $\text{Ta}(\text{CHCMe}_3)(\text{H})\text{Cl}_2(\text{PMe}_3)_3$   
 57b  $\text{Ta}(\text{CDCMe}_3)(\text{D})\text{Cl}_2(\text{PMe}_3)_3$   
 58  $\text{Ta}(\text{C}_5\text{Me}_5)(\text{CHCMe}_3)(\text{H})\text{Cl}(\text{PMe}_3)$   
 59  $[\text{Ta}(\text{CHCMe}_3)_2\text{H}(\text{PMe}_3)_2]_x$   
 60  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}(\text{PMe}_3)_4$   
 61a  $[\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}(\text{PMe}_3)_3]_x(\text{N}_2)$   
 61b  $[\text{Ta}(\text{C}_2\text{H}_4)\text{Br}(\text{PMe}_3)_3]_x(\text{N}_2)$   
 62  $[\text{Nb}(\text{C}_2\text{H}_4)\text{Cl}(\text{PMe}_3)_3]_x(\text{N}_2)$



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## INTRODUCTION

The catalytic reactions of olefins by transition metal complexes has received a great deal of attention during the past two decades. These catalytic reactions are important, especially industrially, because they represent some of the most economical ways to synthesize olefinic monomers or polymers or usable olefins from ones of little industrial value. The more common types of these transformation reactions are dimerization or polymerization of  $\alpha$ -olefins<sup>1</sup> and olefin metathesis.<sup>2</sup> The Shell Higher Olefins Process combines both of these catalytic systems to produce linear  $C_{10}$ - $C_{20}$   $\alpha$ -olefins from ethylene.<sup>3</sup> Such selectivity is uncommon for heterogeneous single catalytic systems.

In contrast, homogeneous catalysts are often highly selective. In these systems, it is frequently possible to vary the catalyst composition and thereby some of the structural features of the catalyst in a systematic fashion. The study of the influence of such modifications on the nature and the distribution of the products is an important method for improving the efficiency of a homogeneous catalyst. Such investigations often give important mechanistic information concerning the relationship between reactivity and the structure of the catalyst.

Recent discoveries by Schrock illustrate the influence ligand modification can have on catalyst activity. Metallacyclopentane complexes of the type  $(C_5R_5)X_2\overline{TaCH_2CHRCH_2}$  catalyze the dimerization of  $\alpha$ -olefins.<sup>4</sup> Simple changes in X cause large variations in the rate of dimerization. Rates increased in the order of alkoxide < Cl < Br.<sup>4b</sup> Apparently, metallacyclopentane complexes are stabilized toward  $\beta$ -elimination when a  $\pi$ -donor ligand such as alkoxide is present.

In general, halide replacement with alkoxides slows all decomposition pathways arising from an  $\alpha$ - or  $\beta$ -hydrogen abstraction. For systems which are poor dimerization catalysts for  $\alpha$ -olefins, such as  $M(\text{CHCMe}_3)\text{Cl}_3(\text{PMe}_3)_2$ , substitution of two chloride ligands with *t*-butoxides effectively stops rearrangement reactions from occurring from the incipient metallacyclobutanes. Instead, the lowest energy pathway is olefin metathesis.<sup>5</sup> Obviously, the ligand environment dramatically affects the electronic nature of the metal which in turn affects its reactivity. These factors which influence the formation of reactive intermediates, such as alkylidene and olefin complexes, form the basis of this research.

In this study of the reaction chemistry of Ta and Nb alkylidenes with olefins, a synthetic approach to the determination of catalytic intermediates is emphasized. Also of utmost importance is the elucidation of the structure and bonding of each class of compounds, and the effect of changes in electron density of the metal center on their reaction chemistry and catalytic activity.

Chapter 1

Characterization of Tantalum and Niobium  
Alkylidene Complexes and  
Their Mechanism of Formation

## Introduction

Transition metal alkyl complexes in which the alkyl contains 1 to 3  $\beta$  hydrogens, often vary in stability. A low energy pathway to the decomposition of these complexes often involves a  $\beta$ -hydrogen elimination.<sup>6</sup> This pathway is blocked if no  $\beta$ -hydrogens are available, therefore, methyl, benzyl, or neopentyl complexes are normally more stable.

Homoleptic methyl complexes are known for many of the early transition metals (e.g.  $Ti^7$  and  $Nb^8$ ). These unstable species can decompose to give alkane by a different mechanism, which has been termed  $\alpha$ -hydrogen elimination.<sup>6</sup> Enhanced stability is often achieved by substituting at least one of the methyl hydrogens with a phenyl group. Hence, benzyl complexes, for example  $Ta(CH_2Ph)_5$  (3), generally decompose at much higher temperatures.<sup>9</sup>

Recently in an attempt to prepare  $Ta(CH_2CMe_3)_5$ , the first primary alkylidene  $Ta(CHCMe_3)(CH_2CMe_3)_3$  (1) was formed, reportedly by an  $\alpha$ -hydrogen abstraction.<sup>10</sup> The chemistry of 1 and its Nb analogue  $[Nb(CHCMe_3)(CH_2CMe_3)_3, 2]$  closely resembles organophosphorous chemistry in that reactions with ketones or aldehydes give the corresponding metal oxide and olefin arising from a Wittig-type reaction.<sup>11</sup> The reactions with electrophiles, confirm the nucleophilicity of the  $\alpha$ -carbon atom of the neopentylidene ligand.

## Results and Discussion

Reactions of  $M(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$ ;  $M = \text{Ta}(1), \text{Nb}(2)$ , Consistent with the Neopentylidene  $\alpha$ -Carbon Atom Being Nucleophilic.<sup>10b</sup>

1, in pentane, reacts with acetyl chloride at 25° to give a pale yellow solution from which nearly white, sublimable crystals of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}[\text{O}(\text{Me})\text{C}=\text{CHCMe}_3]$  (4a), are obtained. Analysis of 4a shows it to be the sum of the reactants. The following evidence suggests that this product is a mixture of E- and Z-isomers of 4a.

The 270 MHz  $^1\text{H}$  NMR spectrum of 4a shows primarily one isomer (~90%). It has a characteristic quartet resonance at  $\delta$  5.3 ppm ( $J = 1.1$  Hz, 1H) and a doublet at 1.92 ppm ( $J = 1.1$  Hz, 3H) for the olefinic proton and methyl resonances, respectively. In addition, there are three singlets, of appropriate area, for the remaining groups (see Experimental). The E configuration is assigned to this isomer for convenience. The olefinic resonance for Z-4a is found at 4.44 ppm and the olefinic methyl resonance at 1.93 ppm.

The gated  $^1\text{H}$  decoupled  $^{13}\text{C}$  NMR spectrum of the 4a mixture shows two olefinic carbon atoms for each isomer. Again, the low and high field sets of resonances are assigned to the E and Z isomers, respectively. Thus, the olefinic carbons for E-4a are at 126 (d,  $^1J_{\text{CH}} = 150$  Hz) and 154 ppm (s), and for Z-4a are at 122 (d,  $^1J_{\text{CH}} = 148$  Hz) and 152 ppm (s), with  $^1J_{\text{CH}}$ , in each case, in the range expected for a tert-butyl substituted olefin.<sup>12</sup>

The infrared spectrum of 4a shows a medium-strength absorbance at  $1655\text{ cm}^{-1}$ , which is consistent with a  $\nu_{\text{C}=\text{C}}$  stretching mode, further confirming the assignment of 4a as an enolate complex.<sup>13</sup>

The reaction between 1 and benzoyl chloride, in pentane, gave a yellow oil. The  $^1\text{H}$  NMR spectrum contains two olefinic resonances (no

longer coupled) in a 2:3 ratio at 5.70 and 4.78 ppm for the E and Z isomers of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}[\text{O}(\text{Ph})\text{C}=\text{CHCMe}_3]$  (4b). However, repeating the same reaction in  $\text{Et}_2\text{O}$  gave Z-4b as a crystalline solid in 57% isolated yield.

Phenylbenzoate, unlike some esters (e.g., ethylformate or acetate),<sup>11</sup> reacts with 1 to give pure E- $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{OPh})[\text{O}(\text{Ph})\text{C}=\text{CHCMe}_3]$  (5) as a white crystalline product in 85% isolated yield.

1 reacts vigorously with acetonitrile to give a 3:1 mixture of E- and Z-6a in essentially quantitative yield. Several recrystallizations from acetonitrile at  $-30^\circ$  gives Z-6a as an acetonitrile adduct. It can be freed of acetonitrile by sublimation to give a yellow crystalline solid. Pure Z- $\text{Ta}(\text{CH}_2\text{CMe}_3)_3[\text{N}(\text{Me})\text{C}=\text{CHCMe}_3]$  (6a) isomerizes to a 1:1 E- and Z-6a mixture, slowly by room light or rapidly (~5 h) upon exposure to broad-band ultraviolet light.

The reaction of 1 with benzonitrile gives a yellow oil which is a 1:9 mixture of E- and Z-6b. Recrystallization from acetonitrile followed by sublimation gives pure Z-6b as a yellow oil.

At  $-78^\circ$  (in toluene, pentane, or ether) 1 reacts instantly with 1 equivalent of HCl to give a bright yellow solution containing  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  (7). The 60 MHz  $^1\text{H}$  NMR spectrum of 7 in toluene- $d_8$  at  $-15^\circ$ , shows only two broadened singlet resonances at 2.10 ( $\text{CH}_2\text{CMe}_3$ ) and 1.25 ppm ( $\text{CH}_2\text{CMe}_3$ ), with relative areas of 2:9. Lowering the temperature to  $-60^\circ$  splits the tert-butyl resonance into two broad singlets, at 1.28 and 1.05 ppm with an area ratio of 3:1. This is consistent with a trigonal bipyramidal structure containing axial and equatorial neopentyl groups. These singlets coalesced, upon warming, at  $-30^\circ$ . The free energy of activation,  $\Delta G^\ddagger$ ,<sup>14</sup> is  $12.5 \pm 0.2 \text{ kcal mol}^{-1}$

for an assumed intramolecular interconversion of the axial and equatorial neopentyl groups. Further confirmation comes from the  $^{13}\text{C}$  NMR spectrum at  $-20^\circ$ ; with singlets, in a ratio of 1:3, at 145 (t,  $^1J_{\text{CH}} \approx 105$  Hz) and 117 ppm (t,  $^1J_{\text{CH}} = 112$  Hz) for the axial and equatorial methylene carbons, respectively.

1 reacts with  $\text{HBF}_4 \cdot \text{ether}$  in ether at  $-78^\circ$  to give white, sublimable  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{F}_2$  as the only organometallic product isolated. Presumably  $[\text{Ta}(\text{CH}_2\text{CMe}_3)_4][\text{BF}_4^-]$  is initially formed which then exchanges a neopentyl ligand for two fluoride ligands from  $\text{BF}_4^-$ . Consistent with this result is the finding that treatment of 7 with  $\text{TlBF}_4$ , in an acetonitrile-ether mixture, gave  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{F}_2$  in 35% yield and  $\text{TlCl}$ .

$\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  (7) can be isolated as yellow crystals from pentane at  $-78^\circ$  which decompose within minutes at  $25^\circ$  under nitrogen. 7 decomposes in pentane at temperatures greater than  $-10^\circ$  to give 2.6 equivalents  $\text{Ta}^{-1}$  of neopentane (by GLC and  $^1\text{H}$  NMR). The organometallic products are 1,  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$  (8) and a brown residue. 7 is considerably more stable in  $\text{Et}_2\text{O}$  and in the presence of other polar groups (see Experimental).

The decomposition of 7 in solution is believed to initially form unstable  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_2\text{Cl}$  (9) which subsequently decomposes.

9 is "trapped" as a 7:2 E and Z mixture of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}[\text{N}(\text{Me})\text{C}=\text{CHCMe}_3]$  (10), by standing, for several hours, a pentane-acetonitrile solution containing 7. Fractional crystallization from acetonitrile, at  $-30^\circ$ , gives pure E-10, a sublimable yellow oil.

Stirring a solution of 7 in the presence of  $\text{MCp}$  ( $\text{M} = \text{Tl}, \text{Na}$ ) for several hours at  $25^\circ$  gives a quantitative yield of  $\text{TaCp}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_2$  (11).<sup>15</sup>  $\text{TlCp}$  is a mild reagent and does not react with  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$  (8).<sup>16</sup>

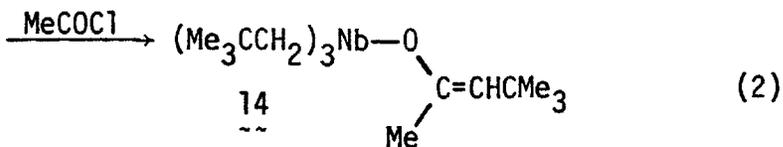
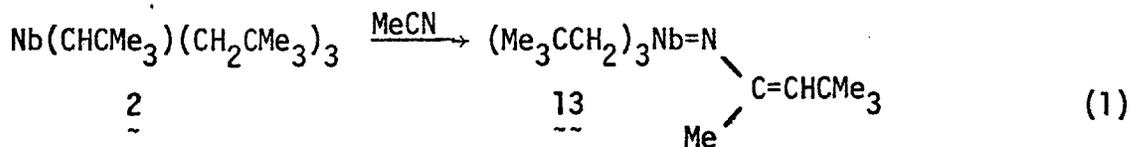
The fact that  $\text{TiCp}$  does react with 7 to give 11 in high yield suggests the intermediacy of 9.

Further evidence for 9 comes from the reaction of 7 with  $\text{LiCH}_2\text{CMe}_3$  to give 1 in quantitative yield, by  $^1\text{H}$  NMR.

Reacting  $\text{Z-Ta}(\text{CH}_2\text{CMe}_3)_3[\text{N}(\text{Me})\text{C}=\text{CHCMe}_3]$  6a in ether with  $\text{HCl}$  at  $-78^\circ$  does not give 10. However, red, crystalline 12 can be obtained in 66% yield. The  $^1\text{H}$  NMR of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}[\text{N}=\text{C}(\text{Me})\text{CH}_2\text{CMe}_3]$  (12), lacking any olefinic resonances, shows singlets at 2.11, 1.82, and 0.93 ppm, with relative areas of 2, 3, and 9 respectively, for the amidine ligand. The infrared spectrum of 12 shows a strong absorbance at  $1655\text{ cm}^{-1}$ , consistent with this formulation.<sup>17</sup>

E-10 in ether also reacts with  $\text{HCl}$  at  $-78^\circ$  to give a product which is similar to 12 (see Experimental).

We believe that most, if not all, of the reactions of 1 with electrophiles would be successful with  $\text{Nb}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$  (2). To demonstrate this postulate, 2 reacts with acetonitrile to give an acetonitrile adduct of 13, a 3:2 E and Z mixture (equation 1). Further evidence from Schrock has shown that 2 reacts with acetyl chloride to give 14 (equation 2).<sup>10b</sup> Each is analogous in nearly every way with



6a and 4a, respectively, the exception being that 13 and 14 are thermally less stable.

The above reactions probably only involve the neopentylidene ligand in the primary step, rather than the neopentyl ligand. The former is clearly more nucleophilic, as the reaction with HCl demonstrates. It has been shown that  $\text{TaCp}(\text{CHCMe}_3)\text{Cl}_2$ <sup>15b</sup> and  $\text{Ta}(\text{CHCMe}_3)\text{Cl}_3(\text{PMe}_3)_2$ <sup>18</sup> each react with acetonitrile to give E and Z mixtures of the corresponding imido complex.

$\text{Ta}(\text{CH}_2\text{Ph})_5$  (3) is known to decompose unimolecularly presumably by  $\alpha$ -hydrogen abstraction, to give toluene.<sup>9b</sup> The intermediate " $\text{Ta}(\text{CHPh})(\text{CH}_2\text{Ph})_3$ " is apparently unstable which subsequently decomposes to unidentified products.  $\text{Ta}(\text{CHPh})(\text{CH}_2\text{Ph})_3$  can be "trapped" using acetonitrile.

Heating a benzene solution of 3 containing 1 mol of acetonitrile, for several hours at 60°, gives ~1 mol per tantalum of toluene and pure Z- $\text{Ta}(\text{CH}_2\text{Ph})_3[\text{N}(\text{Me})\text{C}=\text{CHPh}]$  (15), in nearly quantitative yield, by <sup>1</sup>H NMR. Removal of the solvent gives 15 as a non-volatile red oil. However, if 2 mol of acetonitrile is used a yellow powder is obtained, in 59% yield, which is a 2:1 E- and Z-mixture of the acetonitrile adduct of 15.

#### Five Coordinate Alkoxide Complexes

$\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$  (8), in benzene or toluene, reacts with 2 mol of  $\text{KOCMe}_3$  to give a pale yellow solution from which white, sublimable crystals of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{OCMe}_3)_2$  (16) are obtained. The <sup>1</sup>H NMR at 270 MHz of 16 shows three singlet resonances at 1.63, 1.22, and 1.20 ppm with relative areas of 18:27:6.

16 can also be prepared in 26% yield by reacting an ether solution containing 1 with  $\text{HOCMe}_3$  at -78°. The reaction of 1 in pentane, with  $\text{HOCMe}_3$  at 25° gives instead an insoluble, presumably polymeric, oxide as the only isolable organometallic product.

The reaction of 8 with >2 mol of LiOCMe<sub>3</sub> in ether gives Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>Cl(OCMe<sub>3</sub>) 17, as the major product, and only trace amounts of 16. 17 can be isolated as white, sublimable crystals from pentane at -30°. 17 reacts with 1 mol of KOCMe<sub>3</sub> to give a moderate yield of 16.

The <sup>1</sup>H NMR of 17 in C<sub>6</sub>D<sub>6</sub> shows three singlet resonances at 1.75, 1.38, and 1.22 ppm, with relative areas of 6:9:27. The <sup>13</sup>C NMR of 17 shows that the α-carbon atoms of the neopentyl ligands are equivalent since only one type of methylene carbon resonance (98 ppm; t; <sup>1</sup>J<sub>CH</sub> = 117 Hz) is present in the gated proton decoupled spectrum.

Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub> reacts with [Mg(OCMe<sub>3</sub>)Cl]<sub>x</sub> in ether to give Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>(OCMe<sub>3</sub>) (18) as pale yellow crystals (see Chapter 2 for experimental details). The 270 MHz <sup>1</sup>H NMR spectrum of 18 shows two doublets [2.299 (J = 10.8 Hz) and 1.801 ppm (J = 10.8 Hz)], and two single resonances [1.308 and 1.154 ppm] with relative areas of 2:2:9:18, for the methylene and tert-butyl protons, respectively. 18 contains only one kind of neopentyl α-carbon atom at 105 ppm (t, <sup>1</sup>J<sub>CH</sub> = 118 Hz).

These results indicate that the relative reactivity of these "alkoxylating" reagents increases in the order [Mg(OCMe<sub>3</sub>)Cl]<sub>x</sub> < LiOCMe<sub>3</sub> < KOCMe<sub>3</sub>. Presumably, steric crowding is at least partly responsible for the above finding. Consistent with this is the fact that 8 does not react with [Mg(OCMe<sub>3</sub>)Cl]<sub>x</sub> to give 17, and that Ta(CH<sub>2</sub>Ph)<sub>3</sub>Cl<sub>2</sub> reacts with ~1 mol (slight excess) of LiOCMe<sub>3</sub>, in ether, to give Ta(CH<sub>2</sub>Ph)<sub>3</sub>Cl(OCMe<sub>3</sub>) and Ta(CH<sub>2</sub>Ph)<sub>3</sub>(OCMe<sub>3</sub>)<sub>2</sub> in nearly equal amounts (see Experimental).

The structures of five-coordinate Ta(V) ( $d^0$ ) alkyl/alkoxide complexes are expectedly quite similar to those of analogous organo-phosphorus (V) compounds, that is, trigonal bipyramids with the most electronegative ligands occupying the axial positions.<sup>19</sup> Therefore, molecules such as 16, 17, and 18 almost certainly have structures similar to those found in Figure 1.

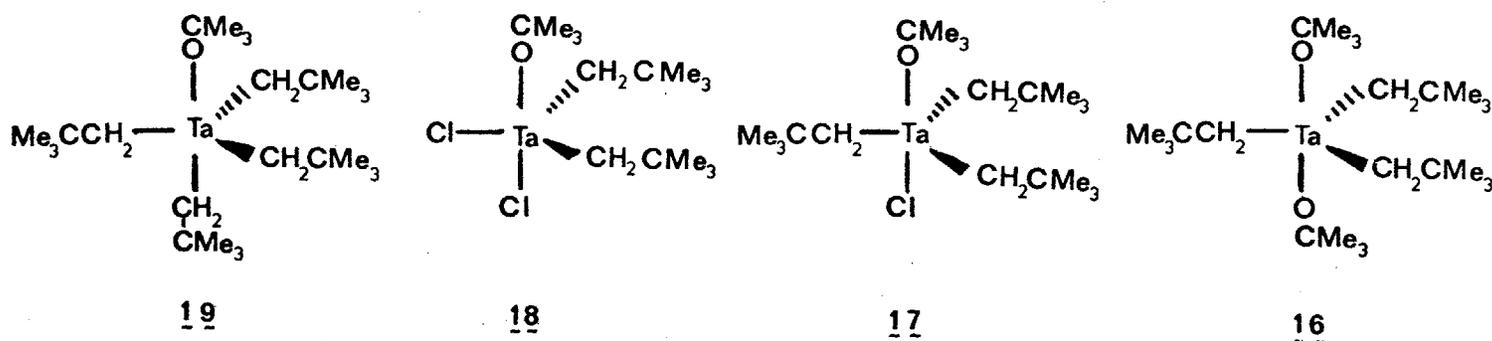


Figure 1

17 Reacts at  $-30^\circ$  with  $\text{LiCH}_2\text{CMe}_3$  in ether or pentane to give  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4(\text{OCMe}_3)$  19. 19 can be isolated as large yellow crystals from concentrated pentane solutions at  $-30^\circ$ . The spectral features of 19 are similar to those found for  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  (7). Most notable in the  $^{13}\text{C}$  NMR (67.89 MHz) spectrum for 19 at  $-30^\circ$ , are two  $\alpha$ -carbon resonances (in 3:1 ratio) at 104 (t,  $^1J_{\text{CH}} = 115$  Hz) and 92 ppm (t,  $^1J_{\text{CH}} = 111$  Hz) for the equatorial and axial neopentyl ligands, respectively. The upfield shift and the larger  $J_{\text{CH}}$  found for the axial  $\alpha$ -carbon atom in 19 (relative to 7), is consistent with the alkoxide ligand being trans to a neopentyl group (see Figure 1) since  $\text{OCMe}_3$  is a better  $\pi$ -donor than  $\text{Cl}$ .<sup>20</sup> Therefore, the axial methylene carbon of 19 would be more shielded and shifts upfield while the  $\text{Ta-H}_\alpha$  interaction<sup>21</sup> is lessened giving rise to the larger  $^1J_{\text{CH}}$ .

The 270 MHz  $^1\text{H}$  NMR spectrum of 19 shows two neopentyl resonances at 1.56 (s, 8H) and 1.27 ppm (s, 36 H) and one tert-butoxide resonance at 1.41 ppm (s, 9 H). Variable-temperature  $^1\text{H}$  NMR shows that the axial and equatorial neopentyl methylene protons coalesce at  $-20^\circ$ , and the neopentyl tert-butyl protons coalesce at  $-25^\circ$ , giving the free energies of exchange ( $\Delta G^\ddagger$ ),  $12.0 \pm 0.8$  and  $12.4 \pm 0.8$  kcal mol $^{-1}$ , respectively.

Heating  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4(\text{OCMe}_3)$  19 in benzene gives  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_2(\text{OCMe}_3)$  (20) and ~1 mol per Ta of neopentane by  $^1\text{H}$  NMR. 20 can be isolated as orange crystals by subliming 19 at  $70^\circ$  and 1-2  $\mu$ . 20 melts at temperatures slightly higher than room temperature and is extremely pentane soluble.

The  $^{13}\text{C}$  NMR of 20 shows resonances at 238 (d,  $^1J_{\text{CH}} = 89$  Hz) and 92 ppm (t,  $^1J_{\text{CH}} = 108$  Hz) for the  $\alpha$ -carbon atoms of the neopentylidene and neopentyl ligands, respectively. Apparently, the tert-butyl resonances are overlapping. The signals for the  $\alpha$ - and  $\beta$ -carbon atoms of the tert-butoxy ligand are at 84(s) and 33 ppm (q,  $^1J_{\text{CH}} \approx 128$  Hz), respectively.

Acetone reacts instantly with 20 in benzene or pentane to give ~1 equivalent  $\text{Ta}^{-1}$  of 2,4,4-trimethyl-2-pentene (diisobutylene), by  $^1\text{H}$  NMR. Removal of the solvent gives an oil which yields lime-green crystals, containing  $\text{Ta}(\text{O})(\text{CH}_2\text{CMe}_3)_2(\text{OCMe}_3)$  21, from an ether-acetonitrile solution at  $-30^\circ$ . Unfortunately, an analytically pure sample of 21 could not be obtained. However, identification of 21 has been made by  $^1\text{H}$  and  $^{13}\text{C}$  NMR and by IR. The  $^1\text{H}$  NMR of 21 contains two AB doublets ( $J \approx 6$  Hz) at 1.75 and 1.32 ppm, and two singlets at 1.48 and 1.29 ppm with relative areas of 2:2:9:18, respectively. The  $^{13}\text{C}$  NMR of 21 shows resonances at 96 (t,  $^1J_{\text{CH}} = 112$  Hz), 36(s) and 35 ppm (q,  $^1J_{\text{CH}} = 125$  Hz) for the

neopentyl ligands, and 81(s) and 31 ppm (q,  $^1J_{CH} = 126$  Hz) for the tert-butoxy ligands. The infrared spectrum of 21 contains a broad, strong absorbance at  $1014\text{ cm}^{-1}$ , assignable to a tantalum-oxygen stretch ( $\nu_{Ta-O}$ ). The solubility of 21 in hydrocarbons suggests a monomeric structure, however, a dimeric (or higher) structure cannot be ruled out.

Formation of Tantalum Alkylidene Complexes:  $Ta(CHCMe_3)(CH_2CMe_3)_2R$ ,  
 $R = OCMe_3$  and  $CH_2CMe_3$

$Ta(CH_2CMe_3)_4(OCMe_3)$  (19), when heated in solution or in the solid state, decomposes to give neopentane and  $Ta(CHCMe_3)(CH_2CMe_3)_2(OCMe_3)$  (20). The decomposition of 19 is first order through at least three half-lives in benzene, xylenes and chloroform. The rate of formation of 20 was measured by: integrating the growth of the  $\alpha$ -hydrogen atom of the neopentylidene or by the neopentane formed versus several internal standards [e.g., diphenylmethane, 1,4-dioxane, hexamethyldisiloxane (HMDS), methylene chloride and tetramethylsilane (TMS)] by  $^1H$  NMR; and by quenching samples at different times with acetone and monitoring the amount of 2,4,4-trimethyl-2-pentene present by GLC. In all cases, a linear least squares plot of time vs.  $\ln[(A_0 - B_i)/(A_0 - B)]$  ( $A_0 \equiv 19$  at  $t = 0$ ;  $B \equiv 20$  at  $t = 0$ ;  $B_i \equiv 20$  at  $t = t_i$ ) was made and these results are tabulated in Table I.

Plotting  $\ln(k/T)$  vs.  $1/T$ , using the data obtained from the diphenylmethane in benzene measurements (1, 2 and 3), gives  $10 \pm 1\text{ kcal mol}^{-1}$  and  $13 \pm 10\text{ eu}$  as values for  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ , respectively. Using these data,  $k$  was found to be  $0.0052$  and  $0.0105\text{ min}^{-1}$  at  $28^\circ$  and  $40^\circ$ , respectively. Comparison of the rate constants shows the relative rates to increase, in different solvents, in the order of benzene(1) < xylenes (~1.5) < chloroform(~2). The rate of decomposition slows markedly when dioxane/HMDS are used as

Table I. Kinetic Data for Decomposition of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4(\text{OCMe}_3)$ 

Run	T(°C) <sup>d</sup>	Standard	Solvent	r <sup>a</sup>	k x 10 <sup>3</sup> min	t <sub>1/2</sub> (min)
1 <sup>e</sup>	50	Ph <sub>2</sub> CH <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	0.91	18	38
2 <sup>e</sup>	38	Ph <sub>2</sub> CH <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	0.98	9.4	74
3 <sup>e</sup>	30	Ph <sub>2</sub> CH <sub>2</sub> /CH <sub>2</sub> Cl <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	0.96	5.9	120
4	21	Dioxane/HMDS <sup>c</sup>	C <sub>6</sub> D <sub>6</sub>	0.99	1.7	400
5	30	Dioxane/HMDS <sup>c</sup>	C <sub>6</sub> D <sub>6</sub>	0.98	3.4	200
6	28	TMS <sup>f</sup>	CDCl <sub>3</sub>	0.99	10	68
7 <sup>b</sup>	40	n-octane	xylene	>0.99	16	45

<sup>a</sup>Correlation coefficient.

<sup>b</sup>Kinetic data obtained from GLC analysis.

<sup>c</sup>Hexamethyldisiloxane.

<sup>d</sup>All temperatures were measured within  $\pm 1^\circ\text{C}$ .

<sup>e</sup>Using  $\ln(k/T) = -\Delta H^\ddagger/RT + \Delta S^\ddagger/R$  gives  $\Delta H^\ddagger = 10.4 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = 12.8 \text{ eu}$  with  $r > 0.99$ .

<sup>f</sup>Tetramethylsilane.

standards, relative to the rate using diphenylmethane. In fact, comparison of the rates at various temperatures shows that 19 decomposes about 0.5 times (at 21°,  $k_{\text{calc.}} = 0.0034 \text{ min}^{-1}$ ) slower in the presence of dioxane/HMDS than in the presence of diphenylmethane.

The decomposition of  $\text{TaCp}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_2$  has been extensively studied by C. D. Wood.<sup>15b</sup> It was found that  $\text{TaCp}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_2$  unimolecularly decomposes to  $\text{TaCp}(\text{CHCMe}_3)\text{Cl}_2$  and neopentane. The rate of decomposition is solvent dependent and increases in the order of ether (1) < pentane (~2) < benzene (~4) < chloroform (~15).  $\text{TaCp}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_2$  is postulated to be in a rapid equilibrium between a cis and a trans form (see Figure 2) with the cis form predominating in more polar solvents (viz. chloroform). Presumably, the cis form is required for  $\alpha$ -hydrogen abstraction to occur.

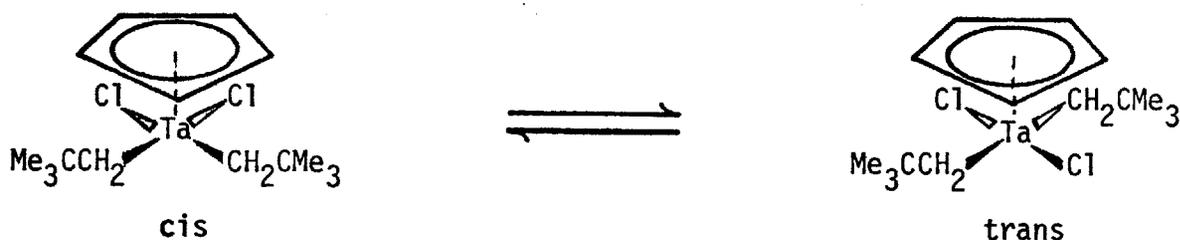


Figure 2

Wood suggests that ether, since it is anomalous and gives the slowest rates, coordinates to tantalum thereby effecting the cis-trans equilibrium leaving the trans isomer to predominate in solution.

Unlike  $\text{TaCp}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_2$ , 19 contains mutually cis neopentyl ligands (see Figure 1) and little or no solvent effect is expected. The

solvent effect that is observed in the decomposition of 19, probably reflects the donor-acceptor properties (or interactions), between the solvent and solvate, which is inherent to the system of study.<sup>22</sup>

Ultimately, the rate determining step, presumably  $\alpha$ -hydrogen abstraction, must be similar for both systems since the kinetic isotope effect ( $k_H/k_D$ ; measured competitively in solution or as a solid) for  $\text{Ta}(\text{CHDCMe}_3)_4(\text{OCMe}_3)$  ( $k_H/k_D = 6 \pm 1$ ) and  $\text{TaCp}(\text{CHDCMe}_3)_2\text{Cl}_2$  ( $k_H/k_D = 7 \pm 1$ ) are virtually the same.

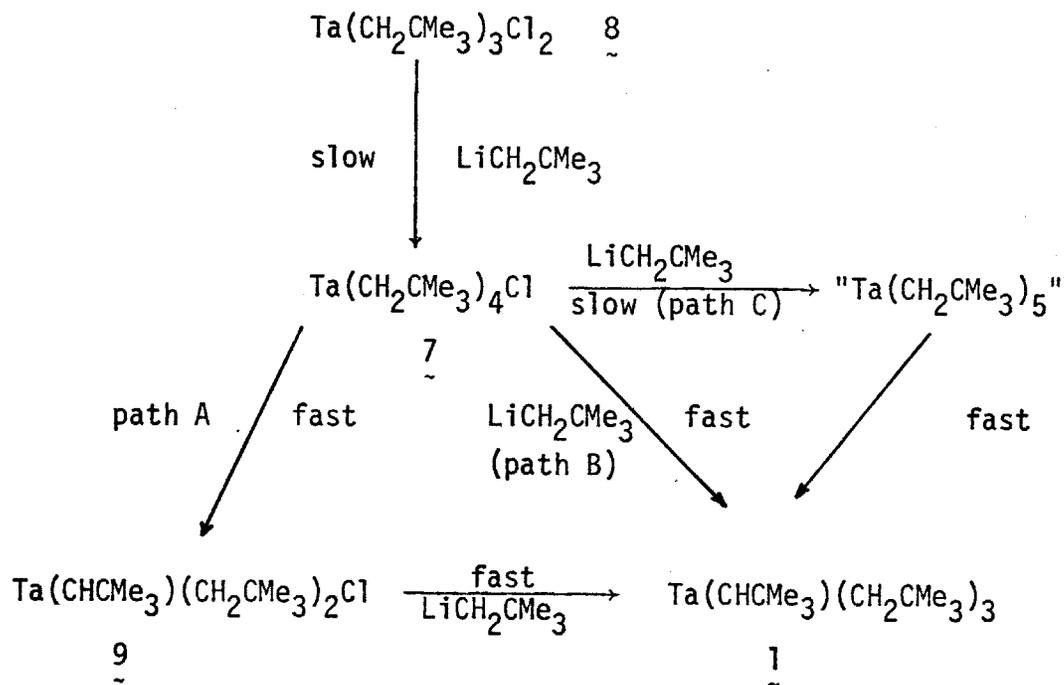
#### Postulated Mechanism of Forming $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$ (1)

The reaction between five-coordinate  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$  (8) and 2 mol of  $\text{LiCH}_2\text{CMe}_3$  gives  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$  (1) in quantitative yield. The intermediacy of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  (7), although implied, has not, as yet, been shown. Attempts to trap 7 with  $\text{TlCp}$  using  $\text{LiCH}_2\text{CMe}_3$  or  $\text{Mg}(\text{CH}_2\text{CMe}_3)_2$  dioxane as alkylating agents with  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$  (8) has had little success (see Experimental). Therefore if 7 is present it must disappear rapidly at 25°.

To test the validity of 7 as an intermediate in the above reaction, the production of  $\text{LiCl}$  and the amount of 1 were followed, in separate experiments, with time (see Experimental). Assuming the reaction to be first-order in tantalum (or lithium) a linear plot using these data, of  $\ln[\text{Ao}/(\text{Ao}-\text{C})]$  ( $\text{Ao} \equiv \text{mmol}$  of 8 at  $t = 0$ ;  $\text{C} \equiv \text{mmol}$  of 1 at any  $t$ ) versus time ( $t$ ) gave half-lives ( $t_{1/2}$ ) of  $9 \pm 3$  min ( $k = 0.08 \pm 0.03 \text{ min}^{-1}$ ) and  $14 \pm 1$  min ( $k = 0.050 \pm 0.005 \text{ min}^{-1}$ ) for the  $\text{LiCl}$  study at 22° and for the GLC study at 20°, respectively. In contrast, a reaction employing  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  (7) and  $\text{LiCH}_2\text{CMe}_3$  was virtually

Scheme I. A Possible Mechanism for the Formation of  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$

Scheme I.



(>99%) complete in 10 min at 22°, as measured by the LiCl method. Clearly, the rate of forming 1 from  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  is greater than the rate of forming 1 from  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ .

If the formation of 7 is rate determining then one possible path (A, Scheme I) seems likely. Since 7 decomposes to give postulated 9, which is four-coordinate, then another  $\text{LiCH}_2\text{CMe}_3$  can probably react with 9 faster than 7 (path C) to give 1. This conjecture seems plausible in alkane solvents.

However, reasoning by analogy to the decomposition of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4(\text{OCMe}_3)$ , the rate of formulation of 1 might be expected to slow down in ether. Schrock has observed that the rate of forming 1 increases (relative to pentane) in ether, suggesting that an alternate mechanism, a dehydrohalogenation (path B), may be operative. Path B is not unreasonable since  $\text{Ph}_3\text{P}=\text{CH}_2$  reacts with 7 (in ether) to give  $\text{Ph}_3\text{P}^+\text{Cl}^-$  and 1 in 76% yield.

Supportive of this view are labeling studies, performed by Schrock,<sup>10b</sup> involving the analysis of neopentane- $\text{d}_x$  produced in the reaction of  $\text{Ta}(\text{CD}_2\text{CMe}_3)_3\text{Cl}_2$  with 1, 2, and 10 mol of  $\text{LiCH}_2\text{CMe}_3$ , showing that the amount of neopentane- $\text{d}_0$  increases with increasing (>2)  $\text{LiCH}_2\text{CMe}_3$ . Moreover, path B must not be exclusively operating since 7 reacts with  $\text{LiMe}$  in ether to give a complex mixture of products containing ca. 30% of 1, by  $^1\text{H}$  NMR.

1 can probably form from  $\text{Ta}(\text{CH}_2\text{CMe}_3)_5$  since  $\text{Ta}(\text{CH}_2\text{Ph})_5$  decomposes to " $\text{Ta}(\text{CHPh})(\text{CH}_2\text{Ph})_3$ ", which can be trapped with acetonitrile. Schrock suggests that " $\text{Ta}(\text{CH}_2\text{CMe}_3)_5$ " must be very short-lived since it must decompose at a rate which is faster than the rate at which the neopentyl groups equilibrate.<sup>10b</sup> Unfortunately, no experiment

distinguishes between the formation of "Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>5</sub>" (path C) and dehydrohalogenation of 7 by LiCH<sub>2</sub>CMe<sub>3</sub> (path B).

The end result of this study leads to the conclusion that probably all pathways (A, B, and C) are operative. The relative contributions from each are quite likely solvent and temperature dependent with 1 being the lowest energy product available for each pathway.

### General Experimental Details

All operations were done under  $N_2$ , unless stated otherwise, either in a Vacuum Atmospheres HE43 glovebox or by Schlenk technique.<sup>23</sup> Ether, benzene and toluene were distilled from sodium benzophenone ketyl under  $N_2$ . Tetrahydrofuran was predried with  $CaH_2$  then distilled from potassium benzophenone ketyl under  $N_2$ . Pentane, hexane, and heptane were purified by an acid wash to remove olefin impurities (3 L of hydrocarbon was shaken successively with three 50 mL portions of concentrated  $H_2SO_4/HNO_3$  (95/5) and three 500 mL portions of distilled water followed by drying over  $CaCl_2$ ), then distilled from sodium benzophenone ketyl or  $LiBu^n$  under  $N_2$ . Chlorobenzene, methyl chloride, chloroform and acetonitrile were distilled from  $P_2O_5$  under  $N_2$ . Benzonitrile was degassed with  $N_2$  and dried with Linde 4A sieves. Acetone (reagent) and 1,4-dioxane were degassed with  $N_2$  and dried with  $CaCl_2$  or Linde 4A molecular sieves. Mesitylene, xylenes, diphenylmethane, olefins, n-alkanes (GLC standards), and NMR solvents were degassed with  $N_2$  and passed through a column of activated alumina. Acetyl chloride and benzoyl chloride were degassed with  $N_2$  and used as received. Phenylbenzoate (Aldrich) was used as received.  $HOCMe_3$  was degassed with  $N_2$  and distilled from Na metal.

$TaCl_5$  (Cerac),  $TaBr_5$  (Cerac),  $KOCMe_3$  (Aldrich),  $LiMe$  (Alfa/Ventron),  $LiBu^n$  (Alfa/Ventron), and  $HCl$  (Matheson CP grade) were used as received.  $HCl$  in ether was prepared by bubbling gaseous  $HCl$  through dry ether, under  $N_2$ , and titrated with base before use.  $LiOCMe_3$  was prepared by reacting  $LiBu^n$  with  $HOCMe_3$  in hexane.  $LiCl$  was obtained from the reaction of  $Ta(CH_2CMe_3)_3Cl_2$  with 2 mol of

$\text{LiCH}_2\text{CMe}_3$ ,  $\text{NaC}_5\text{H}_5$ ,  $\text{Ph}_3\text{P}=\text{CH}_2$ ,  $\text{Me}_3\text{P}=\text{CH}_2$ ,  $\text{TlBF}_4$  and all benzy1 compounds were obtained from L. Messerle.  $\text{LiCHDCMe}_3$  and  $\text{Zn}(\text{CHDCMe}_3)_2$  were obtained from G. Rupprecht.  $\text{Zn}(\text{CD}_2\text{CMe}_3)_2$  was obtained from C. Wood.  $\text{NbCl}_5$  (Alfa/Ventron) and  $\text{TlC}_5\text{H}_5$  (Strem) were sublimed prior to use.  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ ,  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$ ,  $\text{Nb}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ ,  $\text{LiCH}_2\text{CMe}_3$ ,  $\text{Zn}(\text{CH}_2\text{CMe}_3)_2$ ,  $\text{Mg}(\text{CH}_2\text{CMe}_3)_2$  dioxane, and  $\text{Mg}(\text{CH}_2\text{CMe}_3)\text{Cl}$  were prepared by published methods.<sup>10b</sup>

Elemental analyses were done by Alfred P. Bernhardt or Schwarzkopf Microanalytical Labs. Chloride analyses were done titrametrically using an adsorbtion indicator according to published methods.<sup>24</sup> Molecular weights were determined cryoscopically in benzene or cyclohexane. IR spectra were recorded on a Perkin-Elmer 567 spectrometer and are reported in  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectra were done at 60 MHz (Varian T-60, Perkin-Elmer R-20B, and R-24B, and Jeol FX-60Q), 89.9 MHz (Jeol FX-90Q), 200 MHz (Brüker WP-200), 250 MHz (Brüker WM-250) or 270 MHz (Brüker HFX-270) and are reported on the  $\delta$  scale.  $^{13}\text{C}$  NMR were recorded at 15.0 MHz (Jeol), 22.5 MHz (Jeol), 22.63 (Brüker HFX-90), 62.83 MHz (Brüker) or 67.89 MHz (Brüker) and are reported as ppm downfield of  $\text{Me}_4\text{Si}$ . Temperature determination for variable temperature NMR was made using a calibrated temperature controller or measured directly using standard methods. GC/Mass spectra were recorded on a Hewlett-Packard 5990A GC/MS with an ionizing voltage of 60 eV. Analytical GLC was performed on a Hewlett Packard 5730A temperature-programmable gas chromatograph, employing a flame ionizing detector, interfaced to a Hewlett-Packard 3380A integrator.

The columns used for GLC work were:

- A. 1/8" x 8' 10% SP-2100 on Supelcoport 100/120
- B. 1/8" x 15' 10% SE-30 on 100/120 Gas-Chrom Q
- C. 1/8" x 15' 10% Carbowax 20M on 80/100 Gas-Chrom Q

Preparation of Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>Cl[O(Me)C=CHCMe<sub>3</sub>] (I, 50)

Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>Cl[O(Me)C=CHCMe<sub>3</sub>] was prepared according to published procedures.<sup>10b</sup> The ratio of the E isomer to the Z isomer was determined by measuring the relative peak heights for the vinylic hydrogen of the enolate moiety, where E/Z = 7.5/1.

Anal. (I, 50-1; I, 52): Calcd. for TaC<sub>22</sub>H<sub>46</sub>ClO: C, 48.69; H, 8.54.

Found: C, 48.61; H, 8.00.

IR (cm<sup>-1</sup>; Nujol/NaCl; I, 50-1): 1655, m (ν<sub>C=C</sub>).

Preparation of Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>Cl[O(Ph)C=CHCMe<sub>3</sub>] (I, 53)

Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>Cl[O(Ph)C=CHCMe<sub>3</sub>] was prepared according to published procedures.<sup>10b</sup> The ratio of the E isomer to the Z isomer was determined by measuring the relative peak heights for the vinyl hydrogen of the enolate moiety, where E/Z = 1/7.

IR (cm<sup>-1</sup>; Nujol/NaCl; I, 53-1): 1655, m (ν<sub>C=C</sub>).

Preparation of Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>(OPh)[O(Ph)C=CHCMe<sub>3</sub>] (I, 50)

Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>(OPh)[O(Ph)C=CHCMe<sub>3</sub>] was prepared according to published procedures.<sup>10b</sup> The product obtained was the pure E isomer as determined by <sup>1</sup>H NMR.

IR (cm<sup>-1</sup>; Nujol/NaCl; I, 50-2): 1649, m (ν<sub>C=C</sub>).

Preparation of Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>[N(Me)(C=CHCMe<sub>3</sub>)] (I, 66)

Ta(CHCMe<sub>3</sub>)(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub> (2.0 g, 4.3 mmol) was slowly added as a solid to stirred CH<sub>3</sub>CN (10 mL). This reaction is quite vigorous. After stirring for 2 h the solution was filtered and the filtrate stood at -30° for

16 h. The supernatant was decanted from the yellow crystals (ca. 1.7 g) and the remaining solvent was removed in vacuo. The product, isolated as oily crystals, is a 1:3 E/Z mixture and contains weakly coordinated acetonitrile by IR and  $^1\text{H}$  NMR ( $\nu_{\text{CN}} \approx 2280 \text{ cm}^{-1}$ , w; I, 66-1;  $\delta \text{CH}_3\text{CN} = 0.6$ ; I, 66-1). The acetonitrile causes the chemical shifts of several peaks to vary from sample to sample by ca. 1 ppm. Acetonitrile is lost when the product is sublimed at  $70^\circ$ ,  $1\mu$ . Multiple recrystallizations gave the pure Z isomer as a pale yellow, crystalline acetonitrile adduct. Fractional sublimation at  $70^\circ\text{C}$  and  $2\mu$  (1 h) yields a crystalline, acetonitrile-free product, and an oily residue. The pure E isomer has not yet been obtained free of the Z isomer. An analytically pure sample was not obtained due to the photosensitivity of the product (see below).

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 90 MHz; I, 72-4A, 6A;  $25^\circ$ ): E isomer: 5.64 (m, 1,  $J \approx 1 \text{ Hz}$ , olefinic H); 2.24 (d, 3,  $J \approx 1 \text{ Hz}$ , olefinic methyl); 1.26 (s, 9, olefinic  $\text{CMe}_3$ ); 1.21 (s, 27,  $\text{CH}_2\text{CMe}_3$ ); 0.82 (s, 6,  $\text{CH}_2\text{CMe}_3$ ). Z isomer: 4.62 (q, 1,  $J = 1.1 \text{ Hz}$ , olefinic H); 2.20 (d, 3,  $J = 1.1 \text{ Hz}$ , olefinic methyl); 1.45 (s, 9, olefinic  $\text{CMe}_3$ ); 1.15 (s, 27,  $\text{CH}_2\text{CMe}_3$ ); 1.02 (s, 6,  $\text{CH}_2\text{CMe}_3$ ).

IR ( $\text{cm}^{-1}$ ; Nujol/NaCl; I, 72-2): 1610, m ( $\nu_{\text{C}=\text{C}}$ ).

Prolonged exposure ( $\geq 1$  week) of the pure crystalline Z isomer (in vacuo) to indirect sunlight, causes slow isomerization to a 1/4 E/Z mixture, isolated as a green oil. Irradiation with broad-band ultraviolet light on an NMR sample (Pyrex) containing pure Z in  $\text{C}_6\text{D}_6$ , causes rapid isomerization (5 h) to a 1/1 E/Z mixture. Trap to trap distillation of the  $\text{C}_6\text{D}_6$  solution obtained above, showed only neopentane and acetonitrile in small (<10%) amounts (I, 71, 72).

$\text{Ta}(\text{CH}_2\text{CMe}_3)_3[\text{N}(\text{Me})\text{C}=\text{CHCMe}_3]$  gave no reaction with excess  $\text{PMe}_3$  in  $\text{C}_6\text{D}_6$  at  $60^\circ$  after 2 d by  $^1\text{H}$  NMR (I, 71).

Reaction of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3[\text{N}(\text{Me})\text{C}=\text{CHCMe}_3]$  with HCl (II, 22)

Z- $\text{Ta}(\text{CH}_2\text{CMe}_3)_3[\text{N}(\text{Me})\text{C}=\text{CHCMe}_3]$  (0.2 g, 0.4 mmol) was dissolved in  $\text{Et}_2\text{O}$  (20 mL) and cooled to  $-78^\circ$ . 0.3 mL of 1.29 M HCl in  $\text{Et}_2\text{O}$  (0.4 mmol) was added to the cold solution via syringe, causing an immediate color change from yellow to orange. The stirred reaction mixture was held at  $-78^\circ$  for 10 min then rapidly warmed to room temperature and filtered. Removal of the solvent in vacuo gave 0.14 g of orange crystals. Recrystallization from a concentrated pentane solution at  $-30^\circ$  (16 h) gave 0.12 g of bright orange crystals, (crude yield = 0.14 g, 66%, based on the sum of the molecular weights of the starting materials). The product obtained is best formulated as  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}[\text{N}=\text{C}(\text{CH}_3)\text{CH}_2\text{CMe}_3]$  by  $^1\text{H}$  NMR and IR. No further characterization of this product was made.

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 90 MHz; II, 2-2;  $25^\circ\text{C}$ ): 2.11 (s, 2,  $\text{CH}_2\text{CMe}_3'$ ); 1.82 (s, 3,  $\text{CH}_3$ ); 1.76 (s, 6,  $\text{CH}_2\text{CMe}_3$ ); 1.30 (s, 27,  $\text{CH}_2\text{CMe}_3$ ); 0.93 (s, 9,  $\text{CH}_2\text{CMe}_3$ ).

IR ( $\text{cm}^{-1}$ ; Nujol/NaCl; II, 22-1): 1655, s ( $\nu_{\text{C}=\text{N}}$ ).

Preparation of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3[\text{N}(\text{Ph})\text{C}=\text{CHCMe}_3]$  (I, 57)

$\text{Ta}(\text{CH}_2\text{CMe}_3)_3[\text{N}(\text{Ph})\text{C}=\text{CHCMe}_3]$  was prepared according to published procedures.<sup>10b</sup> The crude product was isolated as a 1/8 E/Z mixture. Two recrystallizations from acetonitrile followed by sublimation at  $70^\circ$  and  $1\mu$  for 1 hr gave pure Z as a yellow oil.

IR ( $\text{cm}^{-1}$ ; neat oil/NaCl; II, 8-2A): 1590, m ( $\nu_{\text{C}=\text{C}}$ ).

Preparation of  $\text{Nb}(\text{CH}_2\text{CMe}_3)_3[\text{N}(\text{Me})\text{C}=\text{CHCMe}_3]$  (I, 72)

$\text{Nb}(\text{CH}_2\text{CMe}_3)_3[\text{N}(\text{Me})\text{C}=\text{CHCMe}_3]$  was prepared according to published procedures.<sup>10b</sup> The crude product obtained was an acetonitrile adduct, a 3/2 E/Z mixture as determined by measuring the relative peak heights of the olefinic methyl of the enolate moiety.

IR ( $\text{cm}^{-1}$ ; Nujol/NaCl; I, 72-1B): 1600, br m ( $\nu_{\text{C}=\text{C}}$ ).

Preparation of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  (I, 2)

A solution of  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$  (0.93 g, 2.00 mmol) in 15 mL of pentane was cooled to  $-78^\circ$  and 45 mL of anhydrous HCl (2.0 mmol) was added slowly by syringe. The solution turned brilliant yellow and upon standing (especially when more concentrated) deposited yellow crystals of pure  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  after 1-2 h at  $-78^\circ$ .  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  decomposes at  $>-10^\circ$  in aromatic or aliphatic solvents (more stable in polar solvents, see text) giving 2.6 mol  $\text{Ta}^{-1}$  of neopentane (vs. n-octane) by GLC (column A; I, 63-1,2) using a calculated response factor. Removal of the solvent (in vacuo) gave a brown residue which partially dissolved in pentane, the remaining portion was soluble only in THF. The crystalline solid decomposes (~30 min) at  $25^\circ$  under nitrogen, yielding an intractable green gum. An ether solution of dry HCl (1-4 M) can be substituted for gaseous HCl in the above reaction.  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  can be similarly prepared in situ using toluene or diethyl ether (V, 75).

$\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  decomposes (~24 h) in neat  $\text{Et}_2\text{O}$  giving an insoluble white precipitate, probably a polymeric oxide (IR: II, 29-1;  $\nu_{\text{Ta}-\text{O}} = 1045 \text{ cm}^{-1}$ ),

and a colorless solution (II, 29).

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 60 MHz; I, 26-1 through 6;  $-15$  to  $-65^\circ$ ): ( $-15^\circ$ ): 2.10 (br s, 8,  $\text{CH}_2\text{CMe}_3$ ); 1.25 (s, 36,  $\text{CH}_2\text{CMe}_3$ ). ( $-30^\circ$ ): coalescence of  $\text{CMe}_3$ (axial) and  $\text{CMe}_3$ (equatorial) resonances. ( $-60^\circ$ ): 15 Hz separation between  $\text{CMe}_3$ (axial, br) and  $\text{CMe}_3$ (equatorial, sharpening).

$T_c = 243 \pm 5$  K,  $\Delta\nu = 15 \pm 5$  Hz,  $\Delta G^\ddagger = -12.5 \pm 0.2$  kcal/mol $^{-1}$ .

$^{13}\text{C}$  NMR ( $\delta$ ,  $\text{C}_6\text{D}_5\text{CD}_3$ ; 67.89 MHz; II, 26-1A, 2A;  $\{^1\text{H}\}$  and gated  $\{^1\text{H}\}$ ;  $-20^\circ$ ): 144.6 (t,  $^1J_{\text{CH}} \cong 105$  Hz, axial  $\text{CH}_2\text{CMe}_3$ ); 116.9 (t,  $^1J_{\text{CH}} = 112$  Hz, equatorial  $\text{CH}_2\text{CMe}_3$ ); 40.3 (s, axial  $\text{CH}_2\text{CMe}_3$ ); 35.5 (s, equatorial  $\text{CH}_2\text{CMe}_3$ ); 35.2 (q,  $^1J_{\text{CH}} = 123$  Hz, equatorial  $\text{CH}_2\text{CMe}_3$ ); 34.4 (q,  $^1J_{\text{CH}} \cong 121$  Hz, axial  $\text{CH}_2\text{CMe}_3$ ).

Reaction of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  with  $\text{LiR}$  ( $\text{R} = \text{CH}_2\text{CMe}_3, \text{Me}$ )

1.  $\text{R} = \text{CH}_2\text{CMe}_3$  (I, 2)

$\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  (1 mmol) was prepared in situ with gaseous HCl (see above) in pentane. A pentane solution (5 mL) of  $\text{LiCH}_2\text{CMe}_3$  (1 mmol) added quickly by syringe, gave an immediate precipitate at  $-78$ . The reaction mixture was warmed to room temperature and stirred for 16 h. The orange solution was filtered and the solvent was removed in vacuo. The orange oil (0.44 g) was pure  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$  by  $^1\text{H}$  NMR (yield 96%).

2.  $\text{R} = \text{Me}$  (I, 3,4)

$\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  (0.5 mmol) was prepared in situ ( $-78^\circ$ ) with gaseous HCl (see above) in  $\text{Et}_2\text{O}$  (2-3 ml). 0.73 mL of 1.45 M  $\text{LiMe}$  (0.5 mmol, halide free) added quickly by syringe at  $25^\circ$ , gave an immediate precipitate and some gas evolution. Within 45 min the color changed from yellow

to orange to brown. Removal of the solvent (in vacuo) gave a tacky brown solid which was extracted with 4 ml of pentane. Filtration and removal of the solvent gave a brown oil containing  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$  (~30%) by  $^1\text{H}$  NMR.

Reaction of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  with  $\text{Ph}_3\text{P} = \text{CH}_2$  (II, 21)

The reaction of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  with  $\text{Ph}_3\text{P} = \text{CH}_2$  in  $\text{Et}_2\text{O}$ , previously reported,<sup>10b</sup> gave  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$  as the only isolable organometallic product. (76% yield).

Reaction of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  with  $\text{TlBF}_4$  (II, 24)

A detailed description of the reaction of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  with  $\text{TlBF}_4$  in a 6:1  $\text{Et}_2\text{O}/\text{CH}_3\text{CN}$  solution can be found elsewhere.<sup>10b</sup>  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{F}_2$  was isolated after sublimation at 60-70° (1 $\mu$ ). (35% yield).

An analytically pure sample was obtained after multiple sublimations. Analysis (II, 24-1; II, 31): Calcd. for  $\text{TaC}_{15}\text{H}_{33}\text{F}_2$ : C, 41.67; H, 7.69. Found: C, 41.13; H, 7.91.

IR ( $\text{cm}^{-1}$ ; Nujol/NaCl; II, 6-2A): 1070, br s ( $\nu_{\text{Ta-F}}$ ).

Reaction of  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$  with  $\text{HBF}_4(\text{OMe}_2)$  (II, 31)

The experiment details have been previously reported.<sup>10b</sup> The product,  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{F}_2$ , was isolated by sublimation. (29% yield).

1. With  $\text{TlC}_5\text{H}_5$  (I, 74)

The details for the reaction of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  with  $\text{TlC}_5\text{H}_5$  in toluene, have been reported.<sup>10b</sup>  $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_2$  was isolated in

quantitative yield as a sublimable yellow-orange oil.

2. With  $\text{NaC}_5\text{H}_5$  (I, 73)

A THF solution (10 mL) of  $\text{NaC}_5\text{H}_5$  (0.1 g, 1.1 mmol) was added dropwise to an ether solution (10 mL) containing  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  (1 mmol; prepared by the gaseous HCl method) at  $-78^\circ$ . After stirring for 30 min at  $-78^\circ$  the reaction mixture was warmed to  $0^\circ$  for 1 h, then to  $25^\circ$  for 16 h. Addition of pentane (25 ml) gave a white precipitate (50 mg), which was removed by filtration. The filtrate was stirred to an orange oil, extracted with pentane (25 mL) and filtered. Removal of the solvent (in vacuo) gave  $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_2$  as an orange oil. (>90% yield).

C.D. Wood has previously reported the synthesis of

$\text{Ta}(\eta^5\text{-C}_5\text{H}_5)(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_2$  by a different procedure.<sup>15b</sup>

Trapping " $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_2\text{Cl}$  as  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}[\text{N}(\text{Me})\text{C}=\text{CHCMe}_3]$  (I, 67)

$\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}[\text{N}(\text{Me})\text{C}=\text{CHCMe}_3]$  was prepared and characterized according to published methods.<sup>10b</sup> The crude product isolated as an acetonitrile adduct was a 3.5:1 E/Z mixture, based on the relative peak heights of the imine methyls by  $^1\text{H}$  NMR. (I, 64-4). These methyl resonances are absent if  $\text{CD}_3\text{CN}$  is used instead of  $\text{CH}_3\text{CN}$ .  $\text{LiCH}_2\text{CMe}_3$  was reacted with  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}[\text{N}(\text{Me})\text{C}=\text{CHCMe}_3]$  in pentane. The product, an intractable brown oil, gave a complex  $^1\text{H}$  NMR spectrum and no further investigation was attempted (I, 71).

IR ( $\text{cm}^{-1}$ ; neat oil/NaCl; I, 10-1): 1655 m ( $\nu_{\text{C}=\text{C}}$ ).

Reaction of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}[\text{N}(\text{Me})\text{C}=\text{CHCMe}_3]$  with  $\text{HCl}$  (II, 23)

$\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}[\text{N}(\text{Me})\text{C}=\text{CHCMe}_3]$  (0.44 gm, 0.94 mmol) was dissolved in  $\text{Et}_2\text{O}$  (25 mL) and cooled to  $-78^\circ\text{C}$ . 0.7 ml (0.94 mmol) of an ether solution containing anhydrous  $\text{HCl}$  (1.29 M) added by syringe, reacted immediately, and gave a cloudy red solution. After stirring for 8 h at  $25^\circ$ , the solution was filtered and stripped to an orange solid (0.44 g). Recrystallization from pentane (1.5 mL) gave orange, coral-like crystals. The product obtained has similar (but not identical) spectroscopy to the product isolated from the reaction of  $\text{HCl}$  with  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3[\text{N}(\text{Me})\text{C}=\text{CHCMe}_3]$ . (93% crude yield; based on the sum of the molecular weights of the reactants.)

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 60 MHz; II, 23-1;  $25^\circ$ ): 2.10 (s, 2,  $\text{CH}_2\text{CMe}_3'$ ); 1.80 (s, 3, Me); 1.76 (s, 4,  $\text{CH}_2\text{CMe}_3$ ); 1.30 (s, 18,  $\text{CH}_2\text{CMe}_3$ ); 0.9 (s, 9,  $\text{CH}_2\text{CMe}_3'$ ).

IR ( $\text{cm}^{-1}$ ; Nujol/NaCl; II, 23-1): 1650, s ( $\nu_{\text{C}=\text{N}}$ ).

Miscellaneous Attempts to Trap " $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_2\text{Cl}$ "

1.  $\text{CH}_3\text{COCl}$  (I, 63)

$\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  was reacted with  $\text{CH}_3\text{COCl}$  (1 equivalent) in pentane (10 mL) for 1.5 h at  $25^\circ$ . The brown oil, isolated by removal of the solvent in vacuo, contained 2 olefinic  $^1\text{H}$  resonances ( $\delta$ ) at 5.6 (m) ppm and 4.7 (m) ppm in a 1:2 ratio, respectively (I, 65-1).

2.  $\text{PhCOOPh}$  (I, 64)

$\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  was reacted with  $\text{PhCOOPh}$  (2% excess of 1 equivalent) in pentane (~3 mL) for 1 h at  $25^\circ$ . The resultant oil, isolated by evaporation of the solvent, contained 2 olefinic  $^1\text{H}$  resonances ( $\delta$ )

at 5.6 (s) ppm and 5.4 (s) ppm in a 6:1 ratio, respectively (I, 64-2D).

### 3. $\text{KOOCMe}_3$ (I, 59)

2.0 mmol of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  was prepared in toluene at  $-78^\circ$  using gaseous  $\text{HCl}$ . 4.0 mmol of  $\text{KOOCMe}_3$  was added as a solid and the reaction mixture was slowly brought to room temperature and stirred for 24 h. Removal of the solvent (in vacuo) gave, after extraction with heptane and filtration, a homogeneous red solution. All volatiles of the filtrate were removed in vacuo yielding a glassy red solid that gave a complex  $^1\text{H}$  NMR spectrum (I, 59-1). No sublimate was obtained after 3 h at  $120^\circ$  ( $0.3\mu$ ).

Several attempts were made to directly prepare  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  from  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$  using different alkylating agents in the presence of several "known" trapping agents. (I, 37; II, 6). In each experiment, the only product isolated was unreacted  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ . The best results were obtained from the reaction of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$  in toluene with  $\text{Mg}(\text{CH}_2\text{CMe}_3)_2$ (dioxane) (0.5 equivalents) in the presence of  $\text{TiC}_5\text{H}_5$  (1 equivalent). The major product of the crude reaction mixture was  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ , by  $^1\text{H}$  NMR. Also present was a Cp-containing product (~5-10%) tentatively identified as  $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_2$  (III, 37). Due to the insolubility of  $\text{Mg}(\text{CH}_2\text{CMe}_3)_2$ (dioxane) in toluene, a better method might be obtained utilizing the dioxane free magnesium reagent.

### Preparation of $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}(\text{OCMe}_3)$ (II, 19)

A yellow solution of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$  (1.0 g, 2.15 mmol) and  $\text{LiOCMe}_3$  (0.17 g, 2.15 mmol) was stirred for 16 h at  $25^\circ$ . The solvent was

removed (in vacuo) leaving a white residue which was extracted with pentane (50 mL) and filtered. The volume of the filtrate was reduced to 15 ml, and standing at  $-30^{\circ}$  (16 h) gave 0.78 g of white fibrous crystals, pure by NMR. An analytically pure sample was obtained after repeated sublimations at  $60-100^{\circ}$  ( $1\mu$ ). The additional crops collected from the mother liquor contained some  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{OCMe}_3)_2$  and  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$  (72% yield).  
Anal. (II, 29; II, 27-1): calcd. for  $\text{TaC}_{19}\text{H}_{42}\text{OC}_3$ : C, 45.38; H, 8.41.  
Found: C, 46.09; H, 8.80.

Chlorine Analysis by  $\text{AgNO}_3$  adsorption method (II, 42): Calculated: Cl, 7.04. Found: Cl, 7.05.

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 90 MHz; II, 19-5B;  $25^{\circ}\text{C}$ ): 1.75 (s, 6,  $\text{CH}_2\text{CMe}_3$ ); 1.38 (s, 9,  $\text{OCMe}_3$ ); 1.22 (s, 27,  $\text{CH}_2\text{CMe}_3$ ).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; III, 51-1A through 4A;  $\{^1\text{H}\}$  and gated  $\{^1\text{H}\}$ ;  $25^{\circ}\text{C}$ ): 98.38 (t,  $^1J_{\text{CH}} = 116.5$  Hz,  $\text{CH}_2\text{CMe}_3$ ); 85.6 (s,  $\text{OCMe}_3$ ); 35.43 (q,  $^1J_{\text{CH}} = 124$  Hz,  $\text{CH}_2\text{CMe}_3$ ); 34.17 (s,  $\text{CH}_2\text{CMe}_3$ ); 29.98 (q,  $^1J_{\text{CH}} = 126$  Hz,  $\text{OCMe}_3$ ).

$\text{LiOCMe}_3$  did not react with  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$  in  $\text{C}_6\text{H}_6$  after 36 h at  $25^{\circ}$  by  $^1\text{H}$  NMR. (II, 30)

$\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}(\text{OCMe}_3)$  reacted immediately with 1 mol of  $\text{R}_3\text{P}=\text{CH}_2$  (R = Ph, Me) in  $\text{Et}_2\text{O}$  at  $25^{\circ}$  and gave a >90% yield of  $[\text{R}_3\text{PMe}]^+\text{Cl}^-$  (by IR) and a yellow solution.  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}(\text{OCMe}_3)$  (R = Ph) was recovered unchanged from the reaction mixture in 50% yield. The remaining material was a complex mixture by  $^1\text{H}$  NMR (II, 30, 33).

Preparation of  $\text{Ta}(\text{CHDCMe}_3)_3\text{Cl}(\text{OCMe}_3)$  (II, 68)

$\text{Ta}(\text{CHDCMe}_3)_3\text{Cl}(\text{OCMe}_3)$  was prepared similarly from  $\text{Ta}(\text{CHDCMe}_3)_3\text{Cl}_2$ <sup>10b</sup> and  $\text{LiOCMe}_3$ .

IR ( $\text{cm}^{-1}$ ; Nujol/NaCl; II, 68-1A): 2120, m ( $\nu_{\text{C-D}}$ ); 1150, s ( $\nu_{\text{Ta-O}}$ ).

Preparation of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{OCMe}_3)_2$

1. From  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}(\text{OCMe}_3)$  (II, 27)

$\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}(\text{OCMe}_3)$  (0.63 g, 1.25 mmol) dissolved in 25 mL of toluene reacted immediately with solid  $\text{KOCMe}_3$  (0.14 g, 1.25 mmol). After 1 h the solvent was removed in vacuo. The residue was extracted with pentane (50 mL), and filtration gave 0.1 g of KCl (theory 0.09 g). The filtrate was stripped to 15 mL and left to stand at  $-30^\circ$  for 16 h. The mother liquor was decanted and 0.34 g of white crystals were isolated after drying in vacuo. The mother liquid was reduced in volume to 5 mL. Standing at  $-30^\circ$  overnight, gave an additional crop (0.1 g) of pure material (65% yield).

2. From  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$  (I, 59)

$\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$  (1.0 g, 2.15 mmol) dissolved in toluene (25 mL) was reacted with solid  $\text{KOCMe}_3$  (0.48 g, 4.3 mmol) for 16 h at  $25^\circ$ . Following the above procedure, gave after work-up 0.77 g of white needles.

An analytically pure sample was obtained by sublimation at  $80^\circ$  and  $1\mu$ .

$\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{OCMe}_3)_2$  is stable at  $80^\circ$  in  $\text{C}_6\text{H}_6$  for at least 5 days, by  $^1\text{H}$  NMR (I, 59-2,3) (71% yield).

3. From  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$  (III, 10)

An ether solution (10 mL) containing  $\text{HOCMe}_3$  (0.074 g, 1.0 mmol) was added dropwise to an ether solution of  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$  (0.47 g,

1 mmol) at  $-78^{\circ}$ . No visible reaction was observed after warming to  $25^{\circ}$  for 16 h. The volume was reduced until crystallization occurred (ca. 6 mL), filtration gave 70 mg of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{OCMe}_3)_2$  as a pure product. The mother liquid was stripped to an orange oil, containing  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$  as the major constituent, by  $^1\text{H}$  NMR (26% yield). Anal. (II, 29; I, 59-1): Calcd. for  $\text{TaC}_{23}\text{H}_{51}\text{O}_2$ : C, 51.10; H, 9.50. Found: C, 51.21; H, 9.38.

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 90 MHz; I, 59-1;  $25^{\circ}$ ): 1.63 (s, 18,  $\text{OCMe}_3$ ); 1.22 (s, 27,  $\text{CH}_2\text{CMe}_3$ ); 1.2 (s, 6,  $\text{CH}_2\text{CMe}_3$ ).

$\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$  (0.23 g, 0.5 mmol) pentane (10 mL) reacted throughout a dropwise addition of a pentane solution (2 mL) containing  $\text{HOOCMe}_3$  (0.5 mmol) at  $25^{\circ}$ . Well-formed white crystals (0.11 g), rained from solution, and were isolated by filtration and dried in vacuo.

This completely insoluble product gave an IR spectrum different from the spectrum obtained for the compound formulated as  $[\text{Ta}(\text{O})(\text{CH}_2\text{CMe}_3)_3]_x$ .<sup>11</sup>  
IR ( $\text{cm}^{-1}$ ; Nujol/NaCl; I, 7-1): 990 br s ( $\nu_{\text{Ta-O}}$ ), (I,7)

Preparation of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4(\text{OCMe}_3)$  (II, 54; III, 47)

$\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}(\text{OCMe}_3)$  (5.77 g, 11.5 mmol) dissolved in 60 mL of  $\text{Et}_2\text{O}$  reacted quickly with solid  $\text{LiCH}_2\text{CMe}_3$  (0.9 g, 11.5 mmol) at  $-30^{\circ}$ . After 20 min at  $25^{\circ}$ , the yellow solution was filtered (LiCl isolated, 0.45 g; theory, 0.49 g) and stripped. The remaining yellow solid was extracted with 10-15 mL of pentane, and filtered. The filtrate was cooled to  $-30^{\circ}$  (16 h) and gave 5.8 g of crude product isolated by

filtration as a yellow solid. Recrystallization from concentrated pentane solutions at  $-30^\circ$  gave 2 crops of large yellow prisms (3.69 g), (59% yield).  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4(\text{OCMe}_3)$  is very soluble in hydrocarbon solvents. It is unstable in solution and in the solid state decomposing under nitrogen to  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_2(\text{OCMe}_3)$  after 24 h at  $25^\circ$  (see below).

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 270 MHz; II, 66-1B through 7B;  $+10$  to  $-90^\circ$ ):

( $+10^\circ$ ): 1.555 (s, 8,  $\underline{\text{CH}_2\text{CMe}_3}$ ); 1.408 (s, 9,  $\underline{\text{OCMe}_3}$ ); 1.269 (s, 36,  $\text{CH}_2\text{CMe}_3$ ). ( $-20^\circ$ ): coalescence of  $\text{CMe}_3$  (axial) and  $\text{CMe}_3$  (equatorial) resonances. ( $-40^\circ$ ): 51 Hz separation between  $\text{CMe}_3$  (axial, br) and  $\text{CMe}_3$  (equatorial, br).  $T_c = 253 \pm 10$  K,  $\Delta\nu = 51 \pm 10$  Hz,  $\Delta G^\ddagger = 12.4 \pm 0.8$  kcal mol $^{-1}$ . ( $-25^\circ$ ): coalescence of  $\text{CH}_2$  (axial) and  $\text{CH}_2$  (equatorial) resonances. ( $-70^\circ$ ): 74 Hz separation between  $\text{CH}_2$  (axial, br) and  $\text{CH}_2$  (equatorial, sharpening).  $T_c = 248 \pm 10$  K,  $\Delta\nu = 74 \pm 10$  K,  $\Delta G^\ddagger = 12.0 \pm 0.8$  kcal mol $^{-1}$ .

The  $\text{OCMe}_3$  resonance (assumed axial) exhibits a strong temperature dependent shift over the temperature range studied ( $T = +10^\circ$ ,  $\delta = 1.408$ ;  $T = -90^\circ$ ,  $\delta = 1.254$ ). The weighted average of the chemical shift for the  $\text{CH}_2$  resonances ( $-70^\circ$ ) was 1.550 ppm (found: 1.555 ppm). The weighted average of the chemical shift for the  $\text{CMe}_3$  neopentyl resonances ( $-70^\circ$ ) was 1.283 ppm (found: 1.269 ppm).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 67.89 MHz; II, 66-8B, 9B;  $\{^1\text{H}\}$  and gated  $\{^1\text{H}\}$ ;  $-30^\circ$ ):

104.3 (t,  $^1J_{\text{CH}} = 115$  Hz, equatorial  $\underline{\text{CH}_2\text{CMe}_3}$ ); 92.0 (t,  $^1J_{\text{CH}} = 111$  Hz, axial  $\underline{\text{CH}_2\text{CMe}_3}$ ); 82.1 (s,  $\underline{\text{OCMe}_3}$ ); 46.1 (s, axial  $\underline{\text{CH}_2\text{CMe}_3}$ ); 36.1 (q,

$^1J_{\text{CH}} = 122$  Hz, equatorial  $\underline{\text{CH}_2\text{CMe}_3}$ ); 35.3 (q,  $^1J_{\text{CH}} = 122$  Hz, axial  $\underline{\text{CH}_2\text{CMe}_3}$ ); 30.8 (q,  $^1J_{\text{CH}} = 124$  Hz,  $\underline{\text{OCMe}_3}$ ); 30.3 (s, equatorial  $\underline{\text{CH}_2\text{CMe}_3}$ ).

IR ( $\text{cm}^{-1}$ ; Nujol/NaCl; II, 66-1B): 990, br s ( $\nu_{\text{Ta-O}}$ ).

$\text{Ta}(\text{CHDCMe}_3)_4(\text{OCMe}_3)$  can be prepared from  $\text{Ta}(\text{CHDCMe}_3)_3\text{Cl}(\text{OCMe}_3)$  using a similar procedure (II, 68).

IR ( $\text{cm}^{-1}$ ; Nujol/NaCl; II, 68-1B): 2130, br w ( $\nu_{\text{C-D}}$ ).

Preparation of  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_2(\text{OCMe}_3)$  (II, 38)

In a typical reaction, yellow  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4(\text{OCMe}_3)$  (freshly recrystallized and free of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}(\text{OCMe}_3)$ ) was stirred for 24 h in pentane at 25°, giving a homogeneous orange solution. Removal of the solvent in vacuo gave a >90% yield of  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_2(\text{OCMe}_3)$ , by  $^1\text{H}$  NMR. A more convenient preparation of  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_2(\text{OCMe}_3)$  was obtained from the sublimation of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4(\text{OCMe}_3)$  at 60° and  $1\mu$  depositing orange crystals on an ice cooled probe.  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_2(\text{OCMe}_3)$  is extremely air and water sensitive and can be recrystallized in low yield, from a concentrated pentane solution at -30, as soft crystals which melt at ~28°.

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 90 MHz; II, 38-2A; 25°): 4.12 (s, 1,  $\text{CHCMe}_3$ ); 1.36 (s, 9,  $\text{CHCMe}_3$ ); 1.34 (s, 9,  $\text{OCMe}_3$ ); 1.21 (s, 18,  $\text{CH}_2\text{CMe}_3$ ); 0.83 (s, 4,  $\text{CH}_2\text{CMe}_3$ ).  
 $^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 67.89 MHz; II, 62-5A, 6A; gated  $\{^1\text{H}\}$ ; 25°): 237.9 (d,  $^1J_{\text{CH}} = 89$  Hz,  $\text{CHCMe}_3$ ); 92.0 (t,  $^1J_{\text{CH}} = 108$  Hz,  $\text{CH}_2\text{CMe}_3$ ); 83.7 (s,  $\text{OCMe}_3$ ); 45.7 (s,  $\text{CHCMe}_3$ ); 35 (q,  $^1J_{\text{CH}} \cong 129$  Hz,  $\text{Bu}^t \text{C}_\gamma$ ); 33.1 (q,  $^1J_{\text{CH}} \cong 128$  Hz,  $\text{OCMe}_3$ ).

IR ( $\text{cm}^{-1}$ ; Nujol/NaCl; II, 49-1B): 2800, br w ( $\nu_{\text{C-H}_\alpha}$ ); 1025, s ( $\nu_{\text{Ta-O}}$ ).

$\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_2(\text{OCMe}_3)$  slowly decomposed in benzene in the presence of excess  $\text{PMe}_3$  at 85° (72 h) giving neopentane as the only product by  $^1\text{H}$  NMR (III, 30). Photolysis, with broad-band UV light, of a similar

benzene solution in a Pyrex tube, gave the same result as found thermally, after a 2 hr exposure (II, 38).

Reaction of Ta(CHCMe<sub>3</sub>)(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>(OCMe<sub>3</sub>) with Acetone (III, 53)

Ta(CHCMe<sub>3</sub>)(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>(OCMe<sub>3</sub>) (1.36 g, 2.92 mmol) in 40 mL of pentane reacted immediately with acetone (0.17 g, 2.92 mmol). Removal of the solvent in vacuo gave an oil which was dissolved in 20 mL of Et<sub>2</sub>O. Addition of 5 mL of acetonitrile clouded the solution. Filtering and standing for 16 h at -30° gave 0.52 g of lime-green crystals. After repeated recrystallizations, a product of >90% purity was obtained. The major product was tentatively identified as Ta(O)(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>(OCMe<sub>3</sub>) by <sup>1</sup>H and <sup>13</sup>C NMR and by IR (yield 43%).

The organic product obtained from the above reaction was 2,4,4-trimethyl-2-pentene (ca. 1 equivalent Ta<sup>-1</sup>) by <sup>1</sup>H NMR and by coinjection with an authentic sample by GLC analysis (column A) (II, 59).

<sup>1</sup>H NMR (δ; C<sub>6</sub>D<sub>6</sub>; 90 MHz; III, 53-9; 25°): 1.75 (d, 2, J<sub>HH</sub>, ≈ 6 Hz, CH<sub>A</sub>H<sub>B</sub>CMe<sub>3</sub>); 1.48 (s, 9, OCMe<sub>3</sub>); 1.32 (d, 2, CH<sub>A</sub>H<sub>B</sub>CMe<sub>3</sub>); 1.29 (s, 18, CH<sub>A</sub>H<sub>B</sub>CMe<sub>3</sub>).

<sup>13</sup>C NMR (δ; C<sub>6</sub>D<sub>6</sub>; 15 MHz; III, 53-4 through 8; {<sup>1</sup>H} and gated {<sup>1</sup>H}; 25°): 95.7 (t, <sup>1</sup>J<sub>CH</sub> = 112 Hz, CH<sub>2</sub>CMe<sub>3</sub>); 81.3 (s, OCMe<sub>3</sub>); 36.0 (s, CH<sub>2</sub>CMe<sub>3</sub>); 34.7 (q, <sup>1</sup>J<sub>CH</sub> = 125 Hz, CH<sub>2</sub>CMe<sub>3</sub>); 31.3 (q, <sup>1</sup>J<sub>CH</sub> = 126 Hz, OCMe<sub>3</sub>).

IR (cm<sup>-1</sup>; Nujo1/NaCl; II, 59-1): 1014, br s (ν<sub>Ta-O</sub>).

Thermal Decomposition of Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>4</sub>(OCMe<sub>3</sub>) (IX, 35, 36)

1. Followed by <sup>1</sup>H NMR

The decomposition of Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>4</sub>(OCMe<sub>3</sub>) was studied at different temperatures in C<sub>6</sub>D<sub>6</sub> using several internal NMR standards (e.g. dioxane, Ph<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub> and HMDS).

In a typical experiment, a standard solution of Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>4</sub>(OCMe<sub>3</sub>) (0.64 g, 1.19 mmol) was prepared using 3 mL of C<sub>6</sub>D<sub>6</sub> containing Ph<sub>2</sub>CH<sub>2</sub> (0.10 g, 0.594 mmol). A sample (~0.7 mL) was drawn, sealed in an NMR tube and kept cold until run. The sample was thermally equilibrated to probe temperature and the data was collected by integrating the growth of H<sub>α</sub> for Ta(CH<sub>α</sub>CMe<sub>3</sub>)(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>(OCMe<sub>3</sub>) vs. Ph<sub>2</sub>CH<sub>2</sub>, with time.

Assuming the rate of formation of Ta(CHCMe<sub>3</sub>)(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>(OCMe<sub>3</sub>) follows first-order kinetics, a rate constant k was calculated by a linear least squares fit of time vs. ln[(A<sub>0</sub>-B<sub>i</sub>)/(A<sub>0</sub>-B)] (A<sub>0</sub> ≡ mmol Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>4</sub>(OCMe<sub>3</sub>); B ≡ mmol of Ta(CHCMe<sub>3</sub>)(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>(OCMe<sub>3</sub>) at t). The correlation coefficients (r) and the half-life was calculated for these data (II, 46, 48; III, 43). These results are summarized in the text.

In one experiment the thermal decomposition of Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>4</sub>(OCMe<sub>3</sub>) (0.10 g) in CDCl<sub>3</sub> (~0.7 mL) contained ~1 equivalent Ta<sup>-1</sup> of TMS. The sample was then immediately placed in the NMR and equilibrated. The data was collected by measuring the growth of neopentane relative to the TMS using peak heights. The error for this run was determined to be <50%, due to the method of data collection and the uncertainty in the amount of neopentane produced, since Ta(CHCMe<sub>3</sub>)(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>(OCMe<sub>3</sub>) reacts with CDCl<sub>3</sub> (~24 h) at 25° to give an unidentified product (IV, 28).

The results for this experiment were calculated using the method above and are tabulated in the text.

## 2. Followed by GLC

$\text{Ta}(\text{CH}_2\text{CMe}_3)_4(\text{OCMe}_3)_4$  (0.13 g, 0.25 mmol) was dissolved in freshly dried xylenes (15 mL) containing n-octane (20.3  $\mu\text{L}$ , 0.125 mmol) as an internal GLC standard. An initial sample was taken prior to the placement of the reaction mixture in a constant temperature bath, maintained at  $40 \pm 0.5^\circ\text{C}$ . Samples were then periodically withdrawn and quenched with acetone by the same procedure used in the kinetic study of the reaction of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$  with 2 mol  $\text{LiCH}_2\text{CMe}_3$  (see text). The amount of 2,4,4-trimethyl-2-pentene formed was measured vs. n-octane (column A, isothermal  $70^\circ$ ) using an experimental determined response factor (III, 19). The results for this experiment were calculated using the method above (1) (see text).

## 3. Determination of $k_H/k_D$ (II, 68)

$\text{Ta}(\text{CHDCMe}_3)_4(\text{OCMe}_3)$  (0.15 g) was stirred in pentane (~3 mL) for 24 h at  $30^\circ$ . The reaction mixture was quenched with dry acetone (~0.1 mL) under nitrogen and passed down a short column of alumina. The deuterated 2,4,4-trimethyl-2-pentene formed was analyzed, using column B, by GC/MS.<sup>25</sup> The results obtained gave a competitive isotope effect  $k_H/k_D = 6 \pm 1$  (GC-MS, 2). The competitive isotope effect was similarly measured for deuterium incorporation in a sample of 2,4,4-trimethyl-2-pentene, obtained after quenching with acetone from the product formed from the slow sublimation of  $\text{Ta}(\text{CHDCMe}_3)_4(\text{OCMe}_3)_2$  (0.15 g) at  $50^\circ$ . The value found for  $k_H/k_D$  was  $6 \pm 1$  (GC-MS, 1).

The Rate of Reaction of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$  with  $\text{LiCH}_2\text{CMe}_3$

1. By GLC (III, 45, 46)

$\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$  (0.233 g, 0.500 mmol) was dissolved in pentane (10 mL) containing mesitylene (68.8  $\mu\text{L}$ , 0.501 mmol) as an internal standard, and placed in a constant temperature bath maintained at  $20 \pm 0.5^\circ\text{C}$ .  $\text{LiCH}_2\text{CMe}_3$  (0.078 g, 1.000 mmol), dissolved in pentane (2 mL), was added rapidly to the stirring Ta solution. After equilibration (~10 s), samples were withdrawn periodically (syringe) and quenched with dry acetone (0.1 mL) under nitrogen for ~3 min, then exposed to air. After 40 min, GLC analysis (column A, isothermal  $80^\circ$ ) showed no further change in the amount of 2,4,4-trimethyl-2-pentane (diisobutylene) formed versus mesitylene, using an experimentally determined response factor (III, 46-1A-3A, 46-1B-15B).

Assuming the rate of formation of  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$  was first order in  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$  (or  $\text{LiCH}_2\text{CMe}_3$ ), a rate constant  $k = 0.050 \pm 0.005 \text{ min}^{-1}$  was calculated by a linear least squares fit of time vs. the  $\ln[(A_0)/(A_0 - C)]$  ( $A_0 \equiv \text{mmol Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ ;  $C \equiv \text{mmol Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$  at  $t$ ). The correlation coefficient ( $r$ ) for these data was 0.91, and  $t_{1/2} = 14 \pm 1 \text{ min}$ .

2. By Chloride Analysis (II, 5, 11, 12, 14, 15)

The experimental detail and data have been previously reported.<sup>10b</sup>

Assuming the rate of formation of  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$  was first order in  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$  (or  $\text{LiCH}_2\text{CMe}_3$ ), a rate constant  $k = 0.08 \pm 0.03 \text{ min}^{-1}$  was calculated by a linear least squares fit of time vs.  $\ln[(A_0)/(A_0 - C)]$  ( $A_0 \equiv \text{mmol Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ ;  $C \equiv \text{mmol Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$  at  $t$ ). The correlation coefficient ( $r$ ) for these data was 0.97, and  $t_{1/2} = 9 \pm 3 \text{ min}$ .

The Rate of Reaction of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$  with  $\text{LiCH}_2\text{CMe}_3$  (II, 15)

The experimental detail has been previously reported.<sup>10b</sup> The results obtained from one run at 22°, indicated an essentially complete reaction (99%) after  $11.5 \pm 1.5$  min. No further data was obtained.

Reaction of  $\text{Ta}(\text{CH}_2\text{C}_6\text{H}_5)_5$  with Acetonitrile

1. Using One Equivalent of Acetonitrile (I, 14)

$\text{Ta}(\text{CH}_2\text{C}_6\text{H}_5)_5$  (1.27 g, 2.1 mmol) was dissolved in a benzene solution (30 mL) containing 0.11 mL of acetonitrile (2.1 mmol) and stirred for 28 h at 58°. Removal of the solvent (in vacuo) gave a dark red oil, seemingly pure by  $^1\text{H}$  NMR. Several crystallization attempts from concentrated toluene/pentane and ether/pentane solutions, gave oils. A trace amount of a yellow oil (not characterized) condensed on the water cooled probe during a sublimation attempt. The oil obtained from this reaction has been tentatively characterized as the pure Z isomer of  $\text{Ta}(\text{CH}_2\text{C}_6\text{H}_5)_3[\text{N}(\text{Me})\text{C}=\text{CH}(\text{C}_6\text{H}_5)]$  (>90% yield).

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 60 MHz; I, 13-1; 30°): 8.00, 7.10, 6.65 (m, 20, phenyl resonances); 5.53 (m, 1, vinylic proton); 2.05 (d, 3,  $J_{\text{HH}} \approx 1$  Hz, vinylic Me); 1.75 (s, 6,  $\text{CH}_2\text{C}_6\text{H}_5$ ).

IR ( $\text{cm}^{-1}$ ; neat oil/NaCl; I, 13-1): 1595, s ( $\nu_{\text{C}=\text{C}}$ ).

$\text{Ta}(\text{CH}_2\text{C}_6\text{H}_5)_5$  heated at 58° in a  $\text{C}_6\text{D}_6$  solution containing one equivalent of benzonitrile, gave after 3h, the benzonitrile analog to the above product. This reaction was followed by  $^1\text{H}$  NMR (I, 13-1A through 17A).

2. Using Two Equivalents of Acetonitrile (I, 11, 12)

Ta(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>5</sub> (0.67 g, 1.05 mmol) was dissolved in a benzene solution (30 mL) containing 0.11 mL of acetonitrile (2.1 mmol) and was refluxed for 4 h. The resultant yellow solution was filtered with a fine frit and stripped to dryness. The crude yellow solid was dissolved in a minimal amount of toluene and small volumes of pentane were added until the solution became cloudy. Standing for 16 h at -30° gave 0.36 g of an amorphous yellow solid.

The product obtained has been tentatively identified as a 2:1

E/Z mixture of Ta(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>[N(Me)C=CH(C<sub>6</sub>H<sub>5</sub>)](CH<sub>3</sub>CN) (59% yield).

<sup>1</sup>H NMR (δ; C<sub>6</sub>D<sub>6</sub>; 60 MHz; I, 12-1; 25°): 7.22 (m, 24, phenyl resonances); 6.50 (m, ~0.5, E isomer vinylic proton); 5.80 (m, ~0.2, Z isomer vinylic proton); 2.31 (br s, ~6, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>); 2.24 (m, ~2, E isomer vinylic Me); 2.20 (m, ~1, Z isomer vinylic Me); 0.75 (s, 3, CH<sub>3</sub>CN). IR (cm<sup>-1</sup>; Nujol/NaCl; I, 12-2): 2320, 2280, sh m (ν<sub>C≡N</sub>); 1595, 1570, s (ν<sub>C=C</sub>).

Thermal Decomposition of Ta(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>5</sub> in the Presence of L (L = CH<sub>3</sub>CN, PMe<sub>3</sub>) Followed by <sup>1</sup>H NMR

1. L = CH<sub>3</sub>CN (I, 43)

Ta(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>5</sub> (0.1 g, 0.16 mmol) was dissolved in C<sub>6</sub>D<sub>6</sub> (~0.8 mL) containing acetonitrile (8.2 μL, 0.16 mmol), and dioxane (4.5 μL) as an internal NMR standard. The sample was placed in a 60° bath and the <sup>1</sup>H NMR was recorded periodically. The amount of toluene produced after a complete reaction was ~1 equivalent Ta<sup>-1</sup> vs. dioxane (I, 43-1 through 4).

2. L = PMe<sub>3</sub> (I, 41)

Ta(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>5</sub> (0.1 g, 0.16 mmol) was dissolved in a 0.13 M solution of dioxane in C<sub>6</sub>D<sub>6</sub> (~0.8 mL), and placed in an NMR tube. PMe<sub>3</sub> (~50 mg, 0.7 mmol) was added and the sample was warmed in a constant temperature bath set at 52 ± 2°. The amount of toluene produced was measured by integration (vs. dioxane) during the course of the reaction. After 145 min, 3 equivalents Ta<sup>-1</sup> of toluene were produced. This yield did not change with time (I, 41-1A through 8A). An attempt to isolate the decomposition product formed gave an intractable oil (I, 41).

Reaction of Ta(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Cl<sub>2</sub> with LiOCMe<sub>3</sub> (II, 62)

Ta(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Cl<sub>2</sub> (2.5 g, 4.8 mmol) was dissolved in Et<sub>2</sub>O (50 mL) and stirred with solid LiOCMe<sub>3</sub> (0.42 g, 5.2 mmol) for 10 h. A color change from deep red to orange was observed after 3 h. The reaction mixture was filtered and stripped to an orange solid. Pentane (50 mL) was added and the suspension was filtered removing the LiCl (0.19 g). The solvent was removed in vacuo and the residue was dissolved in a minimal amount of toluene (~6 mL) and filtered. 15 mL of pentane was added and the solution was cooled to -30 for 4 h, yielding 0.7 g of yellow crystals. Two additional crops (0.26 g) were obtained by adding more pentane and cooling to -30°.

All of the obtained material contained Ta(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>(OCMe<sub>3</sub>)<sub>2</sub> in varying amounts (3rd crop was >95%). Fractional crystallization will give pure Ta(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Cl(OCMe<sub>3</sub>).

$\text{Ta}(\text{CH}_2\text{C}_6\text{H}_5)_3\text{Cl}(\text{OCMe}_3)$  was identified by  $^1\text{H}$  NMR and by the reaction with  $\text{Mg}(\text{CH}_2\text{C}_6\text{H}_5)_2$  (dioxane) (0.5 equivalents). The product obtained from the above reaction  $\text{Ta}(\text{CH}_2\text{C}_6\text{H}_5)_4(\text{OCMe}_3)$ , has been reported by L. Messerle<sup>30</sup> (II, 62).

$\text{Ta}(\text{CH}_2\text{C}_6\text{H}_5)_3\text{Cl}(\text{OCMe}_3)$ :

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 60 MHz; II, 61-1A; 25°): 7.1 (m, 14, phenyl resonances); 2.80 (s, 6,  $\text{CH}_2\text{C}_6\text{H}_5$ ); 1.20 (s, 9,  $\text{OCMe}_3$ ).

$\text{Ta}(\text{CH}_2\text{C}_6\text{H}_5)_3(\text{OCMe}_3)_2$ :

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 60 MHz; II, 61-2A; 25°): 7.1 (m, 16, phenyl resonances); 2.41 (s, 6,  $\text{CH}_2\text{C}_6\text{H}_5$ ); 1.40 (s, 18,  $\text{OCMe}_3$ ).

Preparation of Ta(CHDCMe<sub>3</sub>)<sub>3</sub>Br<sub>2</sub> (IV, 38)

Ta(CHDCMe<sub>3</sub>)<sub>3</sub>Br<sub>2</sub> was prepared in pentane using TaBr<sub>5</sub> and Zn(CHDCMe<sub>3</sub>)<sub>2</sub> following a similar procedure used for the preparation of Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>Br<sub>2</sub>.<sup>18</sup> 0.78 g of product was isolated by sublimation at 100° and 1μ (70% yield).

<sup>1</sup>H NMR (δ; C<sub>6</sub>D<sub>6</sub>; 90 MHz; IV, 38-2B; 25°): 2.64 (br, 3, CHDCMe<sub>3</sub>);

1.30 (s, 27, CHDCMe<sub>3</sub>).

<sup>13</sup>C NMR (δ; C<sub>6</sub>D<sub>6</sub>; 15 MHz; IV, 43-3A through 7A; {<sup>1</sup>H} and gated {<sup>1</sup>H}

25°): 121.5 (tt, <sup>1</sup>J<sub>CD</sub> = 18 Hz, <sup>1</sup>J<sub>CH</sub> ≈ 120 Hz, CHDCMe<sub>3</sub>); 35.5 (q,

<sup>1</sup>J<sub>CH</sub> = 125 Hz, CHDCMe<sub>3</sub>); 34.6 (s, CHDCMe<sub>3</sub>).

IR (cm<sup>-1</sup>; Nujol/NaCl; IV, 38-1): 2120, br m (ν<sub>C-D</sub>).

Preparation of Ta(CRCMe<sub>3</sub>)(CHDCMe<sub>3</sub>)<sub>3</sub> R = H or D (IV, 43)

Ta(CHDCMe<sub>3</sub>)<sub>3</sub>Br<sub>2</sub> (0.43 g, 0.78 mmol) was reacted with LiCHDCMe<sub>3</sub> (0.12 g, 1.56 mmol) in 20 mL of pentane (3 h). Ta(CRCMe<sub>3</sub>)(CHDCMe<sub>3</sub>)<sub>3</sub> (R = H or D, 0.33 g) was isolated by sublimation (90% yield).

<sup>13</sup>C NMR (δ; C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 67.89 MHz; IV 73-1A through 5A; {<sup>1</sup>H} and gated

{<sup>1</sup>H}; -50 and 30°): (-50°): 249.3 (d, <sup>1</sup>J<sub>CH</sub> = 90 Hz, CHCMe<sub>3</sub>);

248.3 (t, <sup>1</sup>J<sub>CD</sub> = 13.2 Hz, CDCMe<sub>3</sub>); 114.1 (CH<sub>2</sub>CMe<sub>3</sub>); 113.0 (dt,

<sup>1</sup>J<sub>CD</sub> = 14.9 Hz, J<sub>CH</sub> = 105 Hz, CHDCMe<sub>3</sub>). All other resonances have been reported.<sup>10b</sup>

(30°): 113.0 (dt, <sup>1</sup>J<sub>CD</sub> = 14.9 Hz, J<sub>CH</sub> = 105 Hz, CHDCMe<sub>3</sub>).

Chapter 2

The Synthesis, Characterization, and Reactivity  
of Octahedral Tantalum and Niobium Alkylidene Complexes

## Introduction

Recently, it has been found that complexes of the type  $M(\text{CH}_2\text{R})_2\text{X}_3$  ( $M = \text{Nb}$  or  $\text{Ta}$ ;  $\text{R} = \text{CMe}_3$ ,  $\text{Ph}$ , or  $\text{SiMe}_3$ ;  $\text{X} = \text{Cl}$  or  $\text{Br}$ ) react with 2 or more donor ligands to give a mixture of *cis,mer*- and *trans,mer*- $M(\text{CHR})\text{X}_3\text{L}_2$  ( $\text{L} = \text{PMe}_3$ ,  $\text{PMe}_2\text{Ph}$ ,  $\text{PMePh}_2$ ,  $\text{Py}$ ,  $\text{THF}$ ).<sup>26</sup> The rates of these reactions vary qualitatively in the following order:

for  $\text{R} = \text{CMe}_3 > \text{Ph} \sim \text{SiMe}_3$ ,  $\text{X} = \text{Br} > \text{Cl}$ ,  $\text{L} = \text{PMe}_3 > \text{PMe}_2\text{Ph} > \text{PMePh}_2$ , and for solvent = dichloromethane  $\sim$  chloroform  $>$  pentane.

The reaction of octahedral  $\text{Ta}(\text{CHR})\text{X}_3\text{L}_2$  (where  $\text{X} = \text{Cl}$ ,  $\text{L} = \text{PMe}_3$ ,  $\text{R} = \text{CMe}_3$  or  $\text{Ph}$ ), with an excess of  $\text{R}'\text{CH}=\text{CH}_2$  (where  $\text{R}' = \text{H}$ ,  $\text{Me}$ , or  $\text{Ph}$ ), gives  $\text{Ta}(\text{R}'\text{CH}=\text{CH}_2)\text{Cl}_3(\text{PMe}_3)_2$  in high yields. These reactions give only those organic products which are believed to be formed by rearrangement\* via a metallacyclobutane intermediate.<sup>15c</sup> The intermediacy of metallacyclobutanes in these reactions, is supported by studies involving the reaction of  $\text{Ta}(\text{CHPh})\text{Cl}_3(\text{PMe}_3)_2$  with 4-methylstyrene.<sup>26</sup>

In contrast, the reaction of octahedral  $M(\text{CHR})\text{X}_3\text{L}_2$  ( $M = \text{Nb}$  or  $\text{Ta}$ ,  $\text{X} = \text{Cl}$ ,  $\text{L} = \text{THF}$ ) with  $\alpha$ -olefins gives only metathesis-type products<sup>5,27</sup> rather than rearrangement products. Recently, Schrock found that complexes of the type  $M(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ , (prepared by reacting  $M(\text{CHCMe}_3)\text{Cl}_3(\text{PMe}_3)_2$  with 2 mol of  $\text{LiOCMe}_3$ ),<sup>18</sup> function as active metathesis catalysts for *cis*-2-pentene.<sup>27</sup>

This work deals with the formation, characterization, and reaction chemistry with olefins, of octahedral alkylidene complexes of the type  $M(\text{CHCMe}_3)\text{Cl}_3(\text{PMe}_3)_2$  and their substituted analogs.

\*Rearrangement is defined as a process whereby a metallacyclobutane or pentane complex decomposes by  $\beta$ -hydride elimination forming an alkenyl metal hydride, which may or may not isomerize prior to a reductive elimination step.

## Results and Discussion

### Octahedral Complexes: Halides, Synthesis and Characterization of Dimeric Neopentylidene Complexes

Addition of 1 mol (or an excess) of  $\text{PMe}_3$  to a pentane solution containing  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$  (22) gives an immediate reaction and precipitation of slightly soluble red crystals. The product,  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3(\text{PMe}_3)$  (23), isolated in nearly quantitative yield, has been shown to be of trans,mer-octahedral geometry, by low temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR.<sup>18</sup>

The  $^{31}\text{P}\{^1\text{H}\}$  NMR of 23 (ca. 0.15 M in toluene) at  $-90^\circ$  shows a singlet at -12 ppm. Warming to  $-40^\circ$ , a second singlet appears at +29 ppm (~15% of the mixture). This is apparently due to a second isomer of 23, since with increased temperature both peaks move upfield and broaden at nearly the same rate.

Plotting the chemical shift for the major isomer vs.  $^\circ\text{K}$  gives an exponential function which asymptotically approaches a value of -10.5 ppm at  $0^\circ\text{K}$ . The difference between the observed chemical shift for 23 and the shift of 23 at  $0^\circ\text{K}$  (-10.5 ppm) divided by the difference in shift between free  $\text{PMe}_3$  (-62 ppm) and 23 at  $0^\circ\text{K}$ , times the original concentration of 23 in solution gives a measure of the concentration of 23 at any temperature. Assuming that the concentration of free  $\text{PMe}_3$  equals the concentration of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$  then an equilibrium constant ( $K_{\text{eq}}$ ) can be calculated for the association of  $\text{PMe}_3$  with  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$  according to equation 1 and these results are

$$K_{\text{eq}} = \frac{[\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3(\text{PMe}_3)]}{[\text{PMe}_3][\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3]} \quad (1)$$

Table II. Thermodynamic Data for the Association of  $\text{PMe}_3$  with  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$

T(K)	$\delta^a\text{Ta}(\text{ppm})$	$\Delta^b\text{Ta}$	$\Delta\text{P}^c$	$K_{\text{eq}}^d$
298 <sup>e</sup>	---	---	---	130
293	-23	39	12	91
283	-21	42	10	140
278	-19	43	9	200
273	-19	43	8	220
253	-16	46	5	620
243	-15	47	4	880
233	-14	48	4	1100
213	-13	49	3	2500
183	-12	50	2	5300

<sup>a</sup> $\delta\text{Ta}$  = the chemical shift of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2(\text{PMe}_3)$  ( $\pm 0.5$  ppm) measured downfield of external 85%  $\text{H}_3\text{PO}_4$ .

<sup>b</sup> $\Delta\text{Ta}$  = chemical shift of free  $\text{PMe}_3$  (-62 ppm) -  $\delta\text{Ta}$ .

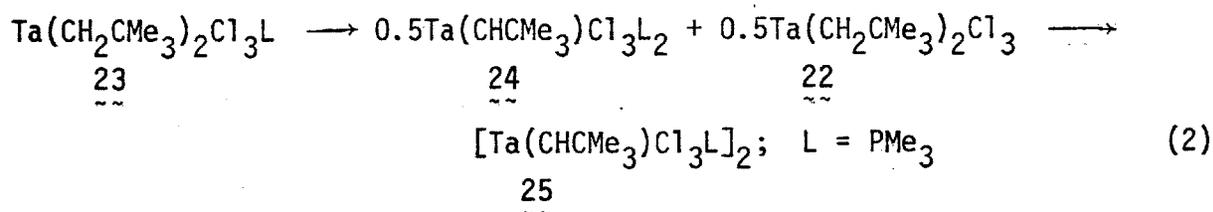
<sup>c</sup> $\Delta\text{P}$  =  $\delta\text{Ta}$  minus the chemical shift of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}(\text{PMe}_3)$  extrapolated to 0°K (-10.5 ppm).

<sup>d</sup> $K_{\text{eq}} = [\text{A}]/[\text{B}][\text{C}] = [\Delta\text{Ta}][343]/[\Delta\text{P}]^2$  with  $[\text{A}] = [\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3(\text{PMe}_3)] = [\Delta\text{Ta}]/343$  and, assuming  $[\text{B}] = [\text{C}] = [\text{PMe}_3]$ ,  $[\text{B}] = [\Delta\text{P}]/343$ , for a  $0.15 \pm 0.05$  M solution of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3(\text{PMe}_3)$  at time zero.

<sup>e</sup>Calculated from a linear least squares plot of  $\ln(K_{\text{eq}})$  vs.  $1/T$ .  $\Delta\text{H}^\circ = 4 \pm 1 \text{ kcal mol}^{-1}$  and  $\Delta\text{S}^\circ = -4 \pm 2 \text{ eu}$  with  $r = 0.97$ .

presented in Table II. Plotting  $\ln[K_{eq}]$  versus  $1/T$  gives a linear plot ( $r = 0.97$ ). From this plot  $\Delta H^\circ$  and  $\Delta S^\circ$  were found to be  $4 \pm 1$  kcal mol<sup>-1</sup> and  $-4 \pm 2$  eu, respectively. This gives a  $\Delta G^{298}$  of  $5 \pm 4$  kcal mol<sup>-1</sup>. Reading from the above plot shows that Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub>(PMe<sub>3</sub>) is ca. 20% dissociated at 25°. This fact sharply contrasts Ta(CH<sub>2</sub>Ph)<sub>2</sub>Cl<sub>3</sub>(PMe<sub>3</sub>) which shows little dissociation at room temperature.<sup>26</sup> These data support that Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub>(PMe<sub>3</sub>) readily disproportionates into Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub> and Ta(CHCMe<sub>3</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub> whereas Ta(CH<sub>2</sub>Ph)<sub>2</sub>Cl<sub>3</sub>(PMe<sub>3</sub>) gives low yields of Ta(CHPh)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub> only under forced conditions.

After several hours (~4) at 25°, 23 (in ether) disproportionates to give a 1:1 mixture of Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub> and Ta(CHCMe<sub>3</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub> (24), thus confirming the lability of PMe<sub>3</sub> in 23. Standing equal amounts of Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub> (22) and Ta(CHCMe<sub>3</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>, or Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub>(PMe<sub>3</sub>), in ether for 48 h gives large deep red crystals of [Ta(CHCMe<sub>3</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>] (25) in high yield (equation 2).



If a more bulky phosphine is used the dimer formation is slowed considerably. For example, the reaction of Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub> with 1 mol of PPr<sub>3</sub><sup>n</sup>, in pentane, gives [Ta(CHCMe<sub>3</sub>)Cl<sub>3</sub>(PPr<sub>3</sub><sup>n</sup>)<sub>2</sub>] only after 5 d at 25°.

The dimeric structure has been confirmed for 25 by molecular weight measurement<sup>18</sup> and recently by neutron diffraction<sup>28</sup> (Figure ~).

The structure of 25 shows that each Ta atom possesses distorted octahedral geometry and forms an edge-sharing dimer with a center of

inversion located midway between two Ta atoms. In the neopentylidene ligand, C(2), C(1), H(1), and Ta form a plane which is aligned along the C(3), Ta, C(1) axis.

The Ta-C(1) (Ta-C<sub>α</sub>) distance of 1.898(2) Å found for 25, suggests a significant amount of multiple bond character in the Ta-neopentylidene bond. In fact, Ta-C<sub>α</sub> is only slightly longer than a Ta-carbon triple-bond length (1.849(8) Å) found in the benzylidyne complex Ta( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)(CCMe<sub>3</sub>)Cl(PMe<sub>3</sub>)<sub>2</sub><sup>29</sup> and is considerably shorter than the average "double bond" length found for three 18-electron complexes of the type TaCp<sub>2</sub>(CHR)X (Ta=C<sub>α</sub> ≈ 2.04 Å)<sup>31</sup>.

A Ta-C(1)-C(2) bond angle of 161.2(1)°, nearly the average of the values found for TaCp<sub>2</sub>(CHCMe<sub>3</sub>)Cl (150.4(5)°)<sup>31</sup> and Ta(C<sub>5</sub>Me<sub>5</sub>)(CCMe<sub>3</sub>)Cl(PMe<sub>3</sub>)<sub>2</sub> (171.8(6)°)<sup>29</sup>, further supports the presence of greater than double bond character in Ta-C<sub>α</sub>.

Another feature of 25 is that the C(1)-H(1) distance, 1.131(3) Å is ca. 0.048 Å longer than the average distance found for the remaining 18 independent methyl C-H distances. Also, the Ta...H(1), (Ta-H<sub>α</sub>) distance, 2.119(4) Å, is less than the sum of van der Waals radii for each atom. In fact, the Ta...H(1) distance is only ca. 0.15 Å longer than what might be expected for a bridging hydride of Ta, Ta-H-Ta.<sup>28a</sup>

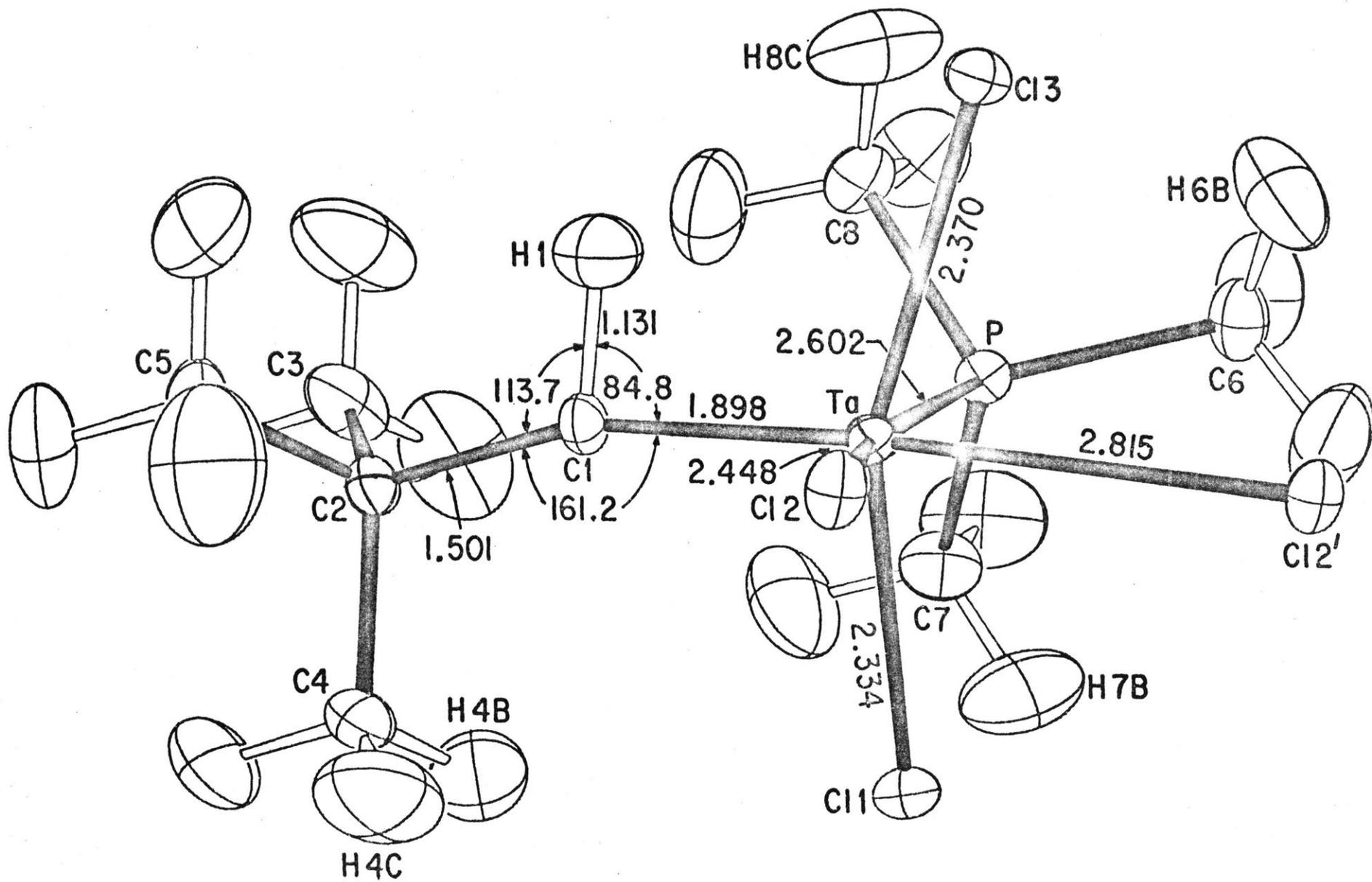
A Ta-C(1)-H(1) bond angle of 84.8(2)°, showing H<sub>α</sub> to be slightly oriented towards Ta, and the greater than normal double bond character in Ta-C<sub>α</sub>, suggest an interaction between Ta and H<sub>α</sub>.

Consistent with the above data, is a valence bond description somewhere between an unsymmetrical bridging hydride in a three-center, two- (or six-) electron bond (I), and a "T" shaped coordination geometry about C<sub>α</sub> arising from a bond between a carbon pure 2p orbital

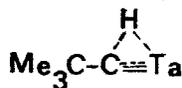
Figure 1a. The Neutron Diffraction Structure of  $[\text{Ta}(\text{CHCMe}_3)\text{Cl}_3(\text{PMe}_3)]_2$



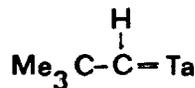
Figure 1b. The Neutron Diffraction of a Single Tantalum Octahedral  
Core in  $[\text{Ta}(\text{CHCMe}_3)\text{Cl}_3(\text{PMe}_3)]_2$



and a hydrogen 1s orbital (II).



I



II

A comparison of  $J_{\text{CH}}$ ,  $\nu_{\text{CH}}$ , and the degree of distortion in the Ta-C<sub>α</sub>-H<sub>α</sub> bond of 25 to another alkylidene complex with less than 18 electrons, Ta(C<sub>5</sub>Me<sub>5</sub>)(CHCMe<sub>3</sub>)(C<sub>2</sub>H<sub>4</sub>)(PMe<sub>3</sub>)<sup>32</sup>, indicates that the  $J_{\text{CH}}$  and  $\nu_{\text{CH}}$  values are a reasonable measure of this distortion. Ta(C<sub>5</sub>Me<sub>5</sub>)(CHCMe<sub>3</sub>)(C<sub>2</sub>H<sub>4</sub>)(PMe<sub>3</sub>) shows lower  $J_{\text{CH}}$  and  $\nu_{\text{CH}}$  values, and, in a recent neutron diffraction study,<sup>28b</sup> a greater distortion than 25 in the Ta-C<sub>α</sub>-H<sub>α</sub> bond (favoring bond description I). In conclusion, the lower the  $J_{\text{CH}}$  and  $\nu_{\text{CH}}$  values observed, the greater the distortion, hence the greater the Ta-H<sub>α</sub> interaction.

### Octahedral Complexes: Halides; Synthesis and Characterization of Olefin Complexes

The reaction of Ta(CHCMe<sub>3</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub> with ethylene to give Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub> (26), has been reported.<sup>18</sup> 26 can also be prepared from Ta(CH<sub>2</sub>CMe<sub>3</sub>)Cl<sub>4</sub>(PMe<sub>3</sub>)<sub>2</sub> and Zn(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> in toluene at -78°, or by reacting ethylene and PMe<sub>3</sub> with [TaCl<sub>3</sub>(THT)]<sub>2</sub>(THT)<sup>33</sup> in toluene at 60° (see Experimental). NMR studies of 26 suggest that the phosphine ligands are trans and equivalent.

26 does not exchange rapidly with free PMe<sub>3</sub> on the NMR timescale, at temperatures below ca. 100°. However, addition of free PMe<sub>2</sub>Ph to a benzene solution containing 26, slowly gives Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> and free PMe<sub>3</sub> after several hours (25°), by <sup>31</sup>P NMR. This indicates slow exchange of PMe<sub>2</sub>Ph for PMe<sub>3</sub> on a chemical time scale.

$[\text{Ta}(\text{CHCMe}_3)\text{Cl}_3\text{L}]_2$ , where  $\text{L} = \text{PMe}_3, \text{PPr}_3^n$ , in toluene, reacts with ethylene to give an insoluble violet powder 27, which reacts quantitatively with added  $\text{L}$  to give  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3\text{L}_2$ . The insolubility of 27 suggests its formulation to be  $[\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{L})]_x$ , where  $x \geq 2$ .

The  $^1\text{H}$  NMR spectrum of 27 ( $\text{L} = \text{PMe}_3$ ) shows a complex pattern (centered at 3.04 ppm) due probably to the olefinic resonances, and a doublet for  $\text{PMe}_3$  at 1.35 ppm ( $J_{\text{HP}} = 9.0$  Hz) merged with several unassignable resonances. Only two  $\text{PMe}_3$  containing complexes must be present since only two singlet resonances are observed at -8 and -12 ppm, in a 3:1 ratio, respectively.

The  $^{13}\text{C}$  NMR of 27 ( $\text{L} = \text{PPr}_3^n$ ) shows a complex spectrum with  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PPr}_3^n)_2$  being the only identifiable species present.

Addition of one equivalent of  $\text{PMe}_2\text{Ph}$  to 27 ( $\text{L} = \text{PMe}_3, \text{PPr}_3^n$ ), yields a mixture of  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3\text{L}_2$  (1 part),  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_2\text{Ph})\text{L}$  (28) (3 parts), and  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_2\text{Ph})_2$  (29) (2 parts).

The  $^1\text{H}$  NMR spectra for the mixtures where  $\text{L} = \text{PMe}_3$  and  $\text{L} = \text{PPr}_3^n$ , show that the patterns observed for the olefinic resonances in  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_2\text{Ph})\text{L}$  (28) (centered at ca. 3 ppm), are consistent with AA'BB'XY multiplets.<sup>34</sup> In addition, the olefinic resonances for each symmetrical phosphine complex (e.g.  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3\text{L}_2$ ) are single resonances coupled to two equivalent phosphine ligands.

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum for a mixture containing 28 where  $\text{L} = \text{PMe}_3$ , shows single resonances at -4 and 7 ppm for the symmetrical phosphine complexes, 26 and 29 respectively, and an AB multiplet ( $J_{\text{pp}} = 151$  Hz) for the mixed phosphine complex. These data are consistent with the phosphine ligands being trans.

The olefinic carbons for  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_2\text{Ph})(\text{PPr}_3^n)$  at 62.2 ( $^1J_{\text{CH}} = 150$  Hz) and 61.1 ppm ( $^1J_{\text{CH}} = 149$  Hz), and the above  $^1\text{H}$  and

$^{31}\text{P}$  NMR data, show that the olefin must be aligned along the L-Ta-L' axis.

$\text{Ta}(\text{PhCH}=\text{CH}_2)\text{Cl}_3(\text{PMe}_3)_2$  also has been shown to contain trans-coupled  $\text{PMe}_3$  ( $J_{\text{pp}}$  = 150 Hz) and is believed to be of the same structure as the above complexes. The 89.9 MHz  $^1\text{H}$  NMR spectrum of  $\text{Ta}(\text{PhCH}=\text{CH}_2)\text{Cl}_3(\text{PMe}_3)_2$  shows two "virtually coupled" triplets for the  $\text{PMe}_3$  ligands. Warming to  $140^\circ$  gives a broad doublet centered near the average of the chemical shifts for the room temperature  $\text{PMe}_3$  triplets, and the olefinic resonances are sharp and coupled. It is difficult to distinguish which process occurs at this temperature, phosphine exchange or olefin rotation. Regardless of this difficulty, the phosphines coalesce at or near  $130^\circ$  to give, for either process, a  $\Delta G^\ddagger \geq 20 \text{ kcal mol}^{-1}$ .

$\text{Ta}(\text{CHCMe}_3)\text{Cl}_3(\text{THF})_2$  in ether or toluene reacts with ethylene to give a brown solution and no isolable organometallic product. However, if the reaction is carried out in THF, blue crystals of  $[\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{THF})_2]_x$  can be isolated in 60% yield.  $[\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{THF})_2]_x$  <sup>33</sup> is soluble in THF and only slightly soluble in aromatic solvents.

$[\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{THF})_2]_x$  reacts with 2 mol of  $\text{PMe}_3$  to give a nearly quantitative yield of  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  and 2.0 equivalents  $\text{Ta}^{-1}$  of THF, by GLC.  $[\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{THF})_2]_x$  has been further characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy (see Experimental). These data indicate that  $[\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{THF})_2]_x$  is present in solution as several isomers, the structures of which cannot be assigned.

In contrast to  $\text{Ta}(\text{CHCMe}_3)\text{Cl}_3(\text{PMe}_3)_2$ , the analogous niobium complex,  $\text{Nb}(\text{CHCMe}_3)\text{Cl}_3(\text{PMe}_3)_2$  when reacted with ethylene, does not give the niobium ethylene complex. <sup>18,56</sup> Instead, a diamagnetic violet powder,

$[\text{NbCl}_3(\text{PMe}_3)_2]_2$  30 is formed, which is soluble in methylene chloride. The identical complex (30), (by  $^1\text{H}$  NMR and IR), can be prepared in 57% yield, by reacting a toluene solution of  $\text{NbCl}_5$  containing 4 mol of  $\text{PMe}_3$  with 2 mol of 0.8% sodium amalgam.

Apparently ethylene does not coordinate strongly to niobium in complexes of this type. The differences between niobium and tantalum in this regard, may well be attributable to the differences in the oxidation potential for each metal. Since third row metal complexes exhibit greater stabilities in their highest oxidation states, and since olefins are  $\pi$ -acceptors,<sup>20</sup> the formation of tantalum olefin complexes may be viewed as an oxidative reaction.

#### Octahedral Complexes: Alkyls; Synthesis and Characterization

Attempts to selectively alkylate octahedral alkylidene or olefin complexes have met with limited success. Generally, alkyl lithium or magnesium reagents are too reactive and substitute all halogens. Zinc reagents typically are not reactive enough. However, when  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  is mixed with 2.0 mol  $\text{Mg}(\text{C}_2\text{H}_5)\text{Br}$  in ether at  $-78^\circ$ , the reaction, upon warming, gives a green-brown solution from which a small yield of a green powder  $\text{Ta}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)_2\text{Cl}(\text{PMe}_3)_2$  (31), can be obtained. The majority of the product is  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$ , (see Chapter 3).

Unfortunately, 31 could not be obtained free from contaminants, and has only been characterized by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  NMR and by IR. These data indicate but do not prove, the presence of two ethyl groups bound to tantalum.

The 67.89 MHz  $^{13}\text{C}$  NMR spectrum of 31, shows only one type of olefinic carbon, one type of ethyl ligand (see Table IV) and a

virtual triplet for the  $\text{PMe}_3$  carbons, indicating equivalent  $\text{PMe}_3$  (which is supported by a singlet in the  $^{31}\text{P}$  NMR). The infrared spectrum of 31, shows no Ta-H stretch suggesting that 31 is not a hydride complex. The  $^1\text{H}$  NMR spectrum of 31 is quite complex, and the assignments can only be tentative since they are based on integral values of merged resonances. This complexity suggests a structure of low symmetry.

The presence of two ethyl groups in this complex is indicated since using only 1 mol of  $\text{Mg}(\text{C}_2\text{H}_5)\text{Br}$  with  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  gives a 1:1 mixture of 31 and  $\text{Ta}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)\text{Cl}_2(\text{PMe}_3)_2$  32 in low yield. 32 can be prepared by an alternate route (see below) and 32 has been successfully analyzed.

31 and 32 can also be prepared as a mixture by reacting  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  with 1 mol of  $[\text{PMe}_3\text{H}]\text{Cl}^-$  (see Experimental), which excludes the possibility of halide exchange when the Grignard reagent was used. Therefore, the loss of symmetry must be due to unsymmetrically bound ethyl groups and not to halide exchange.

Based on these data, the most likely structure of 31 is one containing trans- $\text{PMe}_3$  and cis-ethyl ligands.

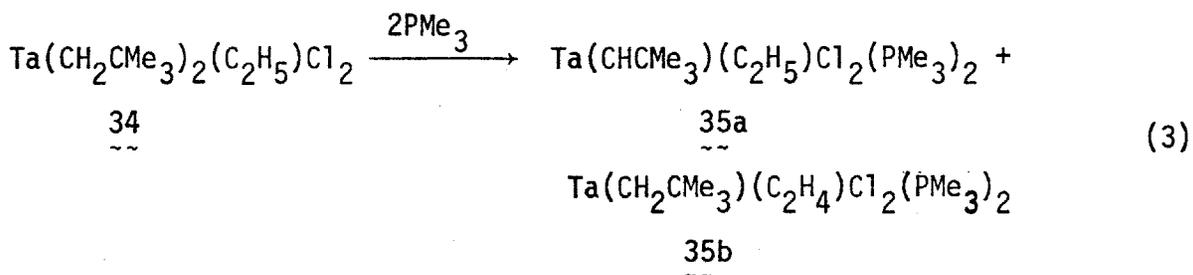
Attempts to alkylate  $\text{Ta}(\text{CHCMe}_3)\text{Cl}_3(\text{PMe}_3)_2$  selectively with  $\text{Mg}(\text{C}_2\text{H}_5)\text{Br}$  or  $\text{Mg}(\text{C}_2\text{H}_5)_2$  dioxane, did not give the expected six-coordinate mono- or diethyl complex. Instead, complete substitution occurred giving five-coordinate  $\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  as the only product observed (see Chapter 3).

A successful method for obtaining mono-substituted six-coordinate complexes, was made possible by reacting  $\text{PMe}_3$  with  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{C}_2\text{H}_5)\text{Cl}_2$  (34), where 34 can be prepared by reacting 0.5 mol  $\text{Zn}(\text{C}_2\text{H}_5)_2$  with  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$  (22), in pentane at  $-30^\circ$ . 34 was isolated as a

yellow oil in quantitative yield and is a solid at  $-30^{\circ}$  where it is indefinitely stable. At  $25^{\circ}$  it slowly decomposes.

The  $^{13}\text{C}$  NMR spectrum of 34, indicates the presence of only one type of neopentyl  $\alpha$ -carbon at 112 ppm (t,  $^1J_{\text{CH}} = 117$  Hz). The resonances at 90.8 (t,  $^1J_{\text{CH}} = 125$  Hz) and 14.4 ppm (q,  $^1J_{\text{CH}} = 129$  Hz) for the  $\alpha$ - and  $\beta$ -carbons respectively, are typical for ethyl complexes of this type (see Chapter 3).

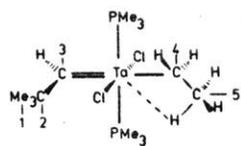
34 reacts quickly with 2 mol of  $\text{PMe}_3$  in pentane at  $-30^{\circ}$ , to give a deep red solution which yields a brown oil after removing the solvent. Examination of the above crude material shows it to contain at least two t-butyl resonances of nearly equal intensities, by  $^1\text{H}$  NMR. Changing the solvent to ether or toluene in the initial reaction does not effect the relative ratios of the two t-butyl containing complexes. Standing a concentrated ether (or pentane) solution containing the reaction product, at  $-30^{\circ}$  for several hours, gives brown needles of 35 (equation 3).



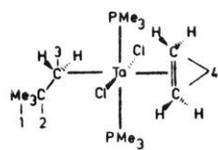
The 67.89 MHz gated  $\{^1\text{H}\}^{13}\text{C}$  NMR spectrum of 35, in toluene- $d_8$  at  $-20^{\circ}$ , shows a complex spectrum attributable to two different species in nearly equal amounts (see Figure 2 and Table IV). The number of resonances present, their respective  $^1\text{H}$  and  $^{31}\text{P}$  coupling constants and the multiplicity arising from the couplings, indicate that the two complexes present are  $\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_5)\text{Cl}_2(\text{PMe}_3)_2$  35a, and  $\text{Ta}(\text{CH}_2\text{CMe}_3)(\text{C}_2\text{H}_4)\text{Cl}_2(\text{PMe}_3)_2$  35b.

Figure 2. The 67.89 MHz Gated  $\{^1\text{H}\}^{13}\text{C}$  NMR Spectrum of  
 $\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_5)\text{Cl}_2(\text{PMe}_3)_2$  and  $\text{Ta}(\text{CH}_2\text{CMe}_3)(\text{C}_2\text{H}_4)\text{Cl}_2(\text{PMe}_3)_2$

<sup>13</sup>C NMR 67.89 MHz; -20 C  
δ<sup>8</sup> toluene



35a



35b

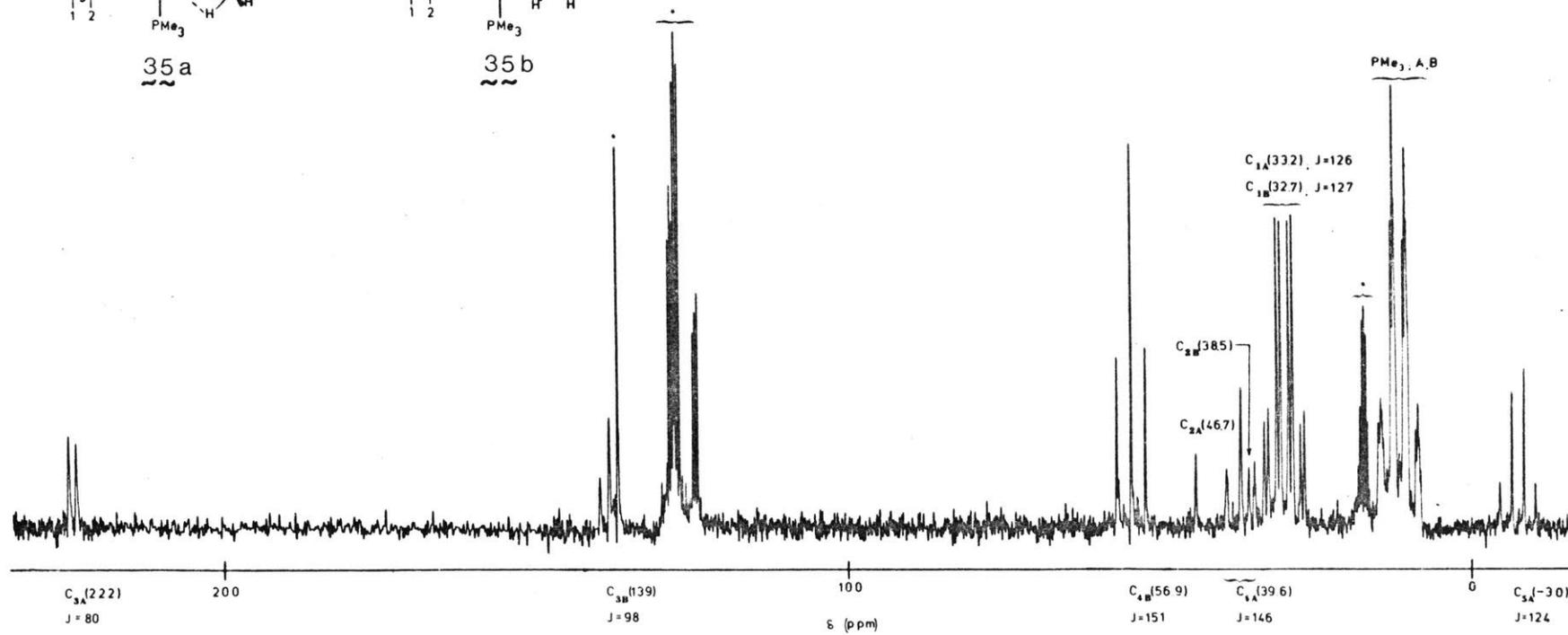


Table III.  $^{13}\text{C}$  NMR Data for Some Tantalum(V) Neopentyl Complexes.

	$C_{\alpha}$ (ppm) <sup>a</sup>	$^1J_{\text{CH}}$ <sup>b</sup>	$C_{\beta}$ (ppm) <sup>a</sup>	Ref.
$\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$	115	119	34.7	c
$\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{C}_2\text{H}_5)\text{Cl}_2$	112	117	34.7	d
$\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{OCMe}_3)\text{Cl}_2$	105	118	36.3	d
$\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$	123	116	37.2	c
$\text{Ta}(\text{CH}_2\text{CMe}_3)\text{Cl}_4$	132	110	40.0	c
$\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3(\text{PMe}_3)$	96.1	121	45.6 <sup>f</sup>	e

<sup>a</sup>Chemical shift, measured downfield from TMS, for the neopentyl ligand only.

<sup>b</sup>Coupling constant, measured in Hertz, for the neopentyl  $\alpha$ -carbon atom.

<sup>c</sup>See Chapter 3 Experimental.

<sup>d</sup>See Chapter 2 Experimental.

<sup>e</sup>Rupprecht, G.A., Ph.D. Thesis.

<sup>f</sup>Questionable shift since  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3(\text{PMe}_3)$  decomposes into  $\text{Ta}(\text{CHCMe}_3)\text{Cl}_3(\text{PMe}_3)_2$  which has a  $C_{\beta}$  shift of 45.8 ppm; see Table IV.

Table IV. Some  $^{13}\text{C}$  NMR Data for Octahedral Neopentylidene and Ethylene Complexes of Tantalum.

Complex	$C_{\alpha}^a$	$J_{\text{CH}}^b$	$C_{\beta}^a$	$J_{\text{CH}}^b$	$C_{\text{O1}}^a$	$J_{\text{CH}}^b$
Ta(CHCMe <sub>3</sub> )(C <sub>2</sub> H <sub>5</sub> )Cl <sub>2</sub> (PMe <sub>3</sub> ) <sub>2</sub> ; neopentylidene:	222	80	46.7	--	--	--
ethyl:	39.6	146	-3.0	124	--	--
Ta(CH <sub>2</sub> CMe <sub>3</sub> )(C <sub>2</sub> H <sub>4</sub> )Cl <sub>2</sub> (PMe <sub>3</sub> ) <sub>2</sub> :	139	98	38.5	--	56.9	151
Ta(CHCMe <sub>3</sub> )(C <sub>2</sub> H <sub>5</sub> )Cl <sub>2</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> ; neopentylidene:	224	--	47.0	--	--	--
ethyl:	45.0	--	-0.58	--	--	--
Ta(CH <sub>2</sub> CMe <sub>3</sub> )(C <sub>2</sub> H <sub>4</sub> )Cl <sub>2</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> :	145	94	38.6	--	59.4	152
Ta(CHCMe <sub>3</sub> )(C <sub>2</sub> H <sub>5</sub> )Br <sub>2</sub> (PMe <sub>3</sub> ) <sub>2</sub> ; neopentylidene:	225.9	87	47.0	--	--	--
ethyl:	39.1	145	-4.7	123	--	--
Ta(CH <sub>2</sub> CMe <sub>3</sub> )(C <sub>2</sub> H <sub>4</sub> )Br <sub>2</sub> (PMe <sub>3</sub> ) <sub>2</sub> :	143	--	36.6	56.7	--	--
Ta(CHCMe <sub>3</sub> )Cl <sub>3</sub> (PMe <sub>3</sub> ) <sub>2</sub> : <sup>c</sup>	256.5	75	45.8	--	--	--
Ta(CHCMe <sub>3</sub> )Br <sub>2</sub> (PMe <sub>3</sub> ) <sub>2</sub> : <sup>c</sup>	258.7	74	45.6	--	--	--
Ta(C <sub>2</sub> H <sub>4</sub> )Cl <sub>3</sub> (PMe <sub>3</sub> ) <sub>2</sub> : <sup>c</sup>	---	--	--	--	59.0	--
Ta(C <sub>2</sub> H <sub>4</sub> )Cl <sub>3</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> : <sup>c</sup>	---	--	--	--	63.6	152
Ta(C <sub>2</sub> H <sub>4</sub> )(C <sub>2</sub> H <sub>5</sub> )Cl <sub>2</sub> (PMe <sub>3</sub> ) <sub>2</sub> :	61.7	132	1.8	125	54.3	151
Ta(C <sub>2</sub> H <sub>4</sub> )(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Cl(PMe <sub>3</sub> ) <sub>2</sub> :	68.9	132	2.6	~123	57.1	152

<sup>a</sup>The chemical shifts for the  $\alpha$ -carbon ( $C_{\alpha}$ ),  $\beta$ -carbon ( $C_{\beta}$ ), and the olefinic carbon ( $C_{\text{O1}}$ ) were measured in ppm downfield of TMS.

<sup>b</sup> $J_{\text{CH}}$  values are listed in Hz.

<sup>c</sup>These data were obtained for the trans,mer-isomer from Rupprecht, G.A., Ph.D. thesis.

35b shows only one olefinic carbon at 56.9 ppm (t,  $J_{CH} = 151$  Hz). The neopentyl methylene carbon at 138.9 ppm and  $\beta$ -carbon at 38.5 ppm, resonate at lower fields than is usually found for Ta(V) neopentyl complexes (see Table III). Indeed, the unusual nature of the neopentyl ligand can be further realized since the  $^1J_{CH}$  for the methylene carbon is 98 Hz and is unusually low for neopentyl complexes. In fact, it is lower than some neopentylidene complexes containing less than 18 electrons.

The neopentylidene resonances for the  $\alpha$ - and  $\beta$ -carbons of 35a, are located at 222 ppm ( $^1J_{CH} = 80$  Hz) and 46.7 ppm (s), respectively, and are in the range expected for an octahedral alkylidene complex. In addition, the  $\alpha$ - and  $\beta$ -carbon atoms for the ethyl ligand are found to be in the range expected for an octahedral ethyl complex (see Table IV). Although the C-H multiplicities for the ethyl ligand (triplet and quartet, respectively) and the  $^1J_{CH}$  observed for the  $\beta$ -carbon atom (124 Hz) are normal, the  $\alpha$ -carbon atom coupling constant is quite high ( $^1J_{CH} = 146$  Hz). In fact, the  $\alpha$ -carbon more closely resembles an olefinic carbon.

35a and 35b were differentiated based on variable temperature  $^{13}C$  NMR data. It was found that 35a lost coupling to phosphorous at lower temperatures than 35b. This is reasonable since the octahedral analogues Ta(CHCMe<sub>3</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub> (24), and Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub> (26), show that 24 exchanges with free PMe<sub>3</sub> at lower temperatures than 26.<sup>26</sup>

Variable temperature  $^{31}P$  NMR studies of 35a and 35b, with added PMe<sub>3</sub>, show that 35a exchanges with free PMe<sub>3</sub> at lower temperatures than 35b. At room temperature 35a shows a broad singlet while 35b shows a sharp singlet. Upon cooling to -67°, 35a collapses and gives an AB multiplet ( $J_{pp} = 150$  Hz). However, 35b remains sharp throughout

that temperature range. At  $-37^\circ$ , P and P' for 35a coalesce giving  $\Delta G^\ddagger = 10.1 \pm 0.2 \text{ kcal mol}^{-1}$  for interconversion. These data are consistent with both 35a and 35b containing trans  $\text{PMe}_3$  ligands. The interconversion of 35a is reversible. Heating 35a and 35b to temperatures greater than  $50^\circ$  in the absence of free  $\text{PMe}_3$ , leads to rapid decomposition of both 35a and 35b at what appears to be the same rate.

The  $^{31}\text{P}$  NMR (36.4 MHz) spectrum at  $-70^\circ$ , of 35a and 35b, shows the relative ratios to be slightly effected by the NMR solvent used (see Experimental). 35b decreases in intensity relative to 35a in polar solvents (i.e. ether or THF). The addition of free  $\text{PMe}_3$  slightly decreases the relative ratio of 35a to 35b. Although these data are somewhat questionable since the observed changes are slight, they do suggest that 35a and 35b are in chemical equilibrium. Due to the decomposition of 35a and 35b (see above), the high temperature limit for the interconversion of 35a into 35b (or the reverse) was never observed.

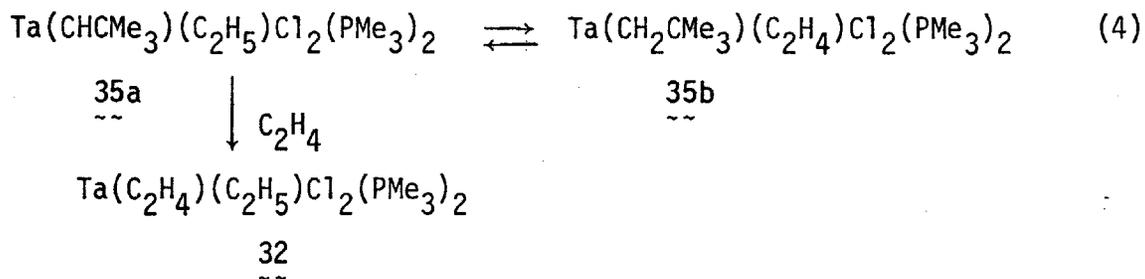
Recently, magnetization transfer or double resonance techniques, have been successfully applied to several systems with lifetimes exceeding approximately one second.<sup>35</sup> A study undertaken with D. D. Trafficante has definitively shown that 35a and 35b are in chemical equilibrium. The rate constant is approximately equal to  $1/T_1$ , where  $T_1$  is the spin lattice relaxation time for the nuclei undergoing the exchange.<sup>36</sup>

Attempts to use the  $\alpha$ -carbon atoms of the neopentyl and neopentylidene were unsuccessful, presumably due to their large chemical shift difference and their short relaxation times.<sup>35c</sup> However, magnetization transfer was achieved by selectively irradiating the  $\beta$ -carbon of the

neopentylidene in 35a and observing the transfer to the  $\beta$ -carbon in the neopentyl group in 35b. The reverse experiment (irradiating  $C_\beta$  for 35b and observing 35a), was also successful (see Figure 3).

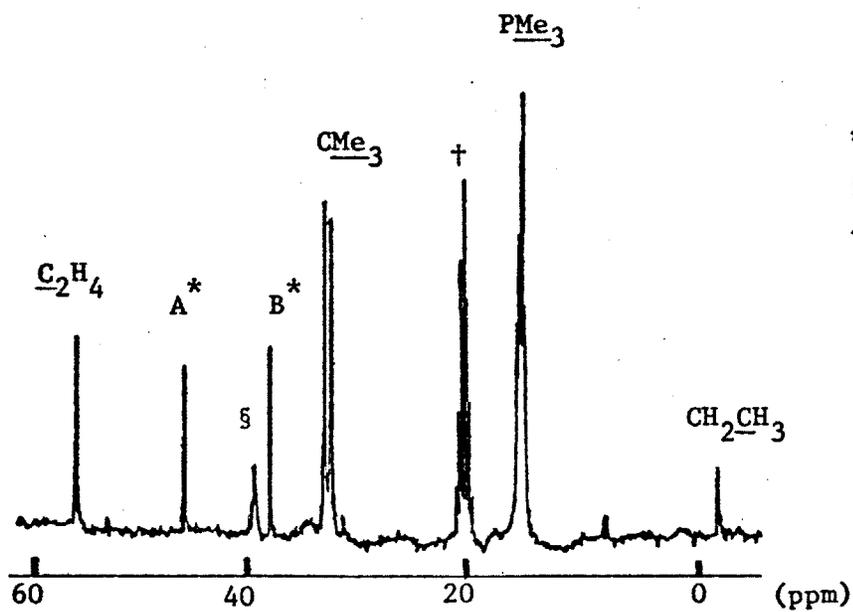
Lowering the decoupling power for the initial pulse (i.e. narrower decoupler frequency distribution), shows that magnetization transfer still occurs with little or no intensity loss for resonances close to the irradiated nuclei .

The equilibrium of 35a and 35b is further supported by the fact that ethylene reacts quickly with this mixture to give a 75% isolated yield of  $Ta(C_2H_4)(C_2H_5)Cl_2(PMe_3)_2$  (32). The only organic products observed are 4,4-dimethyl-1-pentene (0.67 eq.  $Ta^{-1}$ ) and 4,4-dimethyl-trans-2-pentene (0.25 eq.  $Ta^{-1}$ ) which are the products expected from reactions with just 35a. Since no 6,6-dimethyl-1-heptene is observed, it is unlikely that 35b is reacting with ethylene faster than 35a, (where 6,6-dimethyl-1-heptene is the product expected for two ethylene insertions into a Ta-neopentyl bond). Therefore, 35a must be the primary reactant with ethylene and the equilibrium shifts from 35b to 35a to compensate for the loss of 35a, (equation 4).

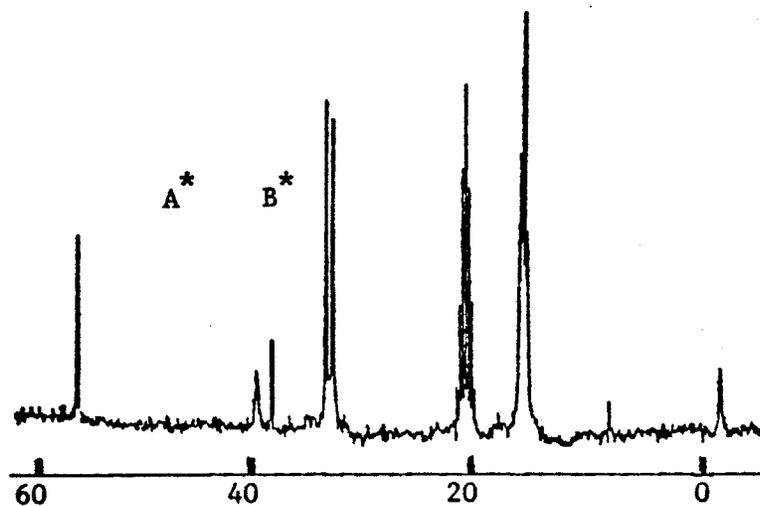
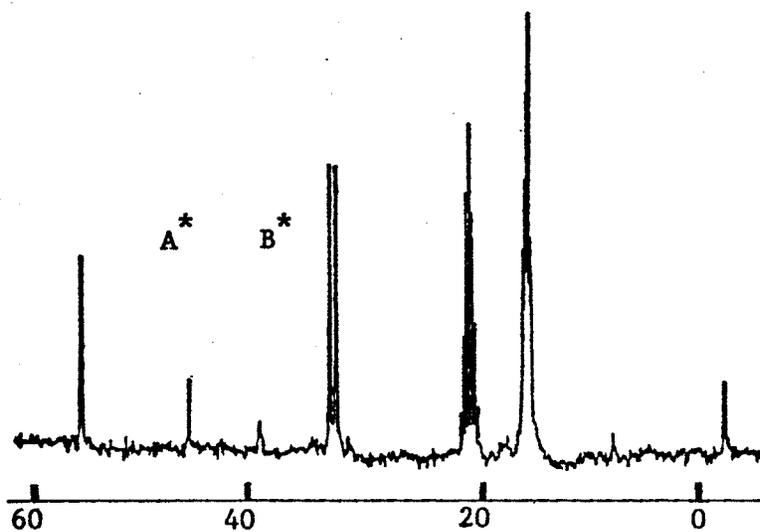


Since 35b and  $Ta(C_2H_4)(C_2H_5)Cl_2(PMe_3)_2$  (32) are monosubstituted ethylene complexes, they may have similar structures. Spectroscopic data (see Table III and experimental) are consistent with trans-phosphines

Figure 3. The 67.89 MHz  $\{^1\text{H}\}^{13}\text{C}$  NMR Magnetization Transfer Experiment of the Equilibrium Mixture,  $\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_5)\text{Cl}_2(\text{PMe}_3)_2$  and  $\text{Ta}(\text{CH}_2\text{CMe}_3)(\text{C}_2\text{H}_4)\text{Cl}_2(\text{PMe}_3)_2$



- \* =  $\text{CMe}_3$
- § =  $\text{CH}_2\text{CH}_3$
- † =  $\text{C}_6\text{D}_5\text{CD}_3$



and cis-chlorine ligands. Unfortunately, the  $^1\text{H}$  NMR spectrum for  $\underline{\underline{35a}}$  and  $\underline{\underline{35b}}$  is extremely complex and little stereochemical information can be obtained. However, based upon similarities to the bromo and  $\text{PMe}_2\text{Ph}$  analogues (see below), a tentative assignment for the neopentyl methylene protons (a singlet at  $-1.95$  ppm) can be made. This fact is quite interesting for two reasons. The first reason being that all known neopentyl and benzyl complexes of Ta containing coordinated  $\text{PMe}_3$  (five- and six-coordinate), show strong  $^{31}\text{P}-^1\text{H}$  coupling (ca. 15 Hz) to the methylene protons, suggesting that in  $\underline{\underline{35b}}$  phosphorous must not be coupling with the methylene protons of the neopentyl ligand. The absence of coupling could arise from some  $\pi$ -bonding character in the Ta-C $_{\alpha}$  bond. Secondly, only one resonance for H $_{\alpha}$  is observed, indicating the presence of a mirror plane. Either H $_{A_{\alpha}}$  and H $_{B_{\alpha}}$  are equivalent, or they are exchanging by a mechanism similar to that demonstrated by Shapely for  $\text{Os}_3(\text{CO})_{10}\text{CH}_2\text{D}_2$ .<sup>37,38a</sup>

Without a crystal structure for  $\underline{\underline{35a}}$  and  $\underline{\underline{35b}}$ , there is no absolute way to determine their structures. Therefore, for convenience, a structure containing both trans-halogens and  $\text{PMe}_3$  ligands, has been assigned for each.

Furthermore, it seems likely that the olefin is oriented in  $\underline{\underline{35b}}$  along the Ta- $\text{PMe}_3$  axis, and the orientation of the alkylidene in  $\underline{\underline{35a}}$  is along the Ta-halogen axis, similar to their monosubstituted analogues (see above).

Complication arises in  $\underline{\underline{35a}}$  due to the inequivalency of the  $\text{PMe}_3$  ligands at low temperature. A  $\Delta G^{\ddagger}$  of  $10.1 \pm 0.2$  kcal mol $^{-1}$  suggests a restricted rotation about a tantalum carbon bond in either the neopentylidene or ethyl ligand. Unfortunately, there is no free energy of activation data available for restricted alkylidene rotation in

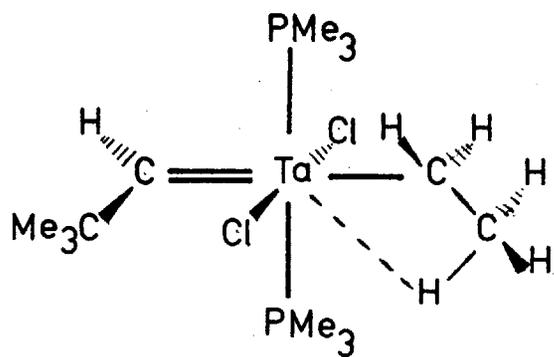
octahedral complexes. However, the lowest value of  $\Delta G^\ddagger$  observed is  $11.2 \text{ kcal mol}^{-1}$  for the four-coordinate complex  $\text{Ta}(\text{C}_5\text{Me}_5)(\text{CHCMe}_3)_2(\text{PMe}_3)$  (see Chapter 3). Since the  $\Delta G^\ddagger$  found for 35a is  $10.1 \text{ kcal mol}^{-1}$  it seems likely that restricted rotation about the Ta-ethyl bond is responsible for the observed  $^{31}\text{P}$  NMR result. This is due to the fact that  $^1J_{\text{CH}}$  for the ethyl  $\alpha$ -carbon atom is  $146 \text{ Hz}$ , suggesting that a  $\text{Ta}\cdots\text{H}_\beta$  interaction gives rise to pseudo-olefinic values for  $^1J_{\text{CH}}$  and is responsible for the observed barrier to rotation. Several well-documented examples of similar CH bond activation are known, supporting this postulate.<sup>38</sup>

The infrared spectrum of 35a and 35b shows further support. The most notable feature is the medium intensity absorbance at  $2460 \text{ cm}^{-1}$  assignable to a  $\nu_{\text{C-H}\alpha}$  stretch in 35a. However, two weak absorbances at  $2680$  and  $2310 \text{ cm}^{-1}$  are also present which may be due to the  $\nu_{\text{C-H}\alpha}$  for the neopentyl ligand in 35b and the  $\nu_{\text{C-H}\beta}$  for the ethyl ligand in 35a, respectively. These assignments are only tentative since they are weak bands and the appropriate labelling studies have not been done.

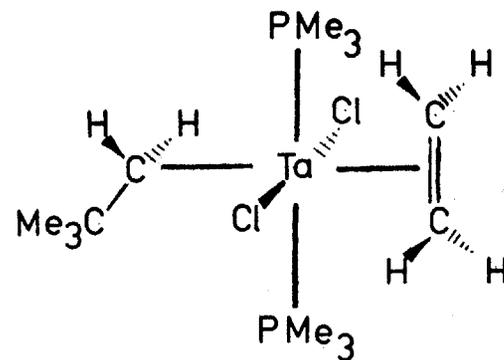
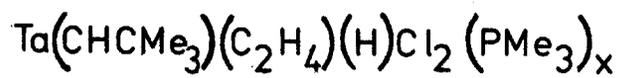
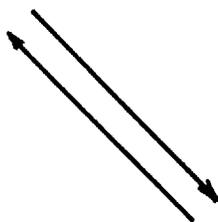
These data indicate that 35a and 35b interconvert through a C-H bond activation mechanism involving a third species which is most likely  $\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_4)\text{HCl}_2(\text{PMe}_3)_x$  (36), (see Scheme II). The intermediacy of 36 is supported by the recent synthesis of  $\text{Ta}(\text{CHCMe}_3)\text{HCl}_2(\text{PMe}_3)_3$  (see Chapter 4).

No distinction can be made between a reversible hydride transfer to the metal and a mechanism not involving the metal center. However, the most likely process is an intramolecular hydride transfer via the metal since  $\beta$ -hydride elimination reactions are known to occur by a similar process.<sup>6</sup>

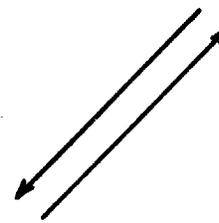
Scheme II. Mechanism in the Equilibrium of  $\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_5)\text{Cl}_2(\text{PMe}_3)_2$   
and  $\text{Ta}(\text{CH}_2\text{CMe}_3)(\text{C}_2\text{H}_4)\text{Cl}_2(\text{PMe}_3)_2$



35a



35b



Scheme II

Addition of 2 mol of  $\text{PMe}_2\text{Ph}$  to a pentane solution of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{C}_2\text{H}_5)\text{Cl}_2$  34, cooled to  $-30^\circ$ , gives an immediate reaction and a brown precipitate. Isolation and recrystallization of the precipitate, did not give a pure product. However,  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_2\text{Ph})_2$  was isolated from the reaction mixture, indicating that free ethylene (formed during the course of the reaction) or alkyl exchange, is responsible for its formation. Although the reaction mixture is impure, the  $^{13}\text{C}$  (see Table IV),  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra show that  $\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_5)\text{Cl}_2(\text{PMe}_2\text{Ph})_2$  37a, and  $\text{Ta}(\text{CH}_2\text{CMe}_3)(\text{C}_2\text{H}_4)\text{Cl}_2(\text{PMe}_2\text{Ph})_2$  37b, are present and are in a 1:2 ratio.

In contrast, preparing the analogous bromide complex (see Experimental), as in 35a and 35b, gives a 5:1 ratio of  $\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_5)\text{Br}_2(\text{PMe}_3)_2$  38a to  $\text{Ta}(\text{CH}_2\text{CMe}_3)(\text{C}_2\text{H}_4)\text{Br}_2(\text{PMe}_3)_2$  38b. The spectroscopic features of 38a and 38b are analogous to the above systems, further confirming the original assignments (see Table IV and Experimental). The factors favoring a particular form, neopentylidene or neopentyl, are unclear and require further investigation.

Octahedral Complexes: Alkoxides; Synthesis, Characterization, and Reactions with Ethylene

$\text{Ta}(\text{CHCMe}_3)\text{Cl}_3(\text{PMe}_3)_2$  (24) reacts with two equivalents of  $\text{LiOCMe}_3$  to give  $\text{Ta}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  (see below).<sup>5,18</sup> Using more reactive reagents, such as  $\text{KOCMe}_3$ , does not give further substitution.<sup>18</sup> Attempts to use one equivalent of  $\text{LiOCMe}_3$  with 24 gives mixtures of  $\text{Ta}(\text{CHCMe}_3)(\text{OCMe}_3)\text{Cl}_2(\text{PMe}_3)_2$  (39) and  $\text{Ta}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ . 39 can be prepared in 80% yield by reacting two equivalents of  $\text{PMe}_3$  with  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{OCMe}_3)\text{Cl}_2$  in methylene chloride.

39 exists as two isomers in solution in a 10:1 ratio. The 270 MHz  $^1\text{H}$  NMR spectrum of 39 at  $-50^\circ$ , shows the neopentylidene  $\alpha$ -hydrogens at 9.19 (t,  $J = 3.3$  Hz) and 8.11 ppm (t,  $J \approx 2.4$  Hz) for the major and minor isomers, respectively. Apparently, the  $\text{PMe}_3$  resonances are coincident for each isomer. The "virtual triplet" pattern observed for the major isomer suggest the  $\text{PMe}_3$  ligands are equivalent. This is supported by the fact that only two singlet resonances, in a 10:1 ratio, are observed by  $^{31}\text{P}$  NMR.

The  $^{13}\text{C}$  NMR spectrum for 39 shows the neopentylidene  $\alpha$ -carbon atom, for the major isomer, is at 282 ppm (dt,  $^2J_{\text{CP}} = 8.4$  Hz,  $^1J_{\text{CH}} = 110$  Hz). Apparently the minor isomer of 39 is in such low concentration that no neopentylidene  $\alpha$ -carbon resonance could be observed. All other resonances are observed for each isomer (see Experimental).

The neopentylidene ligand is probably aligned orthogonal to the Ta-phosphine axis, by analogy to  $\text{trans,mer-Ta}(\text{CHCMe}_3)\text{Cl}_3(\text{PMe}_3)_2$ . Unfortunately there is no way to distinguish between cis- or trans-chlorine ligands in 39.

39, dissolved in ether, reacts with ethylene to give the rearrangement products 4,4-dimethyl-1-pentene (0.65 eq.  $\text{Ta}^{-1}$ ) and 4,4-dimethyl-trans-2-pentene (0.24 eq.  $\text{Ta}^{-1}$ ), and some 1-butene. The organometallic product  $\text{Ta}(\text{C}_2\text{H}_4)(\text{OCMe}_3)\text{Cl}_2(\text{PMe}_3)_2$  (40), can be isolated as orange crystals and gives a satisfactory elemental analysis.

The  $^1\text{H}$  NMR spectrum for 40 shows a complex pattern (possibly an  $\text{AA}'\text{BB}'\text{X}_2$ ) for the olefinic resonances. Only one type of olefinic carbon is present at 44.7 ppm ( $^1J_{\text{CH}} = 152$  Hz) in the  $^{13}\text{C}$  NMR spectrum of 40. The "virtual-coupled" triplets observed for the  $\text{PMe}_3$  ligands, in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for 40, indicate that these ligands are

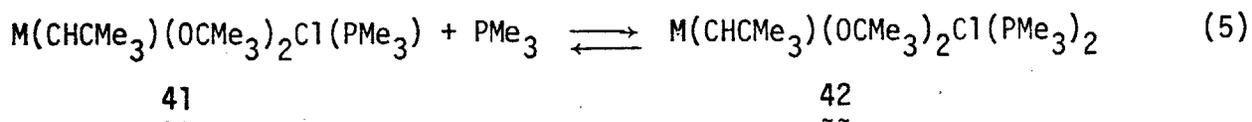
equivalent. These data show that the structure of 40 must be one which contains trans  $\text{PMe}_3$  and cis chlorine ligands, with the olefin aligned either parallel or perpendicular to the Ta- $\text{PMe}_3$  axis.

The preparation of  $\text{M}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ , where M=Ta 41a or Nb 41b, has been reported.<sup>5,18</sup>

The  $^{13}\text{C}$  NMR spectrum for 41a shows the neopentylidene  $\alpha$ -carbon atom at 273 ppm (dt,  $^2J_{\text{CP}} \approx 6$  Hz,  $^1J_{\text{CH}} = 114$  Hz) and the t-butoxy  $\beta$ -carbons are inequivalent and at 79.8 (s) and 78.8 ppm (s).

The structure of 41a is believed to be a trigonal bipyramid with the  $\text{PMe}_3$  ligand occupying an axial site and the neopentylidene ligand equatorial and lying in a plane which is orthogonal to the Ta- $\text{PMe}_3$  axis. This assignment is an analogy to the structure found for  $\text{Ta}(\text{CHCMe}_3)_2(\text{mesityl})(\text{PMe}_3)_2$ .<sup>39</sup> The positions of the alkoxide ligands (either both equatorial or axial-equatorial) cannot be determined at this time. However, the axial-equatorial structure is preferred since steric interactions appear to be minimized. Nb( $\text{CHCMe}_3$ )( $\text{OCMe}_3$ )<sub>2</sub>Cl( $\text{PMe}_3$ ) (41b) is believed to have a similar structure to 41a since the spectral features (NMR) for both complexes are very similar (see Experimental).

Addition of  $\text{PMe}_3$  to a solution containing  $\text{M}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  gives  $\text{M}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  (M = Ta, 42a; Nb, 42b) (equation 5).



42a and 42b can be observed by variable temperature NMR spectroscopy. Low temperature crystallization of pure 41a in the presence of free  $\text{PMe}_3$  gives both 41a and 42a. However, 41a can be regenerated by multiple

recrystallizations of the mixture in the absence of added  $\text{PMe}_3$ , or by prolonged exposure to a vacuum of a toluene solution containing both 41a and 42a.

Since the NMR spectral features are nearly identical for 42a and 42b, only 42a will be discussed in detail.

At  $25^\circ$  free  $\text{PMe}_3$  is not exchanging rapidly on the NMR timescale with coordinated  $\text{PMe}_3$  in either complex (41a or 42a), by  $^{31}\text{P}$  NMR. At  $20^\circ$ , two slightly broadened resonances, in a 10:1 ratio, are observed for 41a and 42a for a 0.15 M toluene solution of 41a with 0.5 equivalents of added  $\text{PMe}_3$ . In a less concentrated solution (0.03 M), under the same conditions, only 41a is observed. However, if excess  $\text{PMe}_3$  (ca. 3 equivalents) is added 41a and 42a are present in a 1:3 ratio, respectively. Upon lowering the temperature for each case (0.5 eq. or 3 eq. of added  $\text{PMe}_3$ ) the resonances sharpen and the ratio of 41a and 42a reaches a limit which does not change with further cooling (ca.  $-30^\circ$ ). At  $-30^\circ$ , 41a and 42a are in a 1:1 ratio if 0.5 equivalents of added  $\text{PMe}_3$  is present, or are in a 1:15 ratio if 3 equivalents of added  $\text{PMe}_3$  is present.

$\text{Nb}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  (41b) with 3 equivalents of added  $\text{PMe}_3$  shows that 41b and 42b are in a 1:15 ratio at  $-60^\circ$ , but are still exchanging since the non-coordinated  $\text{PMe}_3$  resonance is broad at this temperature. Cooling to  $-90^\circ$  sharpens the free  $\text{PMe}_3$  resonance. Where  $\text{M} = \text{Ta}$ , both species (41a and 42a) begin to broaden at nearly the same rate at temperatures greater than ca.  $0^\circ$ . This suggests that for complexes of this type Nb is a weaker Lewis acid than Ta, thus,  $\text{PMe}_3$  binds more effectively to Ta than to Nb.

Observing the equilibrium between 41a and 42a by  $^1\text{H}$  and  $^{13}\text{C}$  NMR gives results similar to those found by  $^{31}\text{P}$  NMR. However, the ratio of 41a to

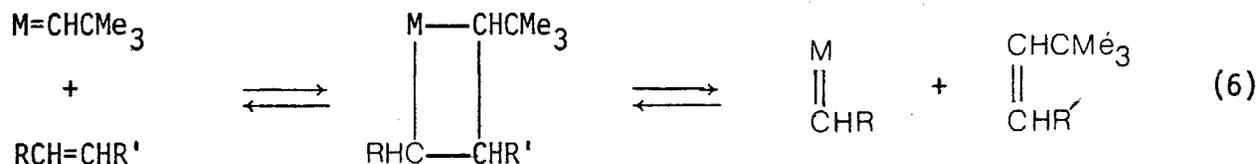
42a is dependent upon the observed nucleus since the amount of added  $\text{PMe}_3$  varied from sample to sample.

The structures of both 42a and 42b are believed similar since the  $\text{PMe}_3$  ligands are trans and equivalent and the alkoxide ligands are trans and inequivalent in each complex (see Experimental). Although it is not possible to determine in which configuration (either cis or trans) the alkoxides are oriented, a trans structure is favored by analogy to  $\text{M}(\text{C}_2\text{H}_4)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  where  $\text{M}=\text{Ta}$  or  $\text{Nb}$  (see below).

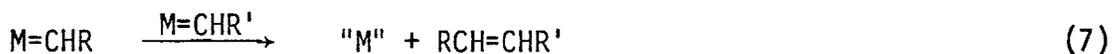
$\text{Nb}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  (41b), in ether with one equivalent of  $\text{PMe}_3$ , reacts with ethylene to give  $\text{Nb}(\text{C}_2\text{H}_4)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  (43). The 270 MHz  $^1\text{H}$  NMR spectrum of 43 at  $-30^\circ$  shows a broad olefinic resonance at 1.70 ppm which does not sharpen with cooling to  $-50^\circ$ . The virtual triplet pattern observed for the  $\text{PMe}_3$  ligands suggests a structure with trans phosphine ligands. Since only one type of t-butyl resonance is observed a trans configuration for the alkoxide ligands must be present. The orientation of the olefin, either parallel or perpendicular to the  $\text{Nb}-\text{PMe}_3$  axis cannot be determined at this time. However, the structure of 43 is believed analogous to that found for  $\text{Ta}(\text{C}_2\text{H}_4)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$ <sup>18</sup>.

#### Octahedral Complexes: Alkoxides; Stoichiometric Metathesis with Styrene and Characterization of Organometallic Products

$\text{M}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  ( $\text{M} = \text{Ta}$ , 41a;  $\text{Nb}$ , 41b) has been shown to be a metathesis catalyst for 1-butene and cis-2-pentene.<sup>5</sup> Results indicate that the mechanism is one involving a metallacyclobutane intermediate which "metathesizes" into a new olefin and a different metal-alkylidene complex (equation 6).<sup>2</sup> The stability of the newly formed alkylidene is highly dependent upon the nature of the R group. Several

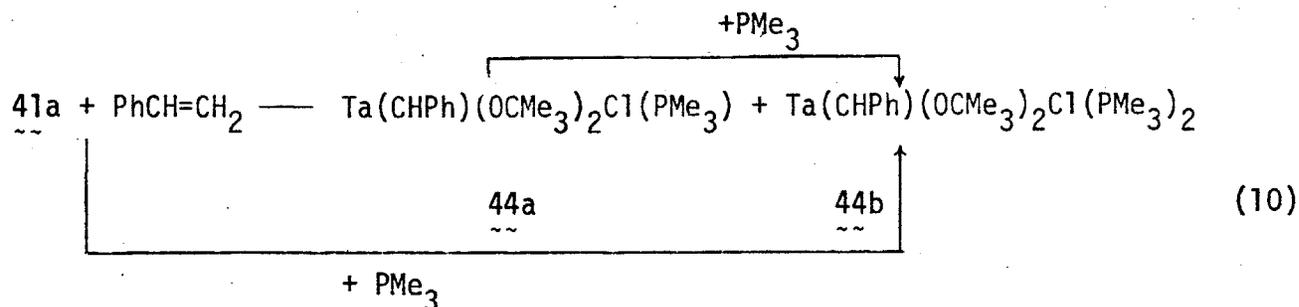


modes of decomposition are possible. The "chain carrying" alkylidene complex can decompose via a bimolecular pathway (equation 7) or via a free carbene which can subsequently abstract proton(s) from a ligand or from the solvent (equation 8), or (for R = Me, Et, etc.) via a rearrangement to form a tautomer, an olefin complex (equation 9). In



order to demonstrate the involvement of an alkylidene complex as the chain carrier in the above metathesis reaction, it is necessary to react olefins with the di-t-butoxy complexes to give a stable alkylidene complex, namely a benzylidene complex.

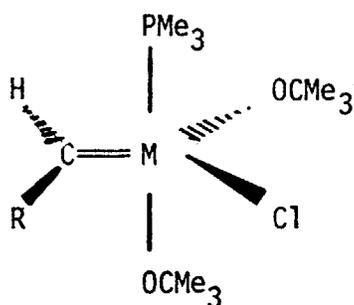
One equivalent of styrene reacts with  $\text{Ta}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  41a to give after 10 min an orange powder in low yield. The product is a 4:1 mixture of  $\text{Ta}(\text{CHPh})(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  (44a) and  $\text{Ta}(\text{CHPh})(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  (44b). Addition of excess  $\text{PMe}_3$  to a solution containing the above mixtures (before and after the reaction with styrene) gives mainly 44b (as green crystals) in high yield (equation 10). Prolonged exposure of 44b to a vacuum, gives mixtures of 44a and 44b, enriched in 44a (see Experimental). Both 44a and 44b show similar  $^1\text{H}$  and



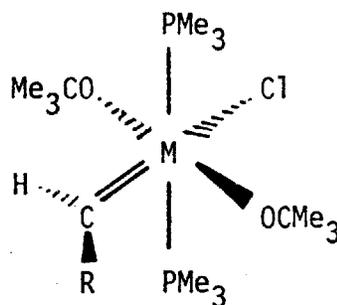
$^{31}\text{P}$  NMR spectroscopy as  $\text{Ta}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  (41a) and  $\text{Ta}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  (42a), respectively. However, the insolubilities of 44a and 44b preclude the possibility of obtaining good  $^{13}\text{C}$  NMR data, although the data obtained is similar to the neopentylidene analogues (41a and 42a, respectively). The only physical difference between the benzylidene and neopentylidene complexes is that 44b and 41a can be isolated in pure form. This difference probably reflects the greater steric demand of a neopentylidene ligand over a benzylidene ligand.

The reaction of  $\text{Nb}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  with styrene in the presence of one equivalent of  $\text{PMe}_3$  gives a mixture of  $\text{Nb}(\text{CHPh})(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ , (45a) (1 part) and  $\text{Nb}(\text{CHPh})(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$ , (45b) (2 parts). Unlike 44b, 45b cannot be isolated in pure form, which further supports the fact that niobium complexes of this type are weaker Lewis acids than tantalum.

The  $^1\text{H}$  NMR spectrum of 45a and 45b is similar to 44a and 44b. Therefore, the most likely structures for all the alkylidene complexes of the type  $\text{M}(\text{CHR})(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  and  $\text{M}(\text{CHR})(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  is believed to be as shown in I and II, respectively.



I



II

Octahedral Complexes: Alkoxides; Organic Products from Stoichiometric  
Metathesis with Styrene, Cis-propenylbenzene, and Stilbene

One equivalent of styrene reacts with  $\text{Ta}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  to give after two hours a 74% yield of the two possible initial metathesis products, 3,3-dimethyl-1-butene (0.69 eq.  $\text{Ta}^{-1}$ ) and trans-1-phenyl-3,3-dimethyl-1-butene (ca. 0.06 eq.  $\text{Ta}^{-1}$ ). In the presence of one equivalent of  $\text{PMe}_3$  the reaction yields only 3,3-dimethyl-1-butene (0.80 eq.  $\text{Ta}^{-1}$ ) after 7 h (runs 1 and 2; see Table V).  $\text{Nb}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ , with and without added  $\text{PMe}_3$ , reacts with styrene to give results similar (runs 3 and 4) to the tantalum case. In each case (runs 1 through 4) trans- and cis-stilbene is slowly formed with slightly more stilbenes being formed in the niobium case without added  $\text{PMe}_3$  (run 3). The formation of stilbenes presumably arises from a bimolecular decomposition of  $\text{M}(\text{CHPh})(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_x$  since the amount of stilbenes continues to grow after the reaction (as measured by % rxn; see Table V) is complete. It is uncertain whether  $\text{M}(\text{CHPh})(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_x$  bimolecularly decomposes when x is one or two. However, more stilbene is observed in the runs without added  $\text{PMe}_3$  implying that  $\text{M}(\text{CHPh})(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  (x = 1) is unstable and is responsible for stilbene formation. Since attempts to isolate  $\text{M}(\text{CHPh})(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  gives low yields of impure products (see previous section), this is supportive of the above postulate.

$\text{M}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  reacts with cis-propenylbenzene to give predominantly 4,4-dimethyl-trans-2-pentene (runs 4 through 8). The amount of 4,4-dimethyl-cis-2-pentene is found only in minor amounts (<5%; run 6). Stilbenes are again formed with the clearer indication that niobium forms stilbenes faster than tantalum, and more slowly in the presence of added  $\text{PMe}_3$ .

Cis-stilbene reacts with  $M(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  to give the only possible metathesis product trans-1-phenyl-3,3-dimethyl-1-butene in good yield (runs 9 through 12).

Finally, inspection of these data shows qualitatively that all the cis-phenyl-substituted olefins (used in this study) react at nearly the same rate with  $M(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  with trans-stilbene reacting the slowest. This would be expected if the olefin must first compete with  $\text{PMe}_3$  for a metal coordination site. Consistent with this is the fact that all of these olefin reactions proceed more readily in the absence of added  $\text{PMe}_3$ .

Clearly these data (and the data in the preceding section) give support to an alkylidene complex as a chain carrier in the metathesis reaction. However, this is a specialized case since the alkylidene formed (a benzylidene) by transalkylidenation is quite stable.

Table V. Organic Products of the Reaction of  $M(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}$  with Styrene, Cis-Propenylbenzene, and Stilbene.<sup>a</sup>

M <sup>b</sup>	Olefin	time(h)	t-stilbene	c-stilbene	t-PhCH=CHCMe <sub>3</sub>	c-PhCH=CHCMe <sub>3</sub>	Me <sub>3</sub> CCH=CH <sub>2</sub>	t-Me <sub>3</sub> CCH=CHMe	% rxn <sup>c</sup>
Ta	PhCH=CH <sub>2</sub>	2 40	2 13(18)	0 3(0)	~6 3(24)	0 ~0	69 73(66)	-- --	74 76(91)
Ta+L	PhCH=CH <sub>2</sub>	7 40	0 11(3)	0 3(~0)	0 1(1)	0	80 (~42)	-- --	80 1(44)
Nb	PhCH=CH <sub>2</sub>	2 40	~0 25(21)	1 2(0)	3 9(44)	0 ~0	69 (~54)	-- --	72 9(98)
Nb+L	PhCH=CH <sub>2</sub>	7 40	1 15(9)	1 3(2)	1 5(13)	0 1	80 (45)	-- --	80 6(59)
Ta <sup>d</sup>	C-PhCH=CHMe	3 40	1 9	1 4	1 2	0 ~0	-- --	68 87	70 90
Ta+L <sup>e</sup>	C-PhCH=CHMe	16	1	1	2	1	--	85 [3] <sup>f</sup>	90
Nb <sup>d</sup>	C-PhCH=CHMe	2 40	15 24	3 2	7 8	0 1	-- --	74 86	80 94
Nb+L <sup>d</sup>	C-PhCH=CHMe	7 40	10 15	4 4	11 7	1 ~0	-- --	68 80	80 87
Ta	c-stilbene	3 40	30 33	1 3	81 87	0 1	-- --	-- --	81 88
Ta+L	c-stilbene	12	24	15	101	0	--	--	101
	t-stilbene	16	82	2	24	1	--	--	25

Table V. (continued)

M <sup>b</sup>	Olefin	time(h)	t-stilbene	c-stilbene	t-PhCH=CHMe <sub>3</sub>	c-PhCH=CHMe <sub>3</sub>	Me <sub>3</sub> CCH=CH <sub>2</sub>	t-Me <sub>3</sub> CCH=CHMe	% rxn <sup>c</sup>
Nb	c-stilbene	2	27	21	91	8	--	--	99
		40	43	3	98	~0	--	--	99
Nb+L	c-stilbene	8	1	62	64	1	--	--	66
		40	27	29	92	1	--	--	93

<sup>a</sup> Approximately one equivalent of olefin at 25° in benzene. Yields of olefin products are in mol % using the decimal value rounded off to the nearest integer. Values in brackets are from the same sample but passed through a short column of activated alumina prior to injection.

<sup>b</sup> L = PMe<sub>3</sub>.

<sup>c</sup> % rxn ≡ the sum of all t-butyl containing metathesis products. Values calculated using decimal values and may differ from the rounded off data.

<sup>d</sup> cis-Me<sub>3</sub>CCH=CHMe is obscured in GLC trace.

<sup>e</sup> Ether was used as a solvent instead of benzene.

<sup>f</sup> Cis-4,4-dimethyl-2-pentene.

Experimental

See Chapter 1 for general information.

$M(\text{CH}_2\text{CMe}_3)_2\text{X}_3$ ,  $\text{Ta}(\text{CH}_2\text{CMe}_3)\text{Cl}_4$ ,  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3(\text{PMe}_3)$ ,  
 $[\text{Ta}(\text{CHCMe}_3)\text{X}_3(\text{PMe}_3)]_2$ ,  $M(\text{CHCMe}_3)\text{X}_3(\text{PMe}_3)_2$ ,  $\text{Ta}(\text{CHCMe}_3)\text{Cl}_3(\text{THF})_2$ ,  
 $M(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ ,  $\text{Ta}(\text{CHSiMe}_3)\text{Cl}_3(\text{PMe}_3)_2$  and  
 $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$ ; for  $M = \text{Ta}, \text{Nb}$  and  $X = \text{Cl}, \text{Br}$ , were prepared  
 similar to the methods previously described by Rupprecht.<sup>18</sup>  
 $\text{Ta}(\text{CH}_2=\text{CHPh})\text{Cl}_3(\text{PMe}_3)_2$  was obtained from Rupprecht.  $\text{PMe}_2\text{Ph}$  and  
 $\text{PPr}_3^n$  were obtained from J. Wengrovius.  $\text{PMe}_3$ ,<sup>40</sup>  
 $\text{Mg}(\text{C}_2\text{H}_5)_2$  dioxane,  $\text{Mg}(\text{C}_2\text{H}_5)\text{Br}$ , and  $[\text{TaCl}_3(\text{THT})]_2(\text{THT})$ <sup>33</sup> were  
 prepared by published methods.  $\text{Zn}(\text{C}_2\text{H}_5)_2$  (Alfa/Ventron) was  
 used as received.

<sup>31</sup>P spectra were recorded at 36.2 MHz (Jeol FX-90Q), 36.4 MHz  
 (Brücker HFX-90) or 109.3 MHz (Brücker HFX-270) and are reported as  
 ppm downfield from external 85%  $\text{H}_3\text{PO}_4$ . <sup>13</sup>C{<sup>1</sup>H} NMR magnetization  
 transfer measurements<sup>41</sup> were made at 67.89 MHz (Brücker WH-270),  
 using 16 K memory and Nicolet software. A dual-channel frequency  
 synthesizer was used to generate narrow (P3) and broad (P1)  
 frequency pulses. Data were collected, using the pulse sequence  
 $\left\langle \text{P3}-\tau-\text{P1} \right\rangle_x$  [P3(saturation pulse) = 4 sec, 1 to 4 W;  
 $\tau = 0.001$  sec; and P1(observation pulse) = 15  $\mu\text{sec}(90^\circ)$ ] waiting  
 $5T_1$  (75 sec) for nine transients, at 0°.

$^{31}\text{P}$  NMR Study of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3(\text{PMe}_3)$  (VIII, 61)

$\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3(\text{PMe}_3)^{18}$  (~0.1 g) was dissolved in cold toluene (~1 mL), transferred to a NMR tube and kept at  $-78^\circ$  until analyzed.

The sample was placed in the NMR probe at  $-90^\circ$  and equilibrated.

$^{31}\text{P}$  { $^1\text{H}$ } NMR spectra, at 36.4 MHz, were recorded from  $-90^\circ$  to  $40^\circ$ .

$\text{Ta}(\text{CHCMe}_3)_2\text{Cl}_3(\text{PMe}_3)$  ( $\delta = -12$  ppm, and trans,mer- $\text{Ta}(\text{CHCMe}_3)_2\text{Cl}_3(\text{PMe}_3)$  ( $\delta = -2$  ppm), were present

at  $-90^\circ$  in a ratio of 30:1. At  $-60^\circ$ , an unidentified peak ( $\delta = 29$  ppm) was growing in

while the other resonances remained unchanged. The peaks at  $-12$

and 29 were broadening with  $\text{Ta}(\text{CHCMe}_3)_2\text{Cl}_3(\text{PMe}_3)$  staying sharp at

$-20^\circ$ . Warming to  $5^\circ$  caused the peak at 29 ppm to disappear with

the  $-12$  resonance becoming more broad. At temperatures greater

than  $5^\circ$ ,  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3(\text{PMe}_3)$  decreased in intensity while

$\text{Ta}(\text{CHCMe}_3)_2\text{Cl}_3(\text{PMe}_3)$  increased (VIII, 61-1A through 11A). The peak

at 29 ppm may be due to a different isomer of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3(\text{PMe}_3)$

since it exchanges at the same rate as the  $-12$  ppm peak. No

further investigations of this system were made.

Preparation of  $[\text{Ta}(\text{CHCMe}_3)_2\text{Cl}_3(\text{PMe}_3)]_2$

1. From  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3(\text{PMe}_3)$  (III, 16)

Standing  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3(\text{PMe}_3)$  (0.5 g, 1.0 mmol) in  $\text{Et}_2\text{O}$  (~3 mL)

for 2d at  $25^\circ$  gives 0.3 g of large ruby-red crystals of

$[\text{Ta}(\text{CHCMe}_3)_2\text{Cl}_3(\text{PMe}_3)]_2$ . The mother liquor was stripped and extracted

with pentane. The pentane soluble fraction, mainly consists of

$\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$  (70% yield).

2. From Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub> and Ta(CHCMe<sub>3</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub> (III, 21)

Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub> (0.43 g, 1.0 mmol) and Ta(CHCMe<sub>3</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub> (0.51 g, 1.0 mmol) were dissolved in 4 mL of Et<sub>2</sub>O, previously cooled to -30°. The reaction mixture was warmed to 25° and left undisturbed for 2d. Filtration gave 0.54 g of large red crystals of [Ta(CHCMe<sub>3</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>] (62% yield).

An analytically pure sample was obtained by fractional crystallization from hot toluene.

Anal. (III, 21; III, 16-1): Calcd. for TaC<sub>8</sub>H<sub>19</sub>Cl<sub>3</sub>P: C, 22.17; H, 4.42; P, 7.15. Found: C, 22.68; H, 4.28; P, 5.60.

<sup>13</sup>C NMR (δ; C<sub>6</sub>D<sub>6</sub>; 15 MHz; III, 21-1A, 2A; {<sup>1</sup>H} and gated {<sup>1</sup>H}; 25°): 276 (dd, <sup>2</sup>J<sub>CP</sub> = 7.3 Hz, <sup>1</sup>J<sub>CH</sub> = 101 Hz, CHCMe<sub>3</sub>); 35.5 (s, CHCMe<sub>3</sub>); 33.5 (q, <sup>1</sup>J<sub>CH</sub> = 126 Hz, CHCMe<sub>3</sub>); 15.8 (qd, <sup>1</sup>J<sub>CP</sub> = 29 Hz, <sup>1</sup>J<sub>CH</sub> = 132 Hz, PMe<sub>3</sub>).

The remaining spectral data have been reported.<sup>18</sup>

[Ta(CH<sub>2</sub>CMe<sub>3</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>], prepared in situ, reacts with excess CX<sub>3</sub>CN (X = H or D) to give Ta[N(CX<sub>3</sub>)C=CHCMe<sub>3</sub>]Cl<sub>3</sub>(PMe<sub>3</sub>) X as a mixture of E and Z isomers. The E/Z ratio was 2:1.

<sup>1</sup>H NMR (δ; CD<sub>3</sub>CN; 60 MHz; III, 13-1C, 2C; 25°): E isomer: 4.92 (m, 1, vinylic H); 1.76 (m, 3, vinylic Me); 1.50 (d, 9, <sup>2</sup>J<sub>PH</sub> ≈ 9 Hz, PMe<sub>3</sub>); 1.09 (s, 9, CMe<sub>3</sub>).

Z isomer: 4.38 (m, 1, vinylic H); 1.76 (m, 3, vinylic Me); 1.52 (d, 9, <sup>2</sup>J<sub>PH</sub> ≈ 9 Hz, PMe<sub>3</sub>); 1.22 (s, 9, CMe<sub>3</sub>).

Preparation of  $[\text{Ta}(\text{CHCMe}_3)\text{Cl}_3(\text{PPr}^n_3)]_2$  (VIII, 21)

$\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$  (2.0 g, 4.66 mmol) dissolved in pentane (15 mL) was reacted with  $\text{PPr}^n_3$  (0.75 g, 4.66 mmol) to give a red solution. After standing undisturbed for 5d at 25°, a few crystals were deposited from solution. Cooling to -30° for 2 h gave 1.36 g of red crystals which were isolated by filtration and dried in vacuo (56% yield).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 62.83 MHz; VIII, 61-1B through 4B;  $\{^1\text{H}\}$  and gated  $\{^1\text{H}\}$ ; 25°): 276.7 (dd,  $^2\text{J}_{\text{CP}} = 7.32$  Hz,  $^1\text{J}_{\text{CH}} = 87.9$  Hz,  $\text{CHCMe}_3$ ); 46.9 (s,  $\text{CHCMe}_3$ ); 33.6 (q,  $^1\text{J}_{\text{CH}} = 127.8$  Hz,  $\text{CHCMe}_3$ ); 28.1 (td,  $^1\text{J}_{\text{CP}} = 24.4$  Hz,  $^1\text{J}_{\text{CH}} = 124.5$  Hz,  $\text{PCH}_2\text{CH}_2\text{CH}_3$ ); 18.3 (t,  $^1\text{J}_{\text{CH}} = 124.5$  Hz,  $\text{PCH}_2\text{CH}_2\text{CH}_3$ ); 16.1 (qd,  $^3\text{J}_{\text{CP}} = 12.2$  Hz,  $^1\text{J}_{\text{CH}} = 126.1$  Hz,  $\text{PCH}_2\text{CH}_2\text{CH}_3$ ).

Preparation of  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$

1. From  $\text{Ta}(\text{CH}_2\text{CMe}_3)\text{Cl}_4$  and  $\text{Zn}(\text{C}_2\text{H}_5)_2$  (IV, 44)

$\text{Ta}(\text{CH}_2\text{CMe}_3)\text{Cl}_4$  (0.39 g, 1.0 mmol) reacts with a 9:1 toluene/pentane solution (8 mL), containing  $\text{PMe}_3$  (0.2 mL), to give a deep red solution of the phosphine adduct at -30°.

$\text{Zn}(\text{C}_2\text{H}_5)_2$  (0.12 g, 1 mmol) reacts with the cold Ta solution as the reaction mixture is slowly warmed to room temperature; changing from red to blue, and finally to brown after 1 h at 25°.

After removal of the solvent in vacuo, the residue was transferred to a sublimator.  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  (0.1 g) was sublimed at 80° and  $1\mu$ , and identified by  $^1\text{H}$  NMR (22% yield). The yield of this reaction should improve by using 0.5 equivalents of  $\text{Zn}(\text{C}_2\text{H}_5)_2$ .

2. From  $[\text{TaCl}_3(\text{THT})]_2(\text{THT})$  and  $\text{PMe}_3$  Under  $\text{C}_2\text{H}_4$  (V, 19)

$[\text{TaCl}_3(\text{THT})]_2(\text{THT})$  (0.1 g, 0.12 mmol) dissolved in toluene (2 mL) containing  $\text{PMe}_3$  (0.08 g, 1.0 mmol, excess), reacts slowly with  $\text{C}_2\text{H}_4$  (30 psi) at  $65^\circ$ . A red precipitate forms in 1 h which redissolves in 2 h to give a homogeneous red solution that becomes deep blue after 16 h. The solvent was removed in vacuo to give 0.1 g of blue crystals which were identified as  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  by  $^1\text{H}$  NMR (90% yield).  $[\text{TaCl}_3(\text{THF})]_2(\text{THT})$  dissolved in  $\text{C}_6\text{H}_6$ , does not react with  $\text{C}_2\text{H}_4$  (30 psi) at  $65^\circ$  after 18 h in the absence of  $\text{PMe}_3$ .

$[\text{TaCl}_3(\text{THT})]_2(\text{THT})$  was isolated in quantitative yield and identified by  $^{13}\text{C}$  NMR (V, 22).

$\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  (0.2 g, 0.43 mmol) reacts with excess butadiene in  $\text{Et}_2\text{O}$  (10 mL) at  $0^\circ$  (24 h), to give 0.1 g of an insoluble yellow powder and a blue solution containing unreacted starting material (III, 32).

Preparation of  $\text{Ta}(\text{C}_2\text{H}_4)\text{Br}_3(\text{PMe}_3)_2$  (V, 15)

$\text{Ta}(\text{CHCMe}_3)\text{Br}_3(\text{PMe}_3)_2$  (3.26 g, 5.07 mmol) was dissolved in  $\text{Et}_2\text{O}$  (40 mL) and pressurized with  $\text{C}_2\text{H}_4$  (30 psi) for 20 h.  $\text{Et}_2\text{O}$  (100 mL) was added to the reaction mixture. Filtration, followed by fractional crystallization, gave 2.8 g of green needles which dissolve in aromatic solvents to give light blue solutions (92% yield).

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{H}_6$ ; 60 MHz; V, 15-2;  $25^\circ$ ): 3.05 (t, 4,  $^3\text{J}_{\text{PH}} \approx 2$  Hz,  $\text{C}_2\text{H}_4$ ); 1.70 (t, 18,  $^2\text{J}_{\text{PH}} \approx 4$  Hz,  $\text{PMe}_3$ ).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{H}_6$ ; 15 MHz; V, 7-5;  $\{^1\text{H}\}$ ;  $25^\circ$ ): 62.8 (br t,  $^2\text{J}_{\text{CP}} \approx 3$  Hz,  $\text{C}_2\text{H}_4$ ); 16.4 (t,  $^1\text{J}_{\text{CP}} \approx 14$  Hz,  $\text{PMe}_3$ ).

Variable Temperature  $^1\text{H}$  NMR of  $\text{Ta}(\text{CH}_2=\text{CHPh})\text{Cl}_3(\text{PMe}_3)_2$  (VIII, 70)

A variable temperature study, by  $^1\text{H}$  NMR at 89.9 MHz, of  $\text{Ta}(\text{CH}_2=\text{CHPh})\text{Cl}_3(\text{PMe}_3)_2$  in  $d_8$ -toluene clearly shows that  $\text{PMe}_3$  is lost reversibly. Some product decomposition giving free styrene was also noted.

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 89.9 MHz; VIII, 70-1A through 22A;  $25^\circ$  to  $140^\circ$ ): ( $140^\circ$ ): 1.55 (br d,  $^2J_{\text{PH}} \approx 8.3$  Hz,  $\text{PMe}_3$ ). ( $132^\circ$ ): coalescence of bound and free  $\text{PMe}_3$ . ( $25^\circ$ ): 1.482 (t,  $^2J_{\text{PH}} = 4.15$  Hz,  $\text{PMe}_3$  (A)); 1.316 (t,  $^2J_{\text{PH}} = 4.15$  Hz,  $\text{PMe}_3$  (B)). Assuming  $\delta$  for free  $\text{PMe}_3$  was 0.9 ppm,  $\Delta\nu(140^\circ) = 59.4$  Hz,  $\Delta G^\ddagger \approx 20$  kcal mol $^{-1}$ . A complete list of the proton resonances for  $\text{Ta}(\text{CH}_2=\text{CHPh})\text{Cl}_3(\text{PMe}_3)_2$  has been reported.<sup>18</sup>

Preparation of  $[\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{THF})_2]_x$  (VIII, 38)

$\text{Ta}(\text{CHCMe}_3)\text{Cl}_3(\text{THF})_2$  (2.50 g, 4.98 mmol) dissolved in THF (~10 mL) reacts with  $\text{C}_2\text{H}_4$  (30 psi) at  $25^\circ$  in 4 h. The blue solution was filtered and the product (0.43 g) was washed with cold THF (~5 mL) and dried in vacuo. The filtrate was reduced to ~3 mL. An equal volume of  $\text{Et}_2\text{O}$  was added and the solution was cooled to  $-30^\circ$  for 4 h. 1.34 g of product was isolated by filtration, combined with the first fraction and recrystallized from a saturated THF solution, containing ~6 mL of  $\text{Et}_2\text{O}$ , at  $-30^\circ$  for 12 h (1.37 g, 60% yield).

$\text{Ta}(\text{CHCMe}_3)\text{Cl}_3(\text{THF})_2$  (0.47 g, 0.94 mmol) dissolved in 5 mL of a 4:1  $\text{Et}_2\text{O}$ /THF solution gives, after reaction with  $\text{C}_2\text{H}_4$  and a similar workup procedure, 70 mg (16%) of  $[\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{THF})_2]_x$  and 0.1 g of tarry green residue (VI, 46).

$[\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{THF})_2]_x$  reacts with excess  $\text{PMe}_3$  in  $\text{C}_6\text{H}_6$  (~1 mL) to give a >90% yield of  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  and 1.92 equivalents  $\text{Ta}^{-1}$  of THF (vs. an internal toluene standard), by  $^1\text{H}$  NMR (VI, 75). In a separate experiment,  $[\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{THF})_2]_x$  (0.209 g, 0.455 mmol) suspended in mesitylene (~5 mL) containing n-octane (30  $\mu\text{L}$ , 0.185 mmol) reacts with excess  $\text{PMe}_3$  liberating THF. GLC analysis, using experimentally determined response factors on columns A and C gave 2.27 and 2.05 equivalents  $\text{Ta}^{-1}$  of THF, respectively (VIII, 33).

$\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_2\text{Ph})_2$  has also been prepared from  $[\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{THF})_2]_x$  and isolated in 83% yield (IX, 25).

$^1\text{H}$  NMR ( $\delta$ ; THF- $d_8$ ; 250 MHz; VIII, 39-5; 25°): 3.63 (br, 15, THF H); 2.87 (s, 4,  $\text{C}_2\text{H}_4$ ); 1.78 (br, 14, THF H).

$^1\text{H}$  NMR at 250 MHz in aromatic solvents at 25° and -60° showed the presence of at least 3 isomers which were not assigned (VIII, 61-1C through 3C).

$^{13}\text{C}$  NMR ( $\delta$ ; THF- $d_8$ ; 22.5 MHz; VIII, 39-1 through 4;  $\{^1\text{H}\}$  and gated  $\{^1\text{H}\}$ ; 25°): 87.4 (t,  $^1J_{\text{CH}} = 152$  Hz;  $\text{C}_2\text{H}_4$ ); 68.4 (br t,  $^1J_{\text{CH}} = 141$  Hz, 2, 5 THF  $\underline{\text{C}}$ ); 26.3 (br t,  $^1J_{\text{CH}} = 131$  Hz, 3,4 THF  $\underline{\text{C}}$ ).

Preparation of  $[\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)]_x$  (VIII, 19)

$[\text{Ta}(\text{CHCMe}_3)\text{Cl}_3(\text{PMe}_3)]_2$  (2.20 g, 2.54 mmol) was dissolved in toluene (~100 mL), filtered and pressurized with  $\text{C}_2\text{H}_4$  (40 psi). The reaction mixture was left under  $\text{C}_2\text{H}_4$  pressure for 24 h without stirring. A color change from red to blue occurred. The solution was filtered leaving 40 mg of blue crystals and a homogeneous blue solution. The

filtrate was stripped to ~40 mL. Addition of pentane (~30 mL) caused precipitation of a violet powder (0.86 g) which was isolated by filtration, washed with pentane and dried in vacuo. A second crop (0.30 g) was collected after more pentane was added to the filtrate (59% yield).

$[\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)]_x$  is insoluble in  $\text{Et}_2\text{O}$ , very slightly soluble in toluene and THF and reacts with chloroform.

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 89.9 MHz; VIII, 72-1A through 3A;  $30^\circ$  to  $-40^\circ$ ): ( $30^\circ$ ): 3.04 (m, olefinic H); 1.353 (d,  $^2J_{\text{PH}} = 9.0$  Hz,  $\text{PMe}_3$ ).

$^{31}\text{P}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 36.3 MHz; VIII, 72-4A;  $\{^1\text{H}\}$ ;  $-60^\circ$ ): -8 (s, 3.2); -12 (s, 1).

Preparation of  $[\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PPr}_3^n)]_x$  (VIII, 24)

$[\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PPr}_3^n)]_x$  was prepared in the same manner as  $[\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)]_x$  (see above) with a 78% yield. The  $^{13}\text{C}$  NMR of  $[\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PPr}_3^n)]_x$  was complicated due to the insolubility of this complex. However, it was possible to assign some of the resonances present as  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PPr}_3^n)_2$  (VIII, 24-1 through 4).

Reaction of  $[\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3\text{L}]_x$ ; L =  $\text{PMe}_3$ ,  $\text{PPr}_3^n$ , with  $\text{PMe}_2\text{Ph}$

1. L =  $\text{PMe}_3$  (VIII, 20)

$[\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)]_x$  (0.5 g, 1.28 mmol) was mixed with toluene (5 mL).  $\text{PMe}_2\text{Ph}$  (0.18 g, 1.30 mmol, excess) added to the stirring suspension caused an immediate reaction giving a blue solution. The reaction mixture was stirred for 1 h. The solvent was removed in vacuo leaving

a residue which was extracted with 25 mL of Et<sub>2</sub>O and filtered. The filtrate was reduced in volume to ~10 mL and filtered yielding 0.32 g of blue powder. An additional crop was collected after cooling the filtrate to -30° for 2 h. NMR analysis (see below) of the product collected showed it to be a 3:1:2 mixture of

Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>(PMe<sub>2</sub>Ph)(PMe<sub>3</sub>), Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub> and Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> (73% yield).

<sup>1</sup>H NMR (δ; C<sub>6</sub>D<sub>6</sub>; 250 MHz; VIII, 73-1A through 5A; 30°):

Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>(PMe<sub>2</sub>Ph)(PMe<sub>3</sub>): 7.5 - 6.7 (m, phenyl H); 2.96 (mt, <sup>3</sup>J<sub>PH</sub> ≈ 2 Hz, olefinic H<sub>A</sub>H<sub>A</sub>'); 2.82 (mt, <sup>3</sup>J<sub>PH</sub> ≈ 2 Hz, olefinic H<sub>B</sub>H<sub>B</sub>'); 2.01 (d, <sup>2</sup>J<sub>PH</sub> = 8.6 Hz, PMe<sub>2</sub>Ph); 1.57 (d, <sup>2</sup>J<sub>PH</sub> = 8.9 Hz, PMe<sub>3</sub>).

Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>: 2.99 (t, <sup>3</sup>J<sub>PH</sub> = 2.2 Hz, C<sub>2</sub>H<sub>4</sub>); 1.59 (t, <sup>2</sup>J<sub>PH</sub> ≈ 4 Hz, PMe<sub>3</sub>).

Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>: 7.5-6.7 (m, phenyl H); 2.66 (t, <sup>3</sup>J<sub>PH</sub> = 2.2 Hz, C<sub>2</sub>H<sub>4</sub>); 2.00 (t, <sup>2</sup>J<sub>PH</sub> = 4.0 Hz, PMe<sub>2</sub>Ph).

<sup>13</sup>C NMR (δ; C<sub>6</sub>D<sub>6</sub>; 22.5 MHz; VIII, 71-1A through 3A; {<sup>1</sup>H}; 30°):

Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>(PMe<sub>2</sub>Ph)(PMe<sub>3</sub>): 137 through 124 (m, phenyl resonances); 62.58 (d, <sup>2</sup>J<sub>PC</sub> = 4.9 Hz, CH<sub>2</sub>=CH<sub>2</sub>); 60.09 (d, <sup>2</sup>J<sub>PC</sub> = 4.9 Hz, CH<sub>2</sub>=CH<sub>2</sub>); 14.95 (d, <sup>1</sup>J<sub>PC</sub> = 15.9 Hz, PMe<sub>3</sub>); 13.36 (d, <sup>1</sup>J<sub>PC</sub> = 13 Hz, PMe<sub>2</sub>Ph).

Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>: 59.0 (t, <sup>2</sup>J<sub>PC</sub> = 3 Hz, C<sub>2</sub>H<sub>4</sub>); 14.4 (t, <sup>1</sup>J<sub>PC</sub> = 13 Hz, PMe<sub>3</sub>).

Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>: 137 through 124 (m, phenyl resonances); 63.61 (t, <sup>2</sup>J<sub>PC</sub> ≈ 3 Hz, C<sub>2</sub>H<sub>4</sub>); 13.5 (t, <sup>1</sup>J<sub>PC</sub> = 12.8 Hz, PMe<sub>2</sub>Ph).

<sup>31</sup>P NMR (δ; C<sub>6</sub>D<sub>6</sub>; 36 MHz; VIII, 71-4A; {<sup>1</sup>H}; 30°): Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>(PMe<sub>2</sub>Ph)(PMe<sub>3</sub>): 6.8 (d, <sup>2</sup>J<sub>PA PB</sub> = 151 Hz, PMe<sub>2</sub>Ph); -3.9 (d, <sup>2</sup>J<sub>PB PA</sub> = 150 Hz, PMe<sub>3</sub>).

Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>: -4.1 (s). Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>: +6.9 (s).

2.  $L = PPr_3^n$  (VIII, 25)

$[Ta(CHCMe_3)Cl_3(PPr_3^n)]_2$  (0.56 g, 0.54 mmol) was reacted with  $C_2H_4$  (30 psi) for 3 h at  $25^\circ$  in  $C_6D_6$  (2 mL).  $PMe_2Ph$  (0.15 g, 1.08 mmol) was added to the reaction mixture and stirred for 30 min. NMR analysis (see below) of the reaction mixture showed a >95% yield of a 3:1:2 mixture of  $Ta(C_2H_4)Cl_3(PMe_2Ph)(PPr_3^n)$ ,  $Ta(C_2H_4)Cl_3(PPr_3^n)_2$  and  $Ta(C_2H_4)Cl_3(PMe_2Ph)_2$ . 4,4-Dimethyl-trans-2-pentene and 4,4-dimethyl-1-pentene were also present in a 9:1 ratio.

$^1H$  NMR ( $\delta$ ;  $C_6D_6$ ; 250 MHz; VIII, 73-6A through 8A;  $30^\circ$ ): olefinic protons only: 2.984 (t,  $^3J_{PH} = 1.7$  Hz,  $Ta(C_2H_4)Cl_3(PPr_3^n)_2$ ); 2.890 (ddt,  $^3J_{PH} = 1.6$  Hz,  $^2J_{HAHA'} = 5.6$  Hz,  $^3J_{HBHA} = 11.1$  Hz,  $Ta(\underline{CH_AH_A'} = \underline{CH_BH_B'})Cl_3(PMe_2Ph)(PPr_3^n)$ ); 2.614 (ddt,  $^3J_{PH} = 1.6$  Hz,  $^2J_{HBHB'} = 6.1$  Hz,  $^3J_{HAHB} = 11.1$  Hz,  $Ta(\underline{CH_AH_A'} = \underline{CH_BH_B'})Cl_3(PMe_2Ph)(PPr_3^n)$ ); 2.614 (t,  $^3J_{PH} = 2.2$  Hz,  $PMe_2Ph$ ). The other resonances were not assigned.

$^{13}C$  NMR ( $\delta$ ;  $C_6D_6$ ; 62.83 MHz; VIII, 25-1 through 16;  $\{^1H\}$  and gated  $\{^1H\}$ ;  $30^\circ$ ):  $Ta(C_2H_4)Cl_3(PMe_2Ph)(PPr_3^n)$ : 136.3 (d,  $^1J_{PC} = 40.2$  Hz, phenyl  $C_\alpha$ ); 130.54 (dd,  $^2J_{PC} = 8.9$  Hz,  $^1J_{CH} \approx 160$  Hz, phenyl ortho C); 129.5, 128.3 (m, phenyl meta and para C); 62.23 (td,  $^2J_{PC} = 5.96$  Hz,  $^1J_{CH} = 150$  Hz,  $\underline{CH_2=CH_2}$ ); 61.14 (td,  $^2J_{PC} = 5.95$  Hz,  $^1J_{CH} = 149$  Hz,  $\underline{CH_2=CH_2}$ ); 25.89 (td,  $^1J_{PC} = 19.4$  Hz,  $^1J_{CH} \approx 128$ ,  $\underline{PCH_2CH_2CH_3}$ ); 17.16 (t,  $^1J_{CH} = 126$  Hz,  $\underline{PCH_2CH_2CH_3}$ ); 16.17 (qd,  $^1J_{PC} = 11.91$  Hz,  $^1J_{CH} \approx 125$  Hz,  $\underline{PMe_2Ph}$ ); 13.49 (qd,  $^3J_{PC} = 13.5$  Hz,  $^1J_{CH} \approx 130$  Hz,  $\underline{PCH_2CH_2CH_3}$ ).  $Ta(C_2H_4)Cl_3(PPr_3^n)_2$ : 59.64 (tt,  $^2J_{PC} \approx 6$  Hz,  $^1J_{CH} = 148$  Hz,  $\underline{C_2H_4}$ ); 25.95 (tt,  $^1J_{PC} = 10.4$  Hz,  $^1J_{CH} \approx 128$  Hz,  $\underline{PCH_2CH_2CH_3}$ ); 16.21 (t,

$^1J_{CH} = 126$  Hz,  $PCH_2CH_2CH_3$ ); 13.29 (qd,  $^3J_{PC} = 10.4$  Hz,  $^1J_{CH} \approx 130$  Hz,  $PCH_2CH_2CH_3$ ).

$Ta(C_2H_4)Cl_3(PMe_2Ph)_2$ : 136.0 (t,  $^1J_{PC} = 20.1$  Hz, phenyl  $C_\alpha$ ); 130.5 (dt,  $^2J_{PC} = 4.5$  Hz,  $^1J_{CH} = 161$  Hz, phenyl ortho C); 129.5, 128.4 (m, phenyl meta and para C); 63.6 (tt,  $^2J_{PC} \approx 4$  Hz,  $^1J_{CH} = 153$  Hz,  $C_2H_4$ ); 13.28 (qt,  $^1J_{PC} = 12.7$  Hz,  $^1J_{CH} = 131$  Hz,  $PMe_2Ph$ ).

Preparation of  $[NbCl_3(PMe_3)_2]_2$  (V, 6)

$NbCl_5$  (1.35 g, 5.0 mmol) was dissolved in toluene (20 mL) and cooled to  $-30^\circ$ .  $PMe_3$  (1.52 g, 20 mmol) was added to the cold Nb solution causing an immediate precipitate of the orange  $PMe_3$  adduct. 0.83% Na/Hg (27.7 g, 10 mmol) was added and the reaction mixture was warmed to  $25^\circ$  and vigorously stirred for 1.5 h. The red solution was filtered through celite and the volume was reduced (in vacuo) to 10 mL. Trituration with pentane (5 mL) gave 1.0 g of purple crystals which were isolated by filtration and dried (in vacuo). An analytically pure sample was obtained by multiple recrystallizations from concentrated  $CH_2Cl_2$  solutions at  $-30^\circ$  (57% yield).

Anal. (V, 6; V, 6-1): Calcd. for  $NbC_6H_{18}Cl_3P_2$ : C, 20.50; H, 5.16.

Found: C, 20.48; H, 5.19.

$^1H$  NMR ( $\delta$ ;  $CH_2Cl_2$ ; 60 MHz; V, 6-1;  $25^\circ$ ): 1.67 (br m,  $PMe_3'$ ); 1.22 (br s,  $PMe_3$ ).

IR ( $cm^{-1}$ ; Nujol/NaCl; V, 6-1A): 960, s ( $\nu_{P-C}$ ).

Preparation of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{C}_2\text{H}_5)\text{Cl}_2$  (V, 20)

$\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$  (1.41 g, 3.28 mmol) was dissolved in pentane (20 mL) and cooled to  $-30^\circ$ .  $\text{Zn}(\text{C}_2\text{H}_5)_2$  (0.21 g, 1.64 mmol), added rapidly, reacts immediately with the cold Ta solution. The solution was warmed to  $25^\circ$  and stirred for 10 min. Filtration gave 0.24 g of  $\text{ZnCl}_2$  (0.22 g theoretical). The yellow filtrate was stripped to an oil (1.36 g) which slowly darkened at  $25^\circ$  (98% yield).

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 60 MHz; V, 20-1;  $-20^\circ$ ): 2.52 (s, 4,  $\text{CH}_2\text{CMe}_3$ ); 2.20 (m, 5, ethyl resonances); 1.22 (s, 18,  $\text{CH}_2\text{CMe}_3$ ).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 15 MHz; V, 20-2,3;  $\{^1\text{H}\}$  and gated  $\{^1\text{H}\}$ ;  $-20^\circ$ ): 112.0 (t,  $^1J_{\text{CH}} = 117$  Hz,  $\text{CH}_2\text{CMe}_3$ ); 90.8 (t,  $^1J_{\text{CH}} = 125$  Hz,  $\text{CH}_2\text{CH}_3$ ); 35.3 (q,  $^1J_{\text{CH}} = 125$  Hz,  $\text{CH}_2\text{CMe}_3$ ); 34.7 (s,  $\text{CH}_2\text{CMe}_3$ ); 14.4 (q,  $^1J_{\text{CH}} = 129$  Hz,  $\text{CH}_2\text{CH}_3$ ).

IR ( $\text{cm}^{-1}$ , neat oil/NaCl; VII, 50-1A): 2725 w ( $\nu_{\text{C-H}}$ ).

Preparation of  $[\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_5)\text{Cl}_2(\text{PMe}_3)_2 \text{ (A)} \rightleftharpoons \text{Ta}(\text{CH}_2\text{CMe}_3)(\text{C}_2\text{H}_4)\text{Cl}_2(\text{PMe}_3)_2 \text{ (B)}]$  (V, 26)

$\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{C}_2\text{H}_5)\text{Cl}_2$  (0.93 g, 2.20 mmol) was dissolved in  $\text{Et}_2\text{O}$  (10 mL) and cooled to  $-30^\circ$ .  $\text{PMe}_3$  (0.35 g, 4.60 mmol, excess) dissolved in  $\text{Et}_2\text{O}$  (5 mL) and cooled to  $-30^\circ$ , was added rapidly to the cold Ta solution. An immediate reaction occurred resulting in a color change from yellow to red. The solution was warmed to  $25^\circ$  and stirred for 10 min. The solvent was removed in vacuo leaving a brown oil. The oil was extracted with pentane (10 mL), filtered and cooled to  $-30^\circ$ . Standing for 12 h gave 0.84 g of brown urchin-like needles. Due to impurities which were difficult to separate from the product, no

additional crops were collected. The crystalline product is indefinitely stable at  $-30^\circ$  but decomposes in 1 h at  $25^\circ$  to give an intractable brown tar (76% yield). Similar results were obtained using pentane as a solvent (V, 31).

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 270 MHz; V, 18-1;  $-40^\circ$ ):  $\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_5)\text{Cl}_2(\text{PMe}_3)_2$ : 1.372 (br m,  $^2\text{J}_{\text{PH}} = 7.37$  Hz,  $\text{PMe}_3$ ); 0.742 (s,  $\text{CHCMe}_3$ );  $-0.087$  (br m,  $\text{CH}_2\text{CH}_3$ ).

$\text{Ta}(\text{CH}_2\text{CMe}_3)(\text{C}_2\text{H}_4)\text{Cl}_2(\text{PMe}_3)_2$ : 2.431 (br m,  $\text{C}_2\text{H}_4$ ); 1.459 (br t,  $^2\text{J}_{\text{PH}} = 3.64$  Hz,  $\text{PMe}_3$ ); 0.556 (s,  $\text{CH}_2\text{CMe}_3$ );  $-1.952$  (s,  $\text{CH}_2\text{CMe}_3$ ).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 67.89 MHz; V, 34-3,4;  $\{^1\text{H}\}$  and gated  $\{^1\text{H}\}$ ;  $-20^\circ$ ):  $\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_5)\text{Cl}_2(\text{PMe}_3)_2$ : 222.3 (dt,  $^2\text{J}_{\text{CP}} = 8.1$  Hz,  $^1\text{J}_{\text{CH}} = 80.3$  Hz,  $\text{CHCMe}_3$ ); 46.7 (s,  $\text{CHCMe}_3$ ); 39.6 (tt,  $^2\text{J}_{\text{CP}} = 9.5$  Hz,  $^1\text{J}_{\text{CH}} = 146$  Hz,  $\text{CH}_2\text{CH}_3$ ); 33.2 (q,  $^1\text{J}_{\text{CH}} = 126$  Hz,  $\text{CHCMe}_3$ ); 15.4 (qt,  $^1\text{J}_{\text{CP}} = 12.5$  Hz,  $^1\text{J}_{\text{CH}} \approx 130$  Hz,  $\text{PMe}_3$ );  $-3.0$  (qt,  $^3\text{J}_{\text{CP}} \approx 3$  Hz,  $^1\text{J}_{\text{CH}} = 124$  Hz,  $\text{CH}_2\text{CH}_3$ ).  $\text{Ta}(\text{CH}_2\text{CMe}_3)(\text{C}_2\text{H}_4)\text{Cl}_2(\text{PMe}_3)_2$ : 138.9 (t,  $^1\text{J}_{\text{CH}} = 98.4$  Hz,  $\text{CH}_2\text{CMe}_3$ ); 56.9 (tt,  $^2\text{J}_{\text{CP}} \approx 3$  Hz,  $^1\text{J}_{\text{CH}} = 150.7$  Hz,  $\text{C}_2\text{H}_4$ ); 38.5 (s,  $\text{CH}_2\text{CMe}_3$ ); 32.7 (q,  $^1\text{J}_{\text{CH}} = 127$  Hz,  $\text{CH}_2\text{CMe}_3$ ); 14.9 (qt,  $^1\text{J}_{\text{CP}} = 12.5$  Hz,  $^1\text{J}_{\text{CH}} \approx 130$  Hz,  $\text{PMe}_3$ ).

$^{31}\text{P}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 109.29 MHz; V, 35-29, 40-1A through 4A;  $\{^1\text{H}\}$ ;  $27^\circ$  to  $-67^\circ$ ):  $\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_5)\text{Cl}_2(\text{PMe}_3)_2$ : ( $27^\circ$ ):  $-12.4$  (br s).

( $-37^\circ$ ): coalescence of  $\text{P}_\text{A}$  and  $\text{P}_\text{B}$  resonances.

( $-67^\circ$ ): ca. low temperature limit;  $-7.4$  (d,  $^2\text{J}_{\text{P}_\text{A}\text{P}_\text{B}} = 124$  Hz,  $\text{PMe}_3(\text{A})$ );

$-17.7$  (d,  $^2\text{J}_{\text{P}_\text{B}\text{P}_\text{A}} = 126$  Hz,  $\text{PMe}_3(\text{B})$ ).

( $-67^\circ$ ):  $1122 \pm 20$  Hz separation between  $\text{P}_\text{A}$  and  $\text{P}_\text{B}$  with  $^2\text{J}_{\text{P}_\text{A}\text{P}_\text{B}} = 125 \pm 2$  Hz,  $\Delta G^\ddagger = 10.1 \pm 0.2$  kcal mol $^{-1}$ .

Ta(CH<sub>2</sub>CMe<sub>3</sub>)(C<sub>2</sub>H<sub>4</sub>)Cl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>: (27°): -11.7 (s, PMe<sub>3</sub>) remained a sharp singlet down to -67°. A small solvent effect was observed at -70°, in the relative amounts of Ta(CHCMe<sub>3</sub>)(C<sub>2</sub>H<sub>5</sub>)Cl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (A) to Ta(CH<sub>2</sub>CMe<sub>3</sub>)(C<sub>2</sub>H<sub>4</sub>)Cl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (B), by <sup>31</sup>P{<sup>1</sup>H} NMR at 36.4 MHz (VIII, 58). These data were normalized (setting A = 1) and are listed below.

solvent	A	B
Toluene <sup>a</sup>	1.0	1.25
Et <sub>2</sub> O <sup>a</sup>	1.0	1.03
THF <sup>a</sup>	1.0	1.09
Toluene <sup>b</sup>	1.0	1.52

<sup>a</sup>Without free PMe<sub>3</sub>.

<sup>b</sup>With >1 mol excess of free PMe<sub>3</sub>.

IR (cm<sup>-1</sup>; Nujol/NaCl; V, 31-1): 2680, br w (ν<sub>C-H<sub>α</sub></sub>, neopentyl); 2460, br m (ν<sub>C-H<sub>α</sub></sub>, neopentylidene); 2310, br w (ν<sub>C-H<sub>β</sub></sub>, ethyl). The ratio of A/B was 1:1 regardless of the solvent used for its preparation, by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR.

Preparation of [Ta(CHCMe<sub>3</sub>)(C<sub>2</sub>H<sub>5</sub>)Br<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (A) ⇌ Ta(CH<sub>2</sub>CMe<sub>3</sub>)(C<sub>2</sub>H<sub>4</sub>)Br<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (B)] (VI, 6)

Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)Br<sub>2</sub> (2 mmol) was prepared in hexane, by the same procedure used for Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)Cl<sub>2</sub>. The product was isolated as an oil and dissolved in cold (-30°) Et<sub>2</sub>O. PMe<sub>3</sub> (0.32 g, 4 mmol) was added to the cold Ta solution, warmed to 25° and stirred for 20 min.

Following the above work-up procedure, 0.21 g of a brown powder was isolated by crystallization from an Et<sub>2</sub>O/hexane solution (15% yield). Using pentane instead of Et<sub>2</sub>O as the solvent in the PMe<sub>3</sub> addition step, gave a 54% yield (VI, 26). The product obtained was impossible to purify. Consequently, no reaction chemistry was investigated.

<sup>1</sup>H NMR (δ; C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 270 MHz; VI, 30-7; -45°):

Ta(CHCMe<sub>3</sub>)(C<sub>2</sub>H<sub>5</sub>)Br<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>: 1.432 (br d, <sup>2</sup>J<sub>PH</sub> = 7.3 Hz, PMe<sub>3</sub>);

1.103 (m, CH<sub>2</sub>CH<sub>3</sub>); 0.679 (s, CHCMe<sub>3</sub>); 0.323 (s, CHCMe<sub>3</sub>); -0.222 (m, CH<sub>2</sub>CH<sub>3</sub>).

Ta(CH<sub>2</sub>CMe<sub>3</sub>)(C<sub>2</sub>H<sub>4</sub>)Br<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>: 1.540 (m, <sup>2</sup>J<sub>PH</sub> = 3.6 Hz, PMe<sub>3</sub>); 0.444 (s, CH<sub>2</sub>CMe<sub>3</sub>).

<sup>13</sup>C NMR (δ; C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 67.89 MHz; VI, 30-1 through 4; {<sup>1</sup>H} and gated

{<sup>1</sup>H}; -20°): Ta(CHCMe<sub>3</sub>)(C<sub>2</sub>H<sub>5</sub>)Br<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>: 225.9 (dt, <sup>2</sup>J<sub>CP</sub> = 8.1 Hz,

<sup>1</sup>J<sub>CH</sub> = 87 Hz, CHCMe<sub>3</sub>); 47.0 (s, CHCMe<sub>3</sub>); 39.1 (tt, <sup>2</sup>J<sub>PC</sub> = 9.5 Hz,

<sup>1</sup>J<sub>CH</sub> = 145 Hz, CH<sub>2</sub>CH<sub>3</sub>); 32.4 (q, <sup>1</sup>J<sub>CH</sub> = 126 Hz, CHCMe<sub>3</sub>); 16.7 (qt,

<sup>1</sup>J<sub>PC</sub> = 13 Hz, <sup>1</sup>J<sub>CH</sub> = 131 Hz, PMe<sub>3</sub>); -4.7 (br q, <sup>1</sup>J<sub>CH</sub> = 123 Hz,

CH<sub>2</sub>CH<sub>3</sub>).

Ta(CH<sub>2</sub>CMe<sub>3</sub>)(C<sub>2</sub>H<sub>4</sub>)Br<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>: 143 (CH<sub>2</sub>CMe<sub>3</sub>); 56.7 (br t, <sup>1</sup>J<sub>CH</sub> =

152 Hz, C<sub>2</sub>H<sub>4</sub>); 36.6 (s, CH<sub>2</sub>CMe<sub>3</sub>).

<sup>31</sup>P NMR (δ; C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 109.29 MHz; VI, 30-5, 6; {<sup>1</sup>H}; 27° and -67°):

Ta(CHCMe<sub>3</sub>)(C<sub>2</sub>H<sub>5</sub>)Br<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>: (27°): -11.1 (s). (-67°): -7.9 (br s,

P<sub>A</sub>); -15.3 (br s, P<sub>B</sub>).

Ta(CH<sub>2</sub>CMe<sub>3</sub>)(C<sub>2</sub>H<sub>4</sub>)Br<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>: (27°): -7.9 (s).

IR (cm<sup>-1</sup>; Nujol/NaCl; VI, 30-8): 2460, br w (ν<sub>C-H<sub>α</sub></sub>, neopentylidene);

950, s (ν<sub>P-C</sub>).

The ratio of A/B was 5:1 by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR.

Preparation of [Ta(CHCMe<sub>3</sub>)(C<sub>2</sub>H<sub>5</sub>)Cl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> (A) + Ta(CH<sub>2</sub>CMe<sub>3</sub>)(C<sub>2</sub>H<sub>4</sub>)Cl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> (B)] (VI, 3, 28)

Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)Cl<sub>2</sub> reacts with 2 equivalents of PMe<sub>2</sub>Ph in Et<sub>2</sub>O to give, after a similar work-up (see above), an 18% yield of a brown powder, and an equal amount of a blue powder which consists mainly of Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>. The products obtained were impossible to purify. Consequently, no reaction chemistry was investigated.

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 270 MHz; VI, 31-5; -45°): The <sup>1</sup>H NMR was difficult to analyze, however it was helpful in confirming some of the assignments made in the other systems.

<sup>13</sup>C NMR (δ; C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 67.89 MHz; VI, 3-1 through 4, 59-1A, 2A, 1B, 2B; {<sup>1</sup>H} and gated {<sup>1</sup>H}); -20°C): Ta(CHCMe<sub>3</sub>)(C<sub>2</sub>H<sub>5</sub>)Cl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>: 224 (br, CHCMe<sub>3</sub>); 138-127 (phenyl resonances); 47.0 (s, CHCMe<sub>3</sub>); 45.0 (br, CH<sub>2</sub>CH<sub>3</sub>); 32.5 (q, <sup>1</sup>J<sub>CH</sub> ≈ 127 Hz, CHCMe<sub>3</sub>); -0.58 (br q, <sup>1</sup>J<sub>CH</sub> = 123 Hz, CH<sub>2</sub>CH<sub>3</sub>).

Ta(CH<sub>2</sub>CMe<sub>3</sub>)(C<sub>2</sub>H<sub>4</sub>)Cl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>: 145 (t, <sup>1</sup>J<sub>CH</sub> = 94 Hz, CH<sub>2</sub>CMe<sub>3</sub>); 138-127 (phenyl resonances); 59.4 (br t, <sup>1</sup>J<sub>CH</sub> = 152 Hz, C<sub>2</sub>H<sub>4</sub>); 38.6 (s, CH<sub>2</sub>CMe<sub>3</sub>); 31.9 (q, <sup>1</sup>J<sub>CH</sub> = 127 Hz, CH<sub>2</sub>CMe<sub>3</sub>).

Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> (VIII, 59-1C through 4C): 63.7 (br t, <sup>1</sup>J<sub>CH</sub> = 151 Hz, C<sub>2</sub>H<sub>4</sub>); 12.9 (qt, <sup>1</sup>J<sub>CP</sub> ≈ 11 Hz, <sup>1</sup>J<sub>CH</sub> = 127 Hz, PMe<sub>2</sub>Ph); 138-127 (phenyl resonances).

<sup>31</sup>P {<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 109.29 MHz; VIII, 60-1A, 2A; -67°):

Ta(CHCMe<sub>3</sub>)(C<sub>2</sub>H<sub>5</sub>)Cl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>: J<sub>PAP<sub>B</sub></sub> = 117 Hz.

IR (cm<sup>-1</sup>; Nujol/NaCl; VI, 31-1): 2480, br w (ν<sub>CH<sub>α</sub></sub>); 945, s (ν<sub>P-C</sub>).

The ratio of A/B was ~1:2, by <sup>13</sup>C NMR.

Preparation of  $\text{Ta}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)\text{Cl}_2(\text{PMe}_3)_2$  (VII, 66)

$[\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_5)\text{Cl}_2(\text{PMe}_3)_2 \rightleftharpoons \text{Ta}(\text{CH}_2\text{CMe}_3)(\text{C}_2\text{H}_4)\text{Cl}_2(\text{PMe}_3)_2]$  (3.38 g, 6.72 mmol) dissolved in  $\text{Et}_2\text{O}$  (20 mL), reacts with  $\text{C}_2\text{H}_4$  (30 psi) in 2.5 h at  $25^\circ$ . The reaction mixture was filtered and stripped to near-black crystals. The crude product was dissolved in a minimal amount of  $\text{Et}_2\text{O}$  (~15 mL). Standing at  $-30^\circ$  for 12 h, deposited 1.95 g of irregular blue-black crystals which were isolated by filtration and dried in vacuo. The mother liquor was reduced in vacuo to ~7 mL and pentane (~3 mL) was added. Standing at  $-30^\circ$  (16 h) gave a second crop of pure compound (0.35 g) (75% yield).

$[\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_5)\text{Cl}_2(\text{PMe}_3)_2 \rightleftharpoons \text{Ta}(\text{CH}_2\text{CMe}_3)(\text{C}_2\text{H}_4)\text{Cl}_2(\text{PMe}_3)_2]$  (0.15 g, 0.298 mmol) was dissolved in  $\text{Et}_2\text{O}$  (~1.5 mL) containing n-heptane (50  $\mu\text{L}$ , 0.340 mmol) and pressurized with  $\text{C}_2\text{H}_4$  (30 psi). Samples were periodically withdrawn at  $0^\circ$  and quenched with air. GLC analysis, on column A using calculated response factors, gave 0.67 equivalents  $\text{Ta}^{-1}$  of 4,4-dimethyl-1-pentene and 0.25 equivalents  $\text{Ta}^{-1}$  of 4,4-dimethyl-trans-2-pentene (V, 29-2). Longer reaction times gave >1 equivalent  $\text{Ta}^{-1}$  of butenes, 0.58 equivalents  $\text{Ta}^{-1}$  of 3-ethyl-1-butene (identified by coinjection with an authentic sample on column A), and ~0.3 equivalents  $\text{Ta}^{-1}$  of assumed  $\text{C}_8$  olefins (V, 29-3). The production of butenes was suppressed in the presence of excess  $\text{PMe}_3$  (V, 14-1).

Anal. (VIII, 12; VIII, 12-2) Calcd. for  $\text{TaC}_{10}\text{H}_{27}\text{Cl}_2\text{P}_2$ : C, 25.82; H, 5.85. Found: C, 25.30; H, 5.91.

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 250 MHz; IX, 18-1A;  $-30^\circ$ ): 1.729 (m, 2, olefinic H); 1.299 (t, 17,  $^2\text{J}_{\text{PH}} = 3.66$  Hz,  $\text{PMe}_3$ ); 1.081 (m, 1,  $\text{CH}_\text{A}\text{H}_\text{B}\text{CH}_3$ ); 0.907 (m, 1,  $\text{CH}_\text{A}\text{H}_\text{B}\text{CH}_3$ ); -0.104 (m, 3,  $\text{CH}_\text{A}\text{H}_\text{B}\text{CH}_3$ ); -1.031 (m, 2, olefinic H).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 15 MHz;  $\nu$ , 58-1 through 4;  $\{^1\text{H}\}$  and gated  $\{^1\text{H}\}$ ;  $25^\circ$ ):  
 61.65 (tt,  $^1J_{\text{PC}} = 8$  Hz,  $^1J_{\text{CH}} = 133$  Hz,  $\text{CH}_2\text{CH}_3$ ); 54.30 (tt,  $^1J_{\text{PC}} \approx 4$  Hz,  
 $^1J_{\text{CH}} = 151$  Hz,  $\text{C}_2\text{H}_4$ ); 14.20 (qt,  $^1J_{\text{PC}} = 11.7$  Hz,  $^1J_{\text{CH}} = 129$  Hz,  $\text{PMe}_3$ );  
 1.8 (br q,  $^1J_{\text{PC}} \approx 4$  Hz,  $^1J_{\text{CH}} = 125$  Hz,  $\text{CH}_2\text{CH}_3$ ).  
 $^{31}\text{P}$  ( $\delta$ ;  $\text{C}_6\text{H}_5\text{CH}_3$ ; 36 MHz;  $\nu$ , 40-49B;  $\{^1\text{H}\}$ ;  $30^\circ$ ): -13 (s).  
 IR ( $\text{cm}^{-1}$ ; Nujol/NaCl;  $\nu$ , 58-1): 950, s ( $\nu_{\text{P-C}}$ ).

Preparation of  $\text{Ta}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)_2\text{Cl}(\text{PMe}_3)_2$  (III, 59, 67)

$\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  (1.5 g, 3.22 mmol) was dissolved in  $\text{Et}_2\text{O}$  (60 mL) and cooled to  $-78^\circ$ . While bubbling  $\text{C}_2\text{H}_4$  through the stirring solution, 5.1 mL of a 1.26 M  $\text{EtMgBr}$  solution (6.44 mmol) diluted with 10 mL of  $\text{Et}_2\text{O}$  was added, dropwise. The reaction mixture was slowly warmed to room temperature (under  $\text{C}_2\text{H}_4$ ). A color change from blue to green occurred at  $-40^\circ$  which finally changed to a green-brown suspension after 30 min at  $25^\circ$ . Filtration gave 1.12 g of a brown solid and a filtrate which was stripped to a brown residue and extracted with pentane (75 mL). This solution was filtered and the volume was reduced in vacuo to 25 mL. Filtration gave 0.41 g of a green powder which was recrystallized from 5 mL of a 4:1  $\text{Et}_2\text{O}$ /pentane solution at  $-30^\circ$ , to give 0.25 g of green needles which were at least 80% pure

$\text{Ta}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)_2\text{Cl}(\text{PMe}_3)_2$  by  $^{13}\text{C}$  NMR (17% yield).

$\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  reacts with 2 equivalents of  $\text{EtMgBr}$  in the absence of  $\text{C}_2\text{H}_4$  to give  $\text{Ta}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)_2\text{Cl}(\text{PMe}_3)_2$  in low yield with  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  as the major product (see Chapter 3) (IV, 50, 71).

Using only 1 equivalent of  $\text{EtMgBr}$ , in a similar reaction with  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  (no  $\text{C}_2\text{H}_4$ ), gave a low yield of a green product containing a 1:1 mixture of  $\text{Ta}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)_2\text{Cl}(\text{PMe}_3)_2$  and

$\text{Ta}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)\text{Cl}_2(\text{PMe}_3)_2$ , identified by  $^{13}\text{C}$  NMR (IV, 49).

$\text{Ta}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)_2\text{Cl}(\text{PMe}_3)_2$  (0.1 g) dissolved in 2 mL of  $\text{Et}_2\text{O}$  and pressurized with  $\text{C}_2\text{H}_4$  (30 psi), was heated for 16 h at  $40^\circ$ . The solution was filtered and stripped to an oil, which contained a single broad resonance centered in the  $\text{PMe}_3$  region, by  $^1\text{H}$  and  $^{13}\text{C}$  NMR (V, 56).

$\text{Ta}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  reacts with 1 equivalent of  $[\text{PMe}_3\text{H}]\text{Cl}$  in THF to give  $\text{Ta}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)_2\text{Cl}(\text{PMe}_3)_2$  in moderate yields (IV, 56, 57).

$\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  (0.42 g, 0.9 mmol) did not react with  $\text{Zn}(\text{C}_2\text{H}_5)_2$  (0.11 g, 0.9 mmol) in  $\text{Et}_2\text{O}$  (~20 mL) after 16 h at  $25^\circ$  under an atmosphere of  $\text{C}_2\text{H}_4$ .  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  (0.4 g) was isolated unchanged from the reaction mixture (III, 59).

$\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  reacts with 0.5 equivalents of  $\text{ZnMe}_2$  in toluene at  $-30^\circ$ . This reaction was not followed up. However, it may be worthwhile to isolate and characterize the product(s) formed using 1.5 equivalents of  $\text{ZnMe}_2$  (IV, 64).

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 250 MHz; IX, 18-1B;  $-30^\circ$ ): 1.793 (m, 2, olefinic H); 1.404 (t, 18,  $^2\text{J}_{\text{PH}} = 3.97$  Hz,  $\text{PMe}_3$ ); 1.052 (m, 3); 0.907 (m, 3); -0.145 (m, 4); -1.346 (m, 2, olefinic H).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 15 MHz; III, 67-3A through 8A;  $\{^1\text{H}\}$  and gated  $\{^1\text{H}\}$ ;  $25^\circ$ ): 68.9 (br t,  $^1\text{J}_{\text{CH}} = 132$  Hz,  $\text{CH}_2\text{CH}_3$ ); 57.1 (br t,  $^1\text{J}_{\text{CH}} = 152$  Hz,  $\text{C}_2\text{H}_4$ ); 15.4 (qt,  $^1\text{J}_{\text{PC}} = 13.2$  Hz,  $^1\text{J}_{\text{CH}} = 129$  Hz,  $\text{PMe}_3$ ); 2.6 (br q,  $^1\text{J}_{\text{CH}} \cong 123$  Hz,  $\text{CH}_2\text{CH}_3$ ).

$^{31}\text{P}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 36 MHz; III, 67-10A;  $\{^1\text{H}\}$ ;  $-20^\circ$ ): -18 (s).

IR ( $\text{cm}^{-1}$ ; Nujol/NaCl; III, 67-1): 950, s ( $\nu_{\text{P-C}}$ ).

Preparation of  $[\text{Mg}(\text{OCMe}_3)\text{Cl}]_x$  (V, 54)

$\text{HOCH}_2\text{Me}_3$  (3.71 g, 50.0 mmol) dissolved in  $\text{Et}_2\text{O}$  (~100 mL), reacts vigorously at  $10^\circ\text{C}$  with 35 mL of a 1.43 M ether solution of  $\text{Bu}^n\text{MgCl}$ . Filtration of the resulting white solid gives, after drying, 6.5 g of  $[\text{Mg}(\text{OCMe}_3)\text{Cl}]_x$  (98% yield).

Preparation of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{OCMe}_3)\text{Cl}_2$  (VI, 2)

$\text{Ta}(\text{CH}_2\text{CMe}_3)\text{Cl}_3$  (2.15 g, 5.00 mmol) reacts slowly with solid  $[\text{Mg}(\text{OCMe}_3)\text{Cl}]_x$  (0.65 g, 4.90 mmol, 2% deficiency) in  $\text{Et}_2\text{O}$  (~50 mL) to give a yellow gelatinous solution. After 12 h the reaction mixture was filtered and the solid was removed (in vacuo) leaving an oily residue which was checked for purity by  $^1\text{H}$  NMR. An additional 0.03 g of  $[\text{Mg}(\text{OCMe}_3)\text{Cl}]_x$  (0.23 mmol) was added to an ether solution (~50 mL) containing the above residue and stirred for 12 h. The reaction mixture was stripped, extracted with hexane (30 mL), and filtered. Removal of the solvent (in vacuo) gave yellow crystals which were recrystallized from a concentrated pentane solution at  $-30^\circ$  (24 h). 1.85 g of yellow crystals were isolated and dried in vacuo (79% yield).  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{OCMe}_3)\text{Cl}_2$  decomposes when sublimed at  $40^\circ$  and  $0.03\mu$ . The product from this sublimation was analyzed.

Anal. (VI, 47; VI, 47-1) Calcd. for  $\text{TaC}_{14}\text{H}_{31}\text{Cl}_2\text{O}$ : C, 35.99; H, 6.69.

Found: C, 26.02; H, 4.64.

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 270 MHz; VII, 43-1A;  $25^\circ$ ): 2.294 (d, 2,  $^2J_{\text{H}_A\text{H}_B} = 10.76$  Hz,  $\text{CH}_A\text{H}_B\text{CMe}_3$ ); 1.801 (d, 2,  $^2J_{\text{H}_B\text{H}_A} = 10.75$  Hz,  $\text{CH}_A\text{H}_B\text{CMe}_3$ ); 1.308 (s, 9,  $\text{OCMe}_3$ ); 1.150 (s, 18,  $\text{CH}_2\text{CMe}_3$ ).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 15 MHz; V, 63-1A, 2A;  $\{^1\text{H}\}$  and gated  $\{^1\text{H}\}$ ;  $25^\circ$ ):

104.6 (t,  $^1J_{\text{CH}} = 118$  Hz,  $\text{CH}_2\text{CMe}_3$ ); 36.3 (s,  $\text{CH}_2\text{CMe}_3$ ); 35.3 (q,  $^1J_{\text{CH}} =$

125 Hz,  $\text{CH}_2\text{CMe}_3$ ); 30.1 (q,  $^1J_{\text{CH}} = 127$  Hz,  $\text{OCMe}_3$ ).  $\text{C}_\beta$  of the  $\text{OCMe}_3$  group was not located.

$\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$  reacts immediately with 1 equivalent of  $\text{LiOCMe}_3$  in 10 mL of  $\text{Et}_2\text{O}$  at  $25^\circ$ . The crude product, isolated similar to the above procedure, contained ~50% of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{OCMe}_3)\text{Cl}_2$ ;  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$  and an unidentified compound were also present (V, 39).

Preparation of  $\text{Nb}(\text{CH}_2\text{CMe}_3)_2(\text{OCMe}_3)\text{Cl}_2$  (VI, 23)

$\text{Nb}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$  (0.64 g, 1.87 mmol) was dissolved in  $\text{Et}_2\text{O}$  (20 mL) and cooled to  $-30^\circ$ . Solid  $[\text{Mg}(\text{OCMe}_3)\text{Cl}]_x$  (0.25 g, 1.87 mmol) was added to the cold solution and the reaction mixture was warmed to  $25^\circ$ . The red solution became dark brown ( $0^\circ$ ) and deposited a blue precipitate (0.35 g) which was filtered off after 1.5 h. The solvent was removed in vacuo and the residue was extracted with pentane (~20 mL), filtered, treated with darco, filtered and concentrated to 1-2 mL. Standing at  $-30^\circ$  (12 h) gave 0.25 g of yellow crystals which darkened after prolonged storage (~1 month) at  $-30^\circ$  (35% yield).

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 60 MHz; VI, 23-1B;  $25^\circ$ ): 2.90 (brd, 2,  $^2J_{\text{H}_\text{A}\text{H}_\text{B}} \approx 10$  Hz,  $\text{CH}_\text{A}\text{H}_\text{B}\text{CMe}_3$ ); 2.50 (br d, 2,  $^2J_{\text{H}_\text{A}\text{H}_\text{B}} \approx 10$  Hz,  $\text{CH}_\text{A}\text{H}_\text{B}\text{CMe}_3$ ); 1.30 (s, 9,  $\text{OCMe}_3$ ); 1.15(s, 18,  $\text{CH}_2\text{CMe}_3$ ).

Preparation of Ta(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)Cl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (VI, 10)

Yellow Ta(CH<sub>2</sub>CMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.47 g, 1.0 mmol) reacts with PMe<sub>3</sub> (0.2 mL, excess) in CH<sub>2</sub>Cl<sub>2</sub> (~10 mL) in 12 h giving an orange solution. The solvent was removed in vacuo leaving a crude orange product (92%), which was extracted with hexane (~20 mL) and filtered. The solvent was reduced (in vacuo) until crystals appeared. Cooling to -30° for 2 h gave 0.44 g of orange crystals (80% yield).

<sup>1</sup>H NMR (δ; C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 270 MHz; VI, 65-1B, 2B; -50°): major isomer: 9.19 (t, 1, <sup>2</sup>J<sub>PH</sub> = 3.26 Hz, CHCMe<sub>3</sub>); 1.33 (t, 18, <sup>2</sup>J<sub>PH</sub> = 4.01 Hz, PMe<sub>3</sub>); 1.30 (s, 9, OCMe<sub>3</sub>); 1.14 (s, 9, CHCMe<sub>3</sub>). minor isomer: 8.11 (t, 1, <sup>2</sup>J<sub>PH</sub> ≈ 2.4 Hz, CHCMe<sub>3</sub>); 1.19 (s, 9, CHCMe<sub>3</sub>).

The major/minor isomer ratio was 13:1.

<sup>13</sup>C NMR (δ; C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 67.89 MHz; VI, 65-1A through 4A; {<sup>1</sup>H} and gated {<sup>1</sup>H}; -50°): major isomer: 281.7 (dt, <sup>2</sup>J<sub>CP</sub> = 8.4 Hz, <sup>1</sup>J<sub>CH</sub> = 110 Hz, CHCMe<sub>3</sub>); 85.6 (s, OCMe<sub>3</sub>); 42.9 (s, CHCMe<sub>3</sub>); 36.3 (q, <sup>1</sup>J<sub>CH</sub> = 125 Hz, CHCMe<sub>3</sub>); 32.0 (q, <sup>1</sup>J<sub>CH</sub> = 128 Hz, OCMe<sub>3</sub>); 15.9 (qt, <sup>1</sup>J<sub>PC</sub> = 12.3 Hz, <sup>1</sup>J<sub>CH</sub> = 131 Hz, PMe<sub>3</sub>). minor isomer: 82.9 (s, OCMe<sub>3</sub>); 44.0 (s, CHCMe<sub>3</sub>); 30.4 (q, <sup>1</sup>J<sub>CH</sub> = 128 Hz, OCMe<sub>3</sub>); 15.9 (t, <sup>2</sup>J<sub>CP</sub> ≈ 14 Hz, PMe<sub>3</sub>).

<sup>31</sup>P (δ; C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 109 MHz; VI, 65-1C, 2C; {<sup>1</sup>H}; -50 and 30°): major isomer: -5.7 (s). minor isomer: -10.1 (s).

The major/minor isomer ratio was 10:1.

Preparation of Ta(C<sub>2</sub>H<sub>4</sub>)(OCMe<sub>3</sub>)Cl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (VI, 12)

Ta(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)Cl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (2.66 g, 4.86 mmol) was dissolved in Et<sub>2</sub>O (25 mL) and pressurized with C<sub>2</sub>H<sub>4</sub> (30 psi). The reaction mixture was heated at 50° for 1 h then cooled to 25° for 12 h under C<sub>2</sub>H<sub>4</sub>. Et<sub>2</sub>O

(~50 mL) was added to the reaction mixture and the solution was filtered. The solvent was removed in vacuo, leaving a crude product which was dissolved in a minimal amount of Et<sub>2</sub>O which contained 10% hexane. Cooling and standing at -30° for 12 h gave 1.55 g of orange crystals. An analytically pure sample was obtained by multiple recrystallization from Et<sub>2</sub>O (59% yield).

Anal. (VI, 12; VI, 12-1): Calcd. for TaC<sub>12</sub>H<sub>31</sub>Cl<sub>2</sub>P<sub>2</sub>O: C, 28.53; H, 6.19. Found: C, 28.71; H, 6.23.

<sup>1</sup>H NMR (δ; C<sub>6</sub>D<sub>6</sub>; 270 MHz, VII, 43-1B; 30°): major isomer: 2.175 (m, 2, olefinic H); 1.591 (m, 2, olefinic H); 1.397 (t, 18, <sup>2</sup>J<sub>PH</sub> = 3.9 Hz, PMe<sub>3</sub>); 0.724 (s, 9, OCMe<sub>3</sub>). minor isomer: 0.738 (s, OCMe<sub>3</sub>).

<sup>13</sup>C NMR (δ; C<sub>6</sub>D<sub>6</sub>; 15 MHz; VII, 42-1A, 2A; {<sup>1</sup>H} and gated {<sup>1</sup>H}); 25°): 83.3 (s, OCMe<sub>3</sub>); 44.7 (tt, <sup>2</sup>J<sub>PC</sub> = 3.7 Hz, <sup>1</sup>J<sub>CH</sub> = 152 Hz, C<sub>2</sub>H<sub>4</sub>); 30.4 (q, <sup>1</sup>J<sub>CH</sub> = 126 Hz, OCMe<sub>3</sub>); 14.3 (qt, <sup>1</sup>J<sub>PC</sub> = 11.73 Hz, <sup>1</sup>J<sub>CH</sub> = 123 Hz, PMe<sub>3</sub>).

Ta(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)Cl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (0.12 g, 0.219 mmol) was dissolved in toluene (~5 mL), containing n-heptane (50 μL, 0.340 mmol) as an internal GLC reference, and reacted with C<sub>2</sub>H<sub>4</sub> (30 psi). The reaction mixture was periodically sampled (0.5 h and 16 h) at 0°, quenched with air, and analyzed using calculated response factors, on column A. The products were 4,4-dimethyl-1-pentene (0.65 eq. Ta<sup>-1</sup>) and 4,4-dimethyl-trans-2-pentene (0.24 eq. Ta<sup>-1</sup>). Also present (16 h) was a small amount of 1-butene (0.25 eq. Ta<sup>-1</sup>) and trans-2-butene (0.43 eq. Ta<sup>-1</sup>). This sample was not analyzed for 3,3-dimethyl-1-butene (VI, 21).

Preparation of Ta(CHSiMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>) (VII, 16)

Ta(CHSiMe<sub>3</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub> (3.54 g, 6.73 mmol) reacts with LiOCMe<sub>3</sub> (1.08 g, 13.47 mmol) in Et<sub>2</sub>O (~50 mL) to give 1.65 g of yellow crystals after following the procedure used in the preparation of Ta(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sup>18</sup> (47% yield).

<sup>1</sup>H NMR (δ; C<sub>6</sub>H<sub>6</sub>; 60 MHz; VII, 13-1; 25°): 10.5 (br, 1, CHSiMe<sub>3</sub>); 1.52 (s, 18, OCMe<sub>3</sub>); 1.12 (d, <sup>2</sup>J<sub>PH</sub> ≈ 9 Hz, PMe<sub>3</sub>); 0.39 (s, 9, CHSiMe<sub>3</sub>).

Ta(CHSiMe<sub>3</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub> reacts with 1 equivalent of HOCMe<sub>3</sub> at -78° in toluene, to give, after work-up, a product which has been tentatively identified as [Ta(CHSiMe<sub>3</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (22% yield) by <sup>1</sup>H NMR (VII, 15).

<sup>1</sup>H NMR (δ; C<sub>6</sub>H<sub>6</sub>; 60 MHz; VII, 15-1; 25°): 3.02 (d, ~1, <sup>3</sup>J<sub>PH</sub> ≈ 2.5 Hz, CHSiMe<sub>3</sub>); 1.05 (d, 9, <sup>2</sup>J<sub>PH</sub> ≈ 10 Hz, PMe<sub>3</sub>); 0.43 (s, 9, CHSiMe<sub>3</sub>).

Spectral Evidence for M(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub> M = Ta and Nb

M(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>) (M = Ta and Nb) reversibly binds PMe<sub>3</sub> to give M(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)Cl(PMe<sub>3</sub>)<sub>2</sub>. This chemical equilibrium was formed by adding ~1 equivalent of PMe<sub>3</sub> to a d<sub>8</sub>-toluene solution of M(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>) and studied by variable temperature <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR. The ratio of the mono-phosphine complex to the bis-phosphine complex depended upon: temperature, concentration, and the nucleus studied. These results have been summarized below.

Ta(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>):

<sup>1</sup>H NMR (δ; C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 270 MHz; VI, 41-1A through 3A; 30° to -60°): (30°): 9.392 (d, 1, <sup>3</sup>J<sub>PH</sub> = 3.29 Hz, CHCMe<sub>3</sub>); 1.405 (s, 9, OCMe<sub>3</sub>); 1.375 (s, 9, OCMe<sub>3</sub>'); 1.253 (s, 9, CHCMe<sub>3</sub>); 1.082 (d, 9, <sup>2</sup>J<sub>PH</sub> = 7.34 Hz, PMe<sub>3</sub>).

(-60°): No changes were observed at this temperature.

<sup>13</sup>C NMR (δ; C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 67.89 MHz; VI, 54-1A, 1B through 5B, {<sup>1</sup>H} and gated

{<sup>1</sup>H}; 30° and -30°); (-30°): 273.2 (dd, <sup>2</sup>J<sub>PC</sub> = 2.9 Hz, <sup>1</sup>J<sub>CH</sub> = 113.7 Hz, CHCMe<sub>3</sub>); 80.7 (s, OCMe<sub>3</sub>); 79.8 (s, OCMe<sub>3</sub>'); 41.6 (s, CHCMe<sub>3</sub>); 35.2 (q, <sup>1</sup>J<sub>CH</sub> = 129 Hz, CHCMe<sub>3</sub>); 32.5 (q, <sup>1</sup>J<sub>CH</sub> = 125 Hz, OCMe<sub>3</sub>); 32.3 (q, <sup>1</sup>J<sub>CH</sub> = 125 Hz, OCMe<sub>3</sub>'); 16.4 (qd, <sup>1</sup>J<sub>PC</sub> = 21.1 Hz, <sup>1</sup>J<sub>CH</sub> = 130 Hz, PMe<sub>3</sub>).

<sup>31</sup>P NMR (δ; C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 36.2 MHz; VI-45-1 through 7; {<sup>1</sup>H}; 20° to -80°):

Ta(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>): (-60°): 1.0 (s).

Ta(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub>: (-60°): -15 (s).

The ratio of Ta(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>) to Ta(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub> was 6:1, at -60°.

Ta(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>) + PMe<sub>3</sub>:

<sup>1</sup>H NMR (δ; C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 270 MHz; VI, 41-1B through 5B; 0° to -60°):

The ratio of Ta(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>) to Ta(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub> was 0.04:1 at -45°. This ratio changes to 1.42:1, 1.92:1, and 5.3:1 at -60°, -20°, and 0°, respectively.

Ta(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub>: (-45°): 9.149 (t, 1, <sup>3</sup>J<sub>PH</sub> = 3.37 Hz, CHCMe<sub>3</sub>); 1.476 (s, 9, OCMe<sub>3</sub>); 1.450 (s, 9, OCMe<sub>3</sub>'); 1.269 (t, 18, <sup>2</sup>J<sub>PH</sub> = 2.99 Hz, PMe<sub>3</sub>); 1.208 (s, 9, CHCMe<sub>3</sub>).

<sup>13</sup>C NMR (δ; C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 67.89 MHz; VI, 43-1A through 4A, 54-2A through 9A; {<sup>1</sup>H} and gated {<sup>1</sup>H}; 30° to -60°):

The ratio of Ta(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>) to Ta(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub> was 1:3.6 at -25°. This ratio changes to 2.5:1, 1:2.7, 1:4, 1:4.6 at 30°, -20°, -40°, and -60°, respectively. Ta(CHCMe<sub>3</sub>)(OCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub>:

(-25°): 275.1 (dt, <sup>2</sup>J<sub>PC</sub> ≈ 8 Hz, <sup>1</sup>J<sub>CH</sub> ≈ 123 Hz, CHCMe<sub>3</sub>); 79.8 (s, OCMe<sub>3</sub>); 78.8 (s, OCMe<sub>3</sub>'); 43.1 (s, CHCMe<sub>3</sub>); 36.0 (q, <sup>1</sup>J<sub>CH</sub> = 130 Hz, CHCMe<sub>3</sub>); 32.9 (q, <sup>1</sup>J<sub>CH</sub> = 123 Hz, OCMe<sub>3</sub>); 32.3 (q, <sup>1</sup>J<sub>CH</sub> = 123 Hz, OCMe<sub>3</sub>'); 16.3 (qt, <sup>1</sup>J<sub>PC</sub> = 11.5 Hz, <sup>1</sup>J<sub>CH</sub> = 133 Hz, PMe<sub>3</sub>).

$^{31}\text{P}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 36.2 MHz; VI, 45-8 through 15;  $\{^1\text{H}\}$ ;  $20^\circ$  to  $-80^\circ$ ):

$\text{Ta}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ : ( $-60^\circ$ ): 1.8 (s).

$\text{Ta}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$ : ( $-60^\circ$ ): -14 (s).

The ratio of  $\text{Ta}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  to  $\text{Ta}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  was 1:24 at  $-60^\circ$ .

$\text{Nb}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ :

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 270 MHz; VI, 42-1A through 4A;  $30^\circ$  to  $-60^\circ$ ):

( $30^\circ$ ): 11.644 (br, 1,  $\text{CHCMe}_3$ ); 1.411 (s, 9,  $\text{OCMe}_3$ ); 1.354 (s, 9,

$\text{OCMe}_3'$ ); 1.191 (s, 9,  $\text{CHCMe}_3$ ); 1.012 (d, 9,  $^2\text{J}_{\text{PH}} = 6.76$  Hz,  $\text{PMe}_3$ ).

( $-60^\circ$ ): 11.644 (d,  $^3\text{J}_{\text{PH}} \approx 3$  Hz,  $\text{CHCMe}_3$ ). No other changes were observed at any temperature.

$^{31}\text{P}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 36.2 MHz; VI, 45-16, 17;  $\{^1\text{H}\}$ ;  $-60^\circ$  and  $-80^\circ$ ):

$\text{Nb}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ : ( $-80^\circ$ ): -10 (br s).

$\text{Nb}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3) + \text{PMe}_3$ :

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 270 MHz; VI, 42-1B through 4B;  $0^\circ$  to  $-45^\circ$ ):

The ratio of  $\text{Nb}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  to  $\text{Nb}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  was 1:3 at  $-45^\circ$ . This ratio changes to 1.9:1 and 7.4:1 at  $-20^\circ$  and  $0^\circ$ , respectively.

$\text{Nb}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ : ( $-45^\circ$ ): 11.707 (d, 1,  $^3\text{J}_{\text{PH}} = 3.69$  Hz,  $\text{CHCMe}_3$ ); 1.406 (s, 9,  $\text{OCMe}_3$ ); 1.336 (s, 9,  $\text{OCMe}_3'$ ); 1.18 (s, 9,  $\text{CHCMe}_3$ ); 1.061 (d, 9,  $^2\text{J}_{\text{PH}} = 6.86$  Hz,  $\text{PMe}_3$ ).

$\text{Nb}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$ : ( $-45^\circ$ ): 11.547 (t, 1,  $^3\text{J}_{\text{PH}} = 4.15$  Hz,  $\text{CHCMe}_3$ ); 1.478 (s, 18,  $\text{OCMe}_3$ ); 1.209 (t, 18,  $^2\text{J}_{\text{PH}} = 2.72$  Hz,  $\text{PMe}_3$ ); 1.144 (s, 9,  $\text{CHCMe}_3$ ).

Free  $\text{PMe}_3$ : ( $-45^\circ$ ): 0.767 (d,  $^2\text{J}_{\text{PH}} = 1.95$  Hz).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 67.89 MHz; VI, 44-1 through 3;  $\{^1\text{H}\}$ ;  $-25^\circ$ ):

$\text{Nb}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ : ~293 (b,  $\underline{\text{CHCMe}_3}$ ); 81 (s,  $\underline{\text{OCMe}_3}$ ); 80.2 (s,  $\underline{\text{OCMe}_3'}$ ); 43.1 (s,  $\underline{\text{CHCMe}_3}$ ); 33.5 (s,  $\underline{\text{CHCMe}_3}$ ); 32.6 (s,  $\underline{\text{OCMe}_3}$ ); 32.0 (s,  $\underline{\text{OCMe}_3'}$ ); 15.6 (d,  $^1J_{\text{P}} = 18.3$  Hz,  $\text{PMe}_3$ ).

$\text{Nb}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$ : ~293 (br,  $\underline{\text{CHCMe}_3}$ ); 80.4 (s,  $\underline{\text{OCMe}_3}$ ); 79.4 (s,  $\underline{\text{OCMe}_3'}$ ); 44.4 (s,  $\underline{\text{CHCMe}_3}$ ); 33.5 (s,  $\underline{\text{CHCMe}_3}$ ); 32.7 (s,  $\underline{\text{OCMe}_3}$ ); 32.2 (s,  $\underline{\text{OCMe}_3}$ ); 16.1 (t,  $^1J_{\text{PC}} = 8.9$  Hz,  $\text{PMe}_3$ ).

$^{31}\text{P}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 36.2 MHz; VI, 45-18, 19;  $\{^1\text{H}\}$ ;  $-60^\circ$  and  $-80^\circ$ ):

$\text{Nb}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ : ( $-80^\circ$ ): -9 (br s).

$\text{Nb}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$ : ( $-80^\circ$ ): -19 (br s). The ratio of

$\text{Nb}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  to  $\text{Nb}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  was 1:9 at  $-80^\circ$ .

Preparation of  $\text{Ta}(\text{CHC}_6\text{H}_5)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  (VII, 72)

$\text{Ta}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  (2.0 g, 3.93 mmol) was dissolved in toluene (10 mL) containing 0.5 mL of  $\text{PMe}_3$  (excess). Styrene (0.50 g, 4.75 mmol, excess) dissolved in toluene (2 mL) was added dropwise to the stirring Ta solution. The first sign of reaction was visible after 2 min with a color change from yellow to orange, and after 1.5 h to green. The reaction mixture stood for 12 h at  $-30^\circ$ . 1.21 g of green flakes were isolated by filtration and dried by passing nitrogen over the crystals. The mother liquor was stripped, and the residue was dissolved in 5 mL of toluene which contained 0.2 mL of  $\text{PMe}_3$ . Standing for 12 h at  $-30^\circ$  gave an additional 0.6 g of product isolated by the same procedure (76% yield).  $\text{Ta}(\text{CHC}_6\text{H}_5)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  can be prepared in 96% yield by adding excess  $\text{PMe}_3$  to a suspension of  $\text{Ta}(\text{CHC}_6\text{H}_5)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  in  $\text{Et}_2\text{O}$ . The product was isolated by the same procedure used above (VII, 20).

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 270 MHz; VII, 44-1B, 2B; VIII, 3-1A;  $-40^\circ$ ,  $-30^\circ$ , and  $30^\circ$ ): 9.963 (t, 1,  $^3\text{J}_{\text{PH}} = 3.76$  Hz,  $\text{CHC}_6\text{H}_5$ ); 7.32, 7.05, 6.72 (m, ~5, aromatic H); 1.589 (s, 9,  $\text{OCMe}_3$ ); 1.499 (s, 9,  $\text{OCMe}_3'$ ); 1.085 (t, 18,  $^2\text{J}_{\text{PH}} = 3.06$  Hz,  $\text{PMe}_3$ ).

$^{13}\text{C}$  NMR ( $\delta$ ; THF- $d_8$ ; 15 MHz; VII, 39-1B;  $\{^1\text{H}\}$ ;  $25^\circ$ ): 258 (br,  $\text{CHC}_6\text{H}_5$ ); 138 (br  $\text{C}_\beta$ ); 129, 128, 127 ( $\text{C}_o$ ,  $\text{C}_m$ ,  $\text{C}_p$ , aromatic C); 80.8 (s,  $\text{OCMe}_3$ ); 79.9 (s,  $\text{OCMe}_3'$ ); 33.2 (s,  $\text{OCMe}_3$ ); 32.4 (s,  $\text{OCMe}_3'$ ); 15.6 (t,  $^1\text{J}_{\text{PC}} = 11$  Hz,  $\text{PMe}_3$ ).

Preparation of  $\text{Ta}(\text{CHC}_6\text{H}_5)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  (VII, 75)

$\text{Ta}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  (2.10 g, 4.13 mmol), dissolved in  $\text{Et}_2\text{O}$  (35 mL), reacts immediately with an  $\text{Et}_2\text{O}$  solution (2 mL) containing styrene (0.55 g, 5.28 mmol, excess), added rapidly at  $25^\circ$ . In 10 min a small amount of orange solid precipitated from solution. The solvent was removed in vacuo leaving an oily solid which was dissolved in THF (15 mL). Standing for 12 h at  $-30^\circ$  gave no product. Trituration with  $\text{Et}_2\text{O}$  (10 mL) gave 0.44 g of a yellow powder which was isolated by filtration, washed with pentane and dried in vacuo. The mother liquor was stripped to a red oil. No additional product was obtained from a saturated pentane solution, containing the red oil, at  $-30^\circ$  (20% yield). The yellow product obtained above was ~80%  $\text{Ta}(\text{CHC}_6\text{H}_5)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  and ~20%  $\text{Ta}(\text{CHC}_6\text{H}_5)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$ , by  $^1\text{H}$  NMR (VII, 75-1).

Similar results were obtained when cis-stilbene was used in the place of styrene. Only trans-stilbene was isolated (VI, 66).

Exposure of a moderate vacuum (~1-10 mm) to a toluene solution containing  $\text{Ta}(\text{CHC}_6\text{H}_5)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$ , or to the crystalline solid, partially

removes bound  $\text{PMe}_3$  giving mixtures of the mono- and bis-phosphine complex. Attempts to prepare pure  $\text{Ta}(\text{CHC}_6\text{H}_5)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ , using this technique, were unsuccessful due to the instability of the product (IX, 6).

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 270 MHz; VII, 44-1A through 4A;  $-40$  and  $30^\circ$ ): 10.44 (d, 1,  $^3\text{J}_{\text{PH}} = 3.57$  Hz,  $\text{CHC}_6\text{H}_5$ ); 7.27, 7.13, 6.74 (m, 5, aromatic H); 1.406 (s, 9,  $\text{OCMe}_3$ ); 1.394 (s, 9,  $\text{OCMe}_3'$ ); 0.813 (d, 9,  $^2\text{J}_{\text{PH}} = 7.88$  Hz,  $\text{PMe}_3$ ).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{THF-d}_8$ ; 15 MHz; VII, 39-1A;  $\{^1\text{H}\}$ ;  $5^\circ$ ): 257 (br,  $\text{CHC}_6\text{H}_5$ ); 145 (br,  $\text{C}_\beta$ ); 129, 127, 125 ( $\text{C}_o$ ,  $\text{C}_m$ ,  $\text{C}_p$ , aromatic C); 81.8 (s,  $\text{OCMe}_3$ ); 80.9 (s,  $\text{OCMe}_3'$ ); 32.2 (br,  $\text{OCMe}_3$ ); 15.5 (d,  $^1\text{J}_{\text{PC}} = 25$  Hz,  $\text{PMe}_3$ ).

Reaction of  $\text{Ta}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  with Cis-Stilbene in the Presence of  $\text{PMe}_3$  (VII, 9)

$\text{Ta}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  (2.74 g, 5.4 mmol) was dissolved in benzene (20 mL) containing 0.5 mL of  $\text{PMe}_3$  (excess). Cis-stilbene (0.94 g, 5.2 mmol), dissolved in benzene (1 mL), was added slowly to the stirring Ta solution. The reaction mixture was stirred in the dark for 12 h at  $25^\circ$ . The solvent was removed in vacuo leaving an orange and green residue. Extraction of the solid with pentane (65 mL) gave, after filtering and drying in vacuo, 1.95 g of an orange solid which was a 2:1 mixture of  $\text{Ta}(\text{CHC}_6\text{H}_5)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  and  $\text{Ta}(\text{CHC}_6\text{H}_5)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  by  $^1\text{H}$  NMR (VII, 44-3A). The mother liquor was reduced in vacuo to 25 mL. Filtration gave 0.62 g of greenish crystals. These crystals were extracted with  $\text{Et}_2\text{O}$  (5 mL) and filtered giving 0.08 g of  $\text{Ta}(\text{CHC}_6\text{H}_5)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ . The mother liquor was triturated with pentane (~5 mL) and cooled for 12 h at  $-30^\circ$ . Isolation by filtration

gave 0.34 g of green flakes which were a 2:1 mixture of trans-stilbene and  $\text{Ta}(\text{CHC}_6\text{H}_5)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$ , by  $^1\text{H}$  NMR (VII, 44-2).

Calcd. yield for  $\text{Ta}(\text{CHC}_6\text{H}_5)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ : 1.31 g, 46%.

Calcd. yield for  $\text{Ta}(\text{CHC}_6\text{H}_5)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$ : 0.75 g, 23%.

Reaction of  $\text{Nb}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  with Styrene in the Presence of  $\text{PMe}_3$  (IX, 3)

$\text{Nb}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  (0.42 g, 1.0 mmol) was dissolved in toluene (8 mL) containing 80 mg of  $\text{PMe}_3$  and cooled to  $-30^\circ$ . Styrene (0.11 g, 1.06 mmol, 6% excess), dissolved in toluene (2 mL), was added dropwise to the stirring Nb solution. The reaction mixture was warmed to  $25^\circ$ , stirred for 2 h, then cooled to  $-30^\circ$  for 16 h. Pentane (~5 mL) was added to the reaction mixture and cooled to  $-30^\circ$  for 4 h, giving orange crystals. Pentane (10 mL) added to the mother liquor gave, after cooling to  $-30^\circ$  for 40 h, a second crop (0.07 g) of orange crystals which were isolated by the above procedure. The product was a 2:1 mixture of  $\text{Nb}(\text{CHC}_6\text{H}_5)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  and  $\text{Nb}(\text{CHC}_6\text{H}_5)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ , by  $^1\text{H}$  NMR (IX, 20-1A, 2A).

Calcd. yield for  $\text{Nb}(\text{CHC}_6\text{H}_5)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$ : 0.30 g, 58%.

Calcd. yield for  $\text{Nb}(\text{CHC}_6\text{H}_5)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ : 0.14 g, 33%.

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 250 MHz; IX, 20-1A, 2A;  $-30^\circ$ ):  $\text{Nb}(\text{CHC}_6\text{H}_5)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ : 12.410 (d, 1,  $^3\text{J}_{\text{PH}} = 4.41$  Hz,  $\text{CHC}_6\text{H}_5$ ); 7.47, 7.18, 6.85 (m, aromatic H); 1.596 (s, 9,  $\text{OCMe}_3$ ); 1.532 (s, 9,  $\text{OCMe}_3'$ ); 0.729 (d, 9,  $^2\text{J}_{\text{PH}} = 7.35$  Hz,  $\text{PMe}_3$ ).

$\text{Nb}(\text{CHC}_6\text{H}_5)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$ : 12.086 (t, 1,  $^3\text{J}_{\text{PH}} = 4.41$  Hz,  $\text{CHC}_6\text{H}_5$ ); 7.47, 7.18, 6.85 (m, aromatic H); 1.449 (s, 9,  $\text{OCMe}_3$ ); 1.414 (s, 9,  $\text{OCMe}_3'$ ); 1.020 (t, 18,  $^2\text{J}_{\text{PH}} = 2.94$  Hz,  $\text{PMe}_3$ ).

Preparation of  $\text{Nb}(\text{C}_2\text{H}_4)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  (VIII, 6)

$\text{Nb}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  (0.76 g, 1.81 mmol), dissolved in toluene (7 mL) containing  $\text{PMe}_3$  (0.3 g, 3.9 mmol, excess), was reacted with  $\text{C}_2\text{H}_4$  (30 psi) for 6 h at 25°. The solution was filtered and stripped to orange crystals. The crude product was extracted with pentane (~125 mL) and filtered. The volume was reduced (in vacuo) to 40 mL. Filtration gave, after drying, 0.62 g of a microcrystalline product. An analytical sample was obtained by fractional crystallization from toluene and  $\text{Et}_2\text{O}$  solutions (91% yield).

Anal. (VIII, 12; VIII, 12-3): Calcd. for  $\text{NbC}_{16}\text{H}_{40}\text{O}_2\text{ClP}_2$ :  
C, 42.26; H, 8.87. Found: C, 41.85; H, 4.63.

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 270 MHz; VII, 42-1E, 2E;  $-50^\circ$ ):

1.700 (m, 4,  $\text{C}_2\text{H}_4$ ); 1.311 (t, 18,  $^2J_{\text{PH}} = 3.06$  Hz,  $\text{PMe}_3$ ); 0.816 (s, 18,  $\text{OCMe}_3$ ).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 15 MHz; VII, 38-1A;  $\{^1\text{H}\}$ ;  $-20^\circ$ ): 76.4 (s,  $\text{OCMe}_3$ ); 42.4 (br s,  $\text{C}_2\text{H}_4$ ); 31.29 (s,  $\text{OCMe}_3$ ); 14.83 (br,  $\text{PMe}_3$ ).

GLC Analysis of the Organic Products Produced in the Reaction of

$\text{M}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)_x$  (M = Nb, Ta; x = 1,2) with olefins (IX, 19)

In a typical experiment,  $\text{Ta}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  (0.153 g, 0.300 mmol) was dissolved in 2 mL of benzene containing n-octane (50  $\mu\text{L}$ , 0.308 mmol) and 30 mg of  $\text{PMe}_3$ . Cis-stilbene (~0.3 mmol) was added to the stirring Ta solution. Samples were withdrawn periodically, quenched with air, or when applicable, passed down a short column (~1 cm) of alumina and analyzed on column A. After 12 h, the products, trans-stilbene (0.24 eq.  $\text{Ta}^{-1}$ ), cis-stilbene (0.15 eq.  $\text{Ta}^{-1}$ ), trans-3,3-dimethyl-1-phenyl-1-butene (1.0 eq.  $\text{Ta}^{-1}$ ) and cis-3,3-dimethyl-1-phenyl-1-butene (0.004 eq.  $\text{Ta}^{-1}$ ),

were identified by coinjection with authentic samples and by  $^1\text{H}$  NMR (VI, 71). The GLC relative responses were either experimentally determined or assumed to be proportional to molecular weight (VI, 70). The reaction of  $\text{M}(\text{CHCMe}_3)(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$  ( $\text{M} = \text{Nb, Ta}$ ) with cis- and trans-stilbene, cis-propenylbenzene, and styrene, with and without excess  $\text{PMe}_3$  in benzene, were similarly analyzed. These results are presented in the text (VII, 7,12,14; IX, 11,16).

Chapter 3

Synthesis and Characterization of Isostructural  
Five-Coordinate Tantalum and Niobium  
Neopentylidene and Ethylene Complexes

## Introduction

The first carbene complex,  $W(C(OMe)Ph)(CO)_5$  was prepared in 1964 by Fischer.<sup>42</sup> Since then a large number of complexes of this general type have been prepared and characterized.<sup>43</sup> Generally, Fischer type carbene complexes are 18-electron complexes in which the transition metal is in a low oxidation state and the carbene ligand is polarized such that the  $\alpha$ -carbon of the carbene is electrophilic.<sup>44</sup>

Electron rich olefins such as  $MeN\overline{CH_2CH_2N(Me)C} = \overline{CN(Me)CH_2CH_2N}$  will add to low oxidation state metal complexes, such as  $Cr(CO)_6$ ,<sup>45</sup> to give biscarbene complexes. Recently biscarbene complexes have been prepared by reacting amines and alcohols with several transition metal isocyanide complexes.<sup>46</sup> In fact, there are several unique complexes containing more than one carbene ligand.<sup>46</sup>

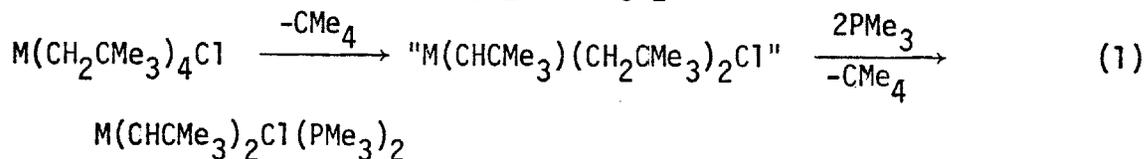
In contrast, nucleophilic alkylidene complexes such as  $Ta(C_5R_5)(CHCMe_3)X_2$ <sup>15b</sup> ( $R = H, Me$ ), have been prepared by a postulated  $\alpha$ -hydrogen abstraction mechanism from  $Ta(C_5R_5)(CH_2CMe_3)_2X_2$ , where the metal remains in the highest oxidation state throughout the course of the reaction.

Until recently no high oxidation state bisalkylidene complexes have been reported.<sup>47</sup> However, a closely related complex, a bisvinylidene,  $Co(C_5H_5)[C=C(SiMe_3)_2]_2$ , has been postulated as an intermediate in the reaction of  $Co(C_5H_5)(CO)_2$  with  $Me_3SiC\equiv CSiMe_3$  to give  $(Me_3Si)_2C=C=C(SiMe_3)_2$ .<sup>48</sup>

This work describes the synthesis and characterization of tantalum and niobium bisneopentylidene complexes of the type  $M(CHCMe_3)_2R(PMe_3)_2$  (where  $M = Ta$  or  $Nb$  and  $R = alkyl$ ). It also describes the study of structurally related five-coordinate complexes in which either one or both of the neopentylidene ligands have been replaced by ethylene.

Results and DiscussionSynthesis and Characterization of Bisneopentylidene Complexes of Tantalum and Niobium

Thermally unstable  $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$ , prepared by adding HCl to  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$  at  $-78^\circ$ , decomposes at temperatures greater than  $-20^\circ$  into postulated  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_2\text{Cl}$  (9) (see Chapter 1). Attempts to trap 9 with  $\text{PMe}_3$  did not give the expected  $\text{PMe}_3$  adduct. Instead, yellow crystalline  $\text{Ta}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  was isolated in quantitative yield. This reaction can also be extended to prepare both Ta and Nb complexes of the type  $\text{M}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$ , (equation 1).

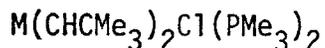
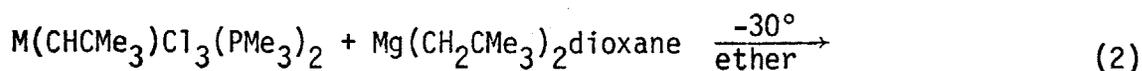


M = Ta, 46a

M = Nb, 46b

46a is soluble in pentane and sublimes (in the dark) at  $80^\circ$  ( $1 \mu$ ) with little decomposition. 46a decomposes in the solid state at ca.  $130^\circ$ . A cryoscopic molecular weight determination showed 46a to be a monomer in cyclohexane (mol. wt. found, 550). The mass spectrum of 46a is consistent with these data. It shows a parent ion at  $m/e$  508.16044 (calcd. 508.16176) but no peaks above this value. Unfortunately, 46a did not give a satisfactory elemental analysis, presumably due to the extreme sensitivity of 46a to air and water (ignites in air).

$\text{M}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  can also be prepared in moderate yields by reacting  $\text{M}(\text{CHCMe}_3)\text{Cl}_3(\text{PMe}_3)_2$  with  $\text{Mg}(\text{CH}_2\text{CMe}_3)_2$  dioxane in ether at  $-30^\circ$ , (equation 2).

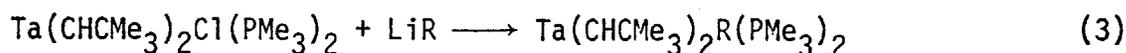


M = Ta, 46a

M = Nb, 46b

For M=Ta, using  $\text{LiCH}_2\text{CMe}_3$ , in ether, gives  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$  after 1 h. Longer reaction times give  $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$  (47d).<sup>18</sup>

$\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$  (47d) can also be prepared by reacting  $\text{Ta}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  with one equivalent of  $\text{LiCH}_2\text{CMe}_3$  in pentane. In general, reacting 46a with an alkyl lithium reagent (in a suitable solvent) gives  $\text{Ta}(\text{CHCMe}_3)_2\text{R}(\text{PMe}_3)_2$  in moderate yields, (equation 3).



R = Me, 47a;  $\text{C}_2\text{H}_5$ , 47b;  $\text{Bu}^n$ , 47c;  $\text{CH}_2\text{CMe}_3$ , 47d; mesityl, 47e

Wood<sup>32,47</sup> has prepared  $\text{Ta}(\text{C}_5\text{H}_5)(\text{CHCMe}_3)_2(\text{PMe}_3)$  (48) by reacting  $\text{Ta}(\text{C}_5\text{H}_5)(\text{CCMe}_3)\text{Cl}(\text{PMe}_3)_2$  with 0.5 equivalents of  $\text{Mg}(\text{CH}_2\text{CMe}_3)_2$  (dioxane) in ether. An analogue containing  $n^5\text{-C}_5\text{Me}_5$  has been prepared similarly employing  $\text{LiCH}_2\text{CMe}_3$  in pentane. 48 can also be prepared by reacting  $\text{Ta}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  with NaCp in an ether/THF solution. It is a monomer in cyclohexane (mol. wt. found, 482).

All known bisalkylidene complexes show similar spectroscopy, ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  NMR, and IR). Therefore, only  $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$  (47d) will be discussed in detail.

47d contains equivalent  $\text{PMe}_3$  ligands as indicated by the "virtually-coupled" triplets in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, and a singlet in the  $^{31}\text{P}$  spectrum.  $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_2\text{Ph})_2$ , prepared by Rupprecht,<sup>18</sup> shows that the methyl groups of the phosphine ligands

are diastereotopic (PMeMe'Ph). Therefore, no plane of symmetry containing the phosphorus nuclei is present. The 270 MHz  $^1\text{H}$  NMR spectrum of  $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$  (47d) shows two distinct  $\alpha$ -hydrogen atom resonances, at 6.93 and 2.08 ppm, due to the inequivalent neopentylidene ligands,<sup>39</sup> (see Figure 1). Also, there are three types of t-butyl resonances as expected; two for the inequivalent neopentylidene ligands and one for the neopentyl ligand. In general,  $\alpha$ -hydrogens for the alkyl ligand resonate at ca. 0 ppm and are strongly coupled to the phosphorous nuclei ( $J_{\text{HP}} \approx 20\text{-}30$  Hz).

The  $^{13}\text{C}$  NMR spectra for  $\text{M}(\text{CHCMe}_3)_2\text{R}(\text{PMe}_3)_2$  confirm the inequivalency of the neopentylidene ligands, with duplicate resonances for the  $\alpha$ -,  $\beta$ - and  $\gamma$ -carbons. Generally, the neopentylidene  $\alpha$ -carbon atoms are separated by about 30-40 ppm, with the lowest field resonance at ca. 275 ppm and a higher field resonance at ca. 245 ppm (see Table VI). In all cases the low field  $\alpha$ -carbon shows a larger  $^1J_{\text{CH}}$  (range 92-105 Hz) than the higher field  $\alpha$ -carbon (range 85-96 Hz).

The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 47d is shown in Figure 2 (spectrum a). Selective  $^1\text{H}$  decoupling of the low field  $^1\text{H}$  resonance (6.93 ppm) indicates that the  $\alpha$ -hydrogen atom giving rise to that resonance, is bound to the  $\alpha$ -carbon atom associated with the low field carbon resonance (275 ppm), (spectrum d). The remaining resonances show almost complete  $^{13}\text{C}\text{-}^1\text{H}$  coupling (comparing spectra b and d) with a significant intensity loss due to loss of NOE.<sup>49</sup> Irradiation of the high field  $\alpha$ -hydrogen resonance (2.08 ppm) decouples the high field  $\alpha$ -carbon resonance (246 ppm; spectrum c). In this case all remaining carbons (except the  $\alpha$ -carbons of the neopentylidenes) show partial proton coupling similar to off resonance decoupling experiments.<sup>49</sup>

Table VI.  $^{13}\text{C}$  and  $^1\text{H}$  NMR Data for Bisneopentylidene Complexes

	$C_{\alpha(1)}$ <sup>a</sup>	$(^1J_{\text{CH}})$ <sup>b</sup>	$C_{\alpha(2)}$ <sup>a</sup>	$(^1J_{\text{CH}})$ <sup>b</sup>	$H_{\alpha(1)}$ <sup>c</sup>	$H_{\alpha(2)}$ <sup>c</sup>
$\text{Ta}(\text{CHCMe}_3)_2\text{R}(\text{PMe}_3)_2$ :						
R = Cl, <u>46a</u> :	273	(98)	241	(86)	8.20	0.45
R = Me, <u>47a</u> :	273	(92)	246	(90)	6.69	2.04
R = Et, <u>47b</u> :	271	(97)	244	(92)	6.92	3.32
R = Bu <sup>n</sup> , <u>47c</u> :	273	(92)	246	(89)	6.86	2.82
R = CH <sub>2</sub> CMe <sub>3</sub> , <u>47d</u> : <sup>d</sup>	274	(95)	246	(85)	6.93	2.08
R = mesityl, <u>47e</u> :	275	(104)	243	(91)	6.72	2.00
$\text{Nb}(\text{CHCMe}_3)_2\text{R}(\text{PMe}_3)_2$ :						
R = Cl, <u>46b</u> :	284	(105)	240	(96)	10.48	1.49
R = CH <sub>2</sub> CMe <sub>3</sub> : <sup>d</sup>	282	(br)	245	(~60)	9.38	4.29
$\text{Ta}(\text{C}_5\text{R}'_5)(\text{CHCMe}_3)_2(\text{PMe}_3)$ :						
R' = H, <u>48</u> : <sup>e</sup>	255	(96)	235	(90)	8.28	2.03
R' = Me: <sup>e</sup>	259	(101)	227	(73)	8.17	0.27

<sup>a</sup>Neopentylidene  $\alpha$ -carbon atom(s) chemical shift measured in ppm downfield from TMS.

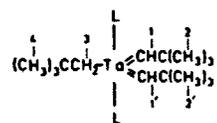
<sup>b</sup> $(^1J_{\text{CH}})$  is reported in Hertz.

<sup>c</sup>Neopentylidene  $\alpha$ -hydrogen atom(s) chemical shift measured in ppm downfield from TMS.

<sup>d</sup>Data taken from Rupprecht, G.A., Ph.D. Thesis.

<sup>e</sup>Data taken from Wood, C.D., Ph.D. Thesis.

Figure 1. The 270 MHz  $^1\text{H}$  NMR Spectrum of  $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$



L = PMe<sub>3</sub>

270 MHz <sup>1</sup>H NMR

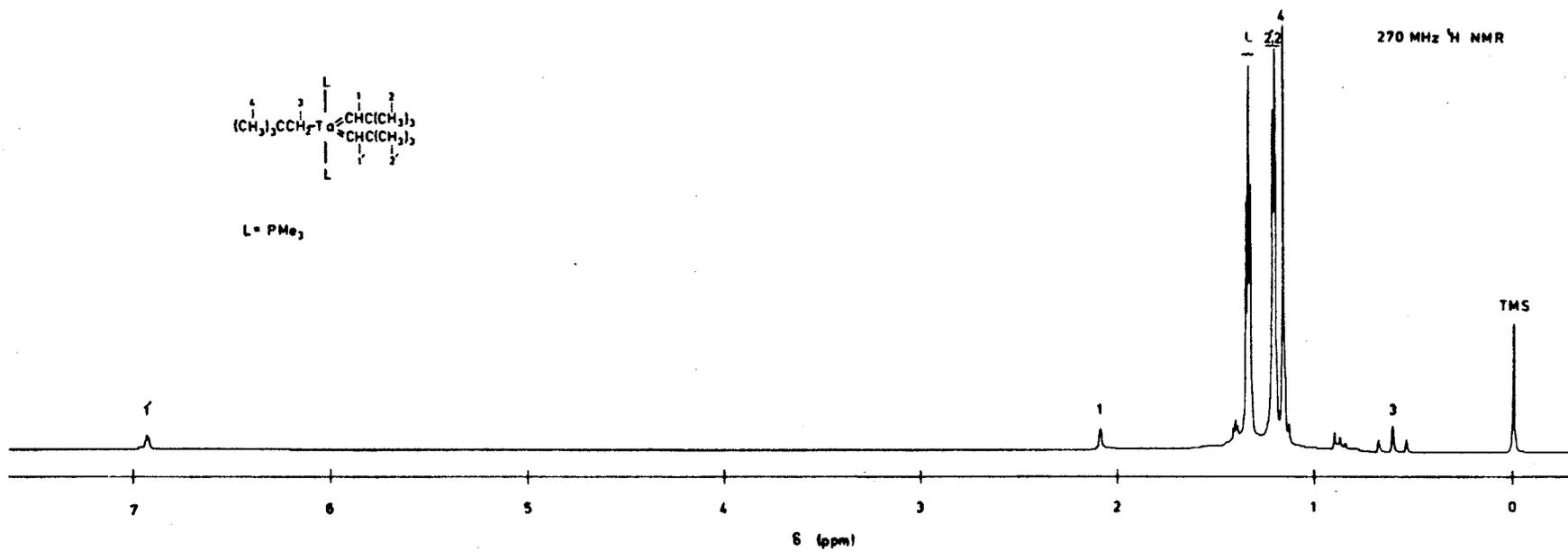
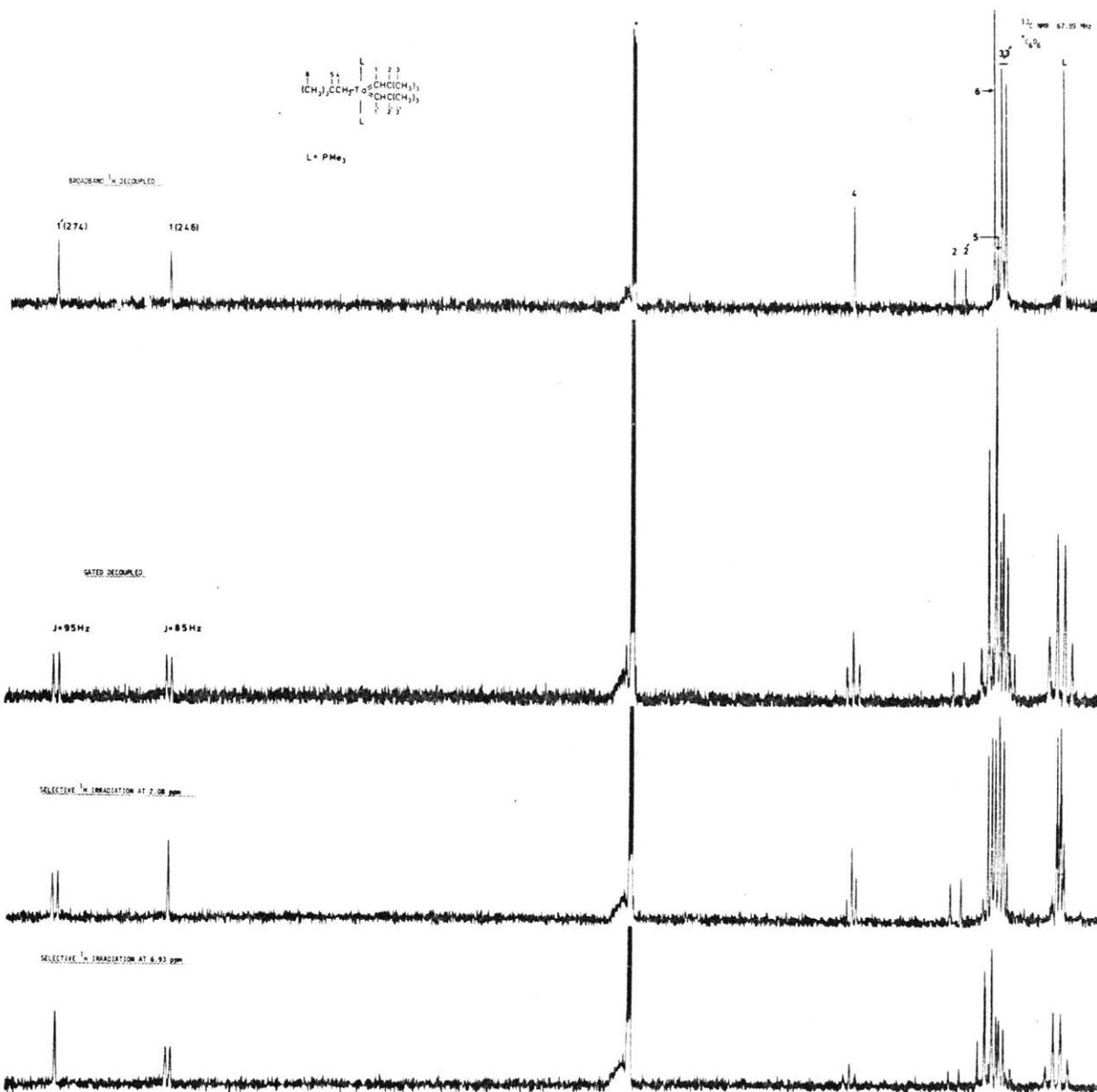
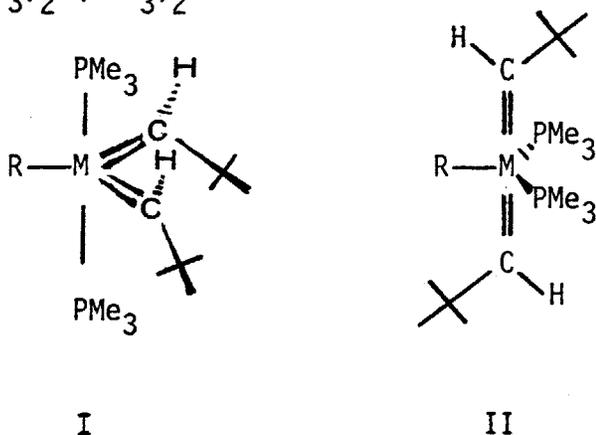


Figure 2. The 67.89 MHz  $^{13}\text{C}$  NMR Spectra of  $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$   
(a),  $\{^1\text{H}\}$  ; (b) gated  $\{^1\text{H}\}$ ; (c) selective  $^1\text{H}$  decoupled at  
2.08 ppm; (d) selective  $^1\text{H}$  decoupled at 6.93 ppm.



The similarities between the NMR spectroscopy obtained for complexes of the type  $M(\text{CHCMe}_3)_2\text{R}(\text{PMe}_3)_2$  indicate that the coordination geometries about the metal center are the same. The two most likely geometries for  $M(\text{CHCMe}_3)_2\text{R}(\text{PMe}_3)_2$  are I and II.

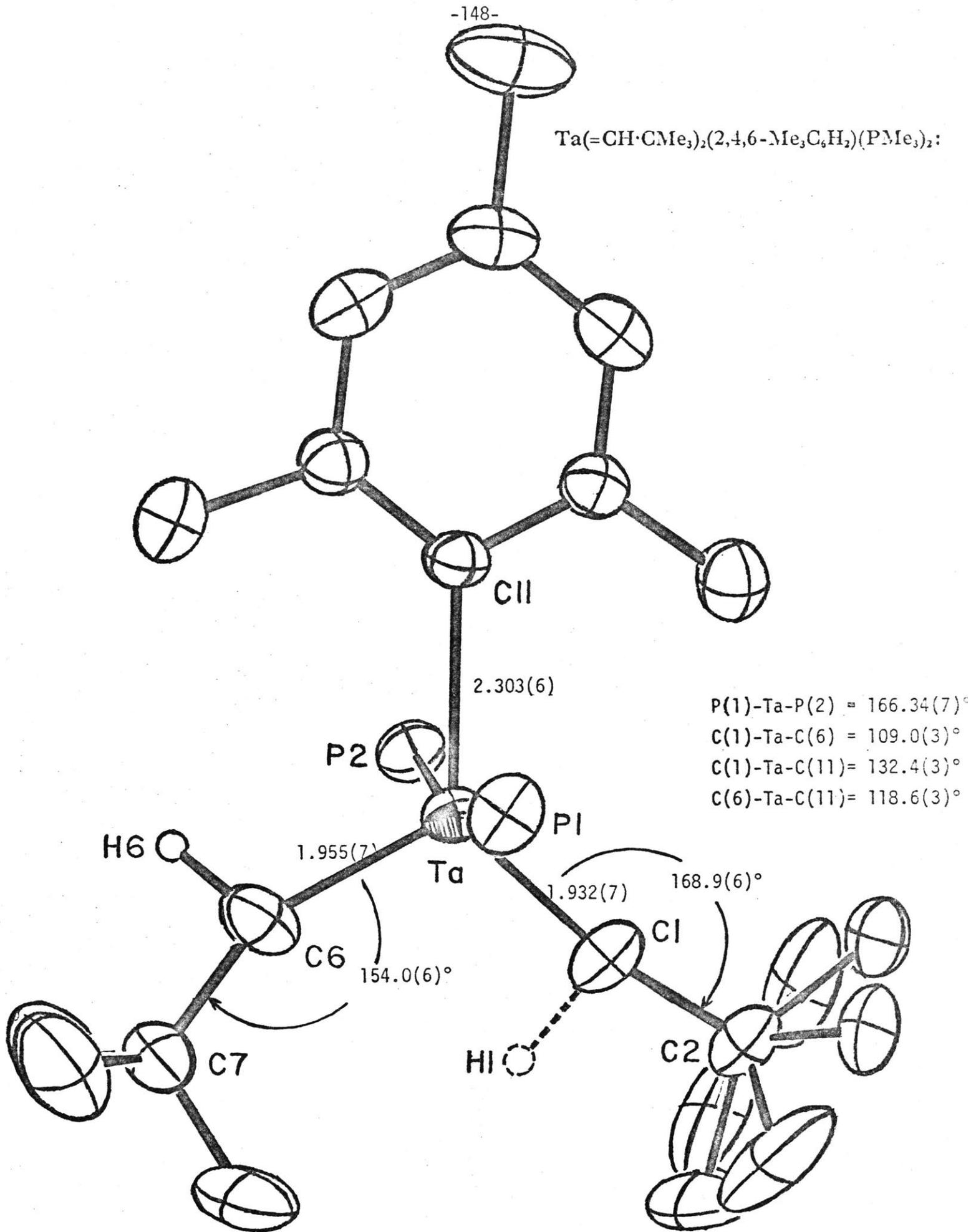
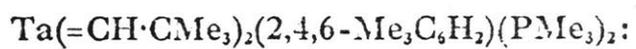


In order to distinguish between structures I and II, x-ray structural studies were attempted by Churchill for several complexes where  $\text{R} = \text{CH}_2\text{CMe}_3$  and  $\text{Cl}$ , and  $\text{M} = \text{Ta}$  and  $\text{Nb}$ . Unfortunately the crystals were disordered. However, the structure of  $\text{Ta}(\text{CHCMe}_3)_2(\text{mesityl})(\text{PMe}_3)_2$  was solved and reported by Churchill,<sup>39</sup> (Figure 3).

Structural determination of  $\text{Ta}(\text{CHCMe}_3)_2(\text{mesityl})(\text{PMe}_3)_2$  confirms that there is a slightly distorted trigonal bipyramidal geometry about the metal. The neopentylidene ligands lie in the equatorial plane and point in the same direction confirming their inequivalency. The mesityl ligand is normal and also lies in the equatorial plane. The  $\text{PMe}_3$  ligands are axial with a  $\text{PMe}_3\text{-Ta-PMe}_3$  angle of  $166.34(7)^\circ$ . These ligands are probably bent off axis in order to minimize steric interactions with the neopentylidene ligands.

The most notable features are: the difference in distances between  $\text{Ta-C}(6)$  and  $\text{Ta-C}(1)$ , ( $1.955(7)$  and  $1.932(7)$  Å, respectively), and the difference in bond angles between  $\text{Ta-C}(6)\text{-C}(7)$  and  $\text{Ta-C}(1)\text{-C}(2)$ , ( $154.0(6)^\circ$  and  $168.9(6)^\circ$ , respectively). These data indicate that the neopentylidene

Figure 3. The X-Ray Molecular Structure of  $\text{Ta}(\text{CHCMe}_3)_2(\text{mesityl})(\text{PMe}_3)_2$



ligand containing C(6), is bound to Ta in a similar fashion as found for the 18-electron complex  $\text{Ta}(\text{C}_5\text{H}_5)_2(\text{CHCMe}_3)\text{Cl}$ ,<sup>31</sup> whereas the neopentylidene containing C(1), is bound to Ta in a similar fashion as found for the electron deficient (<18 e) complex  $[\text{Ta}(\text{CHCMe}_3)\text{Cl}_3(\text{PMe}_3)]_2$ <sup>28</sup> (see Chapter 2). This is consistent with the observed  $^1\text{H}$  and  $^{13}\text{C}$  NMR data for  $\text{M}(\text{CHCMe}_3)\text{R}(\text{PMe}_3)_2$ . Typically 18-electron alkylidene complexes show lower field  $^1\text{H}$  and  $^{13}\text{C}$  resonances than those found in electron deficient complexes. This indicates that  $\text{Ta}(\text{CHCMe}_3)_2(\text{mesityl})(\text{PMe}_3)_2$  has the same (or similar) solution and solid state structures (see Figure 4).

Variable temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR studies of several four- and five-coordinate bisneopentylidene complexes show that the neopentylidene ligands equilibrate at a rate which is on the order of the NMR time scale (see Table VII). This process is assumed to be intramolecular since the  $\text{PMe}_3$  ligands observed by  $^1\text{H}$  or  $^{13}\text{C}$  NMR remained sharp and coupled to the nucleus observed. The most reasonable mechanism for the interconversion of the neopentylidene ligands is that the alkylidene(s) equilibrate by rotation about the Ta-neopentylidene bond (Scheme III).

It is difficult to decide between path A, equilibration of the neopentylidene ligands via rotation about only one alkylidene-Ta bond; or path B, equilibration due to a synchronous rotation of the neopentylidene ligands. Ignoring electronic effects, it is expected that both pathways are sensitive to steric changes in Ta: i.e., changes in

Table VII. Free Energies of Activation for the Interconversion of Neopentylidene Ligands in  $\text{Ta}(\text{CHCMe}_3)_2\text{R}(\text{PMe}_3)_x$

$\text{Ta}(\text{CHCMe}_3)_2\text{R}(\text{PMe}_3)_x$	$T_c$ (K) <sup>b</sup>	$\Delta G^\ddagger$ (kcal mol <sup>-1</sup> ) <sup>a</sup>	Reference
$x = 1, R = \text{C}_5\text{Me}_5:$	273	$11.3 \pm 0.2$	d
$x = 1, R = \text{C}_5\text{H}_5:$	273	$12.4 \pm 0.5$	this work
$x = 2, R = \text{Cl}:$	273(298)	$12.2 \pm 0.5$ ( $13.2 \pm 0.8$ )	this work
$x = 2, R = \text{Me}:$	345	$16.0 \pm 0.5$	this work
$x = 2, R = \text{CH}_2\text{CMe}_3:$	c	$\sim 17.2$	e

<sup>a</sup> $\Delta G^\ddagger$  in kcal mol<sup>-1</sup> estimated from the coalescence of the two neopentylidene  $\text{H}_\alpha$  resonances. Number in brackets is the  $\Delta G^\ddagger$  calculated from coalescence of neopentylidene  $\text{C}_\alpha$  resonances.

<sup>b</sup> $T_c \equiv$  coalescence temperature in K accurate within  $\pm 10\text{K}$ .

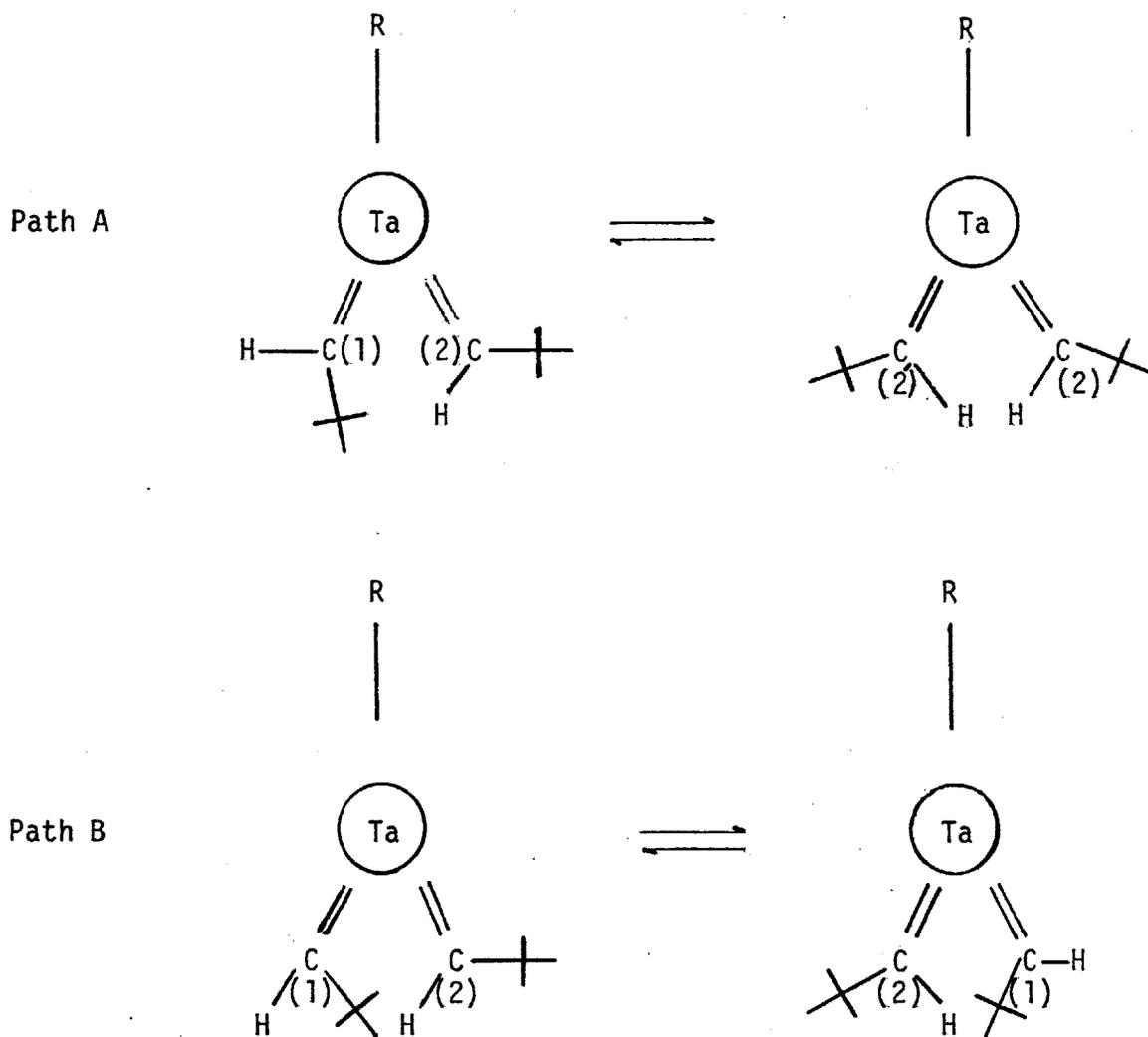
<sup>c</sup>Not reported.

<sup>d</sup>Wood, C.D., Ph.D. Thesis.

<sup>e</sup>Rupprecht, G A., Ph.D. Thesis.

Scheme III. Possible Mechanisms for the Interconversion of  
Neopentylidene Ligands in Bisneopentylidene Complexes

Scheme III.<sup>a</sup> Possible Mechanisms for the Interconversion of Neopentylidene Ligands in Bisneopentylidene Complexes



<sup>a</sup>PMe<sub>3</sub> ligands are orthogonal to the plane of the paper.

coordination number and/or changes in the steric bulk of the ligands.

For five-coordinate complexes  $\Delta G^\ddagger$  increases in the order expected;  $\text{Cl} < \text{Me} < \text{CH}_2\text{CMe}_3$ , and is consistent with both pathways. Lowering the coordination number only slightly effects  $\Delta G^\ddagger$  and the change is in the correct direction.

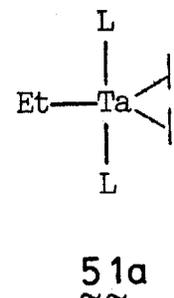
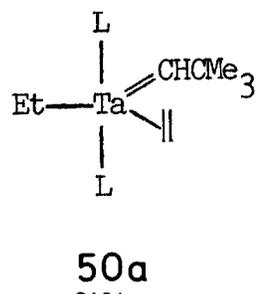
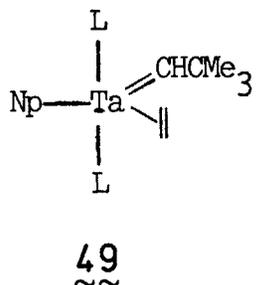
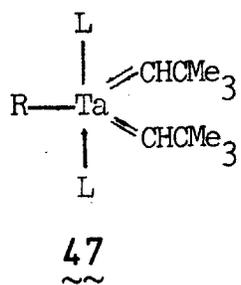
Determining which pathway is responsible for the neopentylidene interconversion is of little practical value. The important result is that rotation about Ta-neopentylidene can occur in electron deficient alkylidene complexes. In fact, the free energies of activation found for bisneopentylidene complexes are lower than the reported values in 18 electron complexes of the type  $\text{Ta}(\text{C}_5\text{H}_5)_2(\text{CHR}')\text{X}$  (where  $\text{R}' = \text{H}, \text{Ph}, \text{CMe}_3$ ).<sup>30</sup>

Synthesis and Characterization of  $\text{M}(\text{CHCMe}_3)(\text{C}_2\text{H}_4)\text{R}(\text{PMe}_3)_2$ ;  $\text{M} = \text{Ta}$  and  $\text{Nb}$

$\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  in ether reacts with 1.5 equivalents of  $\text{Mg}(\text{CH}_2\text{CMe}_3)_2$  (dioxane) to give large yellow crystals of  $\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_4)(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$  49 in moderate yields. 49 is thermally sensitive and decomposes in solution at temperatures greater than  $40^\circ$ .

The  $^{13}\text{C}$  NMR spectrum of 49 at  $-20^\circ$  shows the neopentylidene  $\alpha$ -carbon atom at 247 ppm (dt,  $^2J_{\text{CP}} = 11.3$  Hz,  $^1J_{\text{CH}} = 93$  Hz). Only one olefinic resonance is observed, at 33.6 ppm (t,  $^1J_{\text{CH}} = 145$  Hz). The neopentyl  $\alpha$ -carbon resonance is at 75.2 ppm ( $J_{\text{CH}} = 108$  Hz). Also, two different t-butyl resonances are observed, as expected. A virtual triplet is observed for the  $\text{PMe}_3$  ligands. The  $^1\text{H}$  NMR shows two multiplets at 1.27 (2 H) and -0.15 ppm (2 H) for the olefinic protons at  $-30^\circ$ . Warming to  $30^\circ$  still shows only two ethylene multiplets, however, the olefinic

Figure 4. Proposed Structures of Some Five-Coordinate Olefin and Alkylidene Complexes

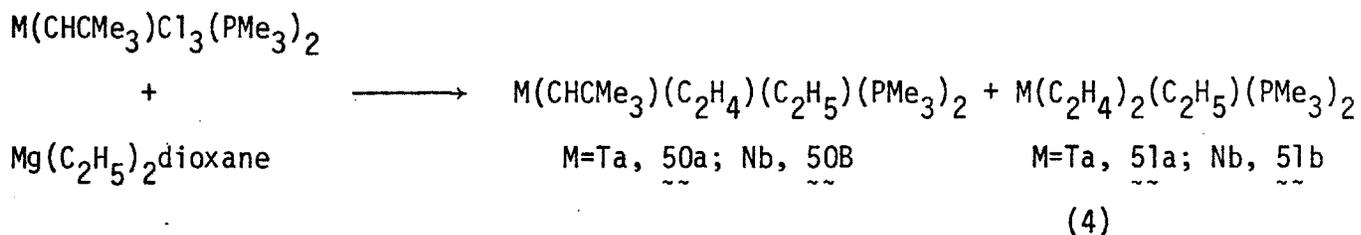


protons are no longer coupled to phosphorous due to phosphine dissociation at this temperature.

The structure of 49, based on these data, is probably similar to that found for bisneopentylidene complexes; a trigonal bipyramid with axial  $\text{PMe}_3$  ligands and the neopentylidene ligand lying in the equatorial plane. The ethylene ligand, also in the equatorial plane, must be aligned parallel to the Ta- $\text{PMe}_3$  axis (see Figure 4).

This supports the general observation that olefins are usually oriented orthogonal to the plane containing an alkylidene ligand, as seen for structurally analogous complexes (c.f. *trans,mer*-Ta( $\text{C}_2\text{H}_4$ )- $\text{Cl}_3(\text{PMe}_3)_2$  and *trans,mer*-Ta( $\text{CHCMe}_3$ ) $\text{Cl}_3(\text{PMe}_3)_2$ ).

Reaction of  $\text{M}(\text{CHCMe}_3)\text{Cl}_3(\text{PMe}_3)_2$  (where M = Ta or Nb) with 1.5 equivalents of  $\text{Mg}(\text{C}_2\text{H}_5)_2$ dioxane gives a red oil which contains  $\text{M}(\text{CHCMe}_3)(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  and  $\text{M}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  (equation 4).



For M = Ta the ratio of 50a to 51a is 7:3, and for M = Nb the ratio of 50b to 51b is 3:2. Ta( $\text{C}_2\text{H}_4$ ) $_2$ ( $\text{C}_2\text{H}_5$ )( $\text{PMe}_3$ ) $_2$  (51a) can be isolated from the reaction mixture as red crystals leaving a red oil enriched with Ta( $\text{CHCMe}_3$ )( $\text{C}_2\text{H}_4$ )( $\text{C}_2\text{H}_5$ )( $\text{PMe}_3$ ) $_2$  (50a).  $\text{M}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  (M = Ta, Nb) will be discussed in the following section.

The 67.89 MHz  $^{13}\text{C}$  NMR spectrum for 50a (shown in Figure 5) adequately separates all resonances so that a complete assignment of 50a can be made. At  $-50^\circ$ , 50a is present as two isomers. Each

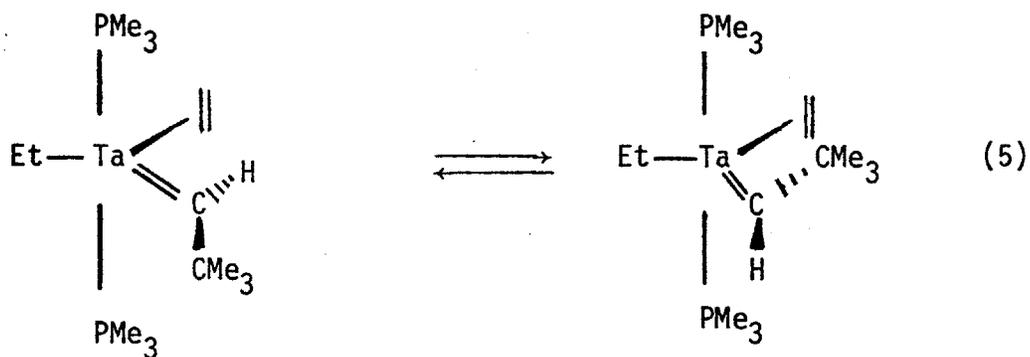
neopentylidene  $\alpha$ -carbon for the minor (260 ppm;  $^1J_{CH} = 80$  Hz) and major (238 ppm;  $^1J_{CH} = 92$  Hz) isomers are equally coupled ( $^2J_{CP} = 10.3$  Hz) to equivalent phosphorous nuclei. Only one type of ethylene carbon is observed for each isomer. All remaining resonances were found for each isomer and are consistent with the formulation  $Ta(CHCMe_3)(C_2H_4)(CH_2CMe_3)(PMe_3)_2$ .

Increasing the temperature shows that the neopentylidene and ethyl ligands, for each isomer, equilibrate and give a high temperature form which is similar to the major isomer. Although the  $PMe_3$  resonances are overlapped for each isomer, it is clear that the virtual triplet for at least the major isomer remains coupled throughout the temperature range studied ( $-50^\circ$  to  $60^\circ$ ). At  $-60^\circ$  only two resonances are present at 0.0 and  $-7.8$  ppm for the major and minor isomers respectively, in the  $^{31}P$  NMR spectrum of 50a. As the temperature is raised, the resonance for the minor isomer moves downfield and merges with the major isomer. Neither isomer exchanges on the order of the NMR timescale with added  $PMe_3$  throughout the equilibration process. These data indicate that both isomers equilibrate by an intramolecular process ( $\Delta G^\ddagger \approx 13$  kcal mol $^{-1}$ ) involving two rotameric forms of 50a.

The structure for each rotamer of  $Ta(CHCMe_3)(C_2H_4)(C_2H_5)(PMe_3)_2$  (50a) must be similar, and analogous to the structure postulated for  $Ta(CHCMe_3)(C_2H_4)(CH_2CMe_3)(PMe_3)_2$  (see Figure 4). Although there is no way to assign a specific structure for either rotamer their structures must only differ in the orientation (either pointing towards or away from the ethyl ligand) of the neopentylidene ligand (equation 5).

Figure 5. The 67.89 MHz  $\{^1\text{H}\}^{13}\text{C}$  NMR Spectrum of  $\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  at  $-50^\circ\text{C}$ .





There are some questions which arise as to why alkylidene olefin complexes are stable toward the formation (and/or rearrangement) of a metallacyclobutane complex. Since the alkylidene and ethylene ligands are bound to the metal in equatorial plane of a trigonal bipyramid the distance which separates these ligands must be sufficiently large to stop the formation of a metallacyclobutane complex. Recent structural data for  $\text{Ta}(\text{C}_5\text{Me}_5)(\text{CHCMe}_3)(\text{C}_2\text{H}_4)(\text{PMe}_3)$  partially illustrates the point.<sup>28b</sup>

This view overlooks any electronic factors as being responsible for the stability these species exhibit toward cyclization. Detailed examination of the structural data for the ethylene ligand in  $\text{Ta}(\text{C}_5\text{Me}_5)(\text{CHCMe}_3)(\text{C}_2\text{H}_4)(\text{PMe}_3)$  shows, as suggested by the authors, that perhaps the bonding of ethylene is best described as that arising from a metallacyclopropane. If this is true, then the oxidation state of Ta, in this complex, would be formally +5 rather than +3. This is not too surprising since Ta complexes are generally more stable in higher oxidation states (see Chapter 4).<sup>20</sup>

With this description in mind, the formation of a metallacyclobutane complex would effectively reduce the metal and would therefore be

unfavorable. Furthermore, just changing the coordination number of the complex by adding a ligand such as  $\text{PMe}_3$  may not be enough to force the cyclization to occur. Instead, addition of an effective  $\pi$ -bonding ligand, such as ethylene, would not only increase the coordination number but also stabilize the high oxidation state of the metal.

Implicit in this argument is that if ethylene is removed from  $\text{Ta}(\text{C}_5\text{Me}_5)(\text{CHCMe}_3)(\text{C}_2\text{H}_4)(\text{PMe}_3)$  then the complex should rearrange in such a way as to maintain a +5 oxidation state (see Chapter 4).

These postulates (steric and electronic) are supported by the fact that  $\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_4)(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$  does not rearrange, even under forced conditions in the presence of  $\text{PMe}_3$ , to give

$\text{Ta}(\text{CHCMe}_3)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$ , whereas  $\text{Ta}(\text{CH}_2\text{CMe}_3)(\text{C}_2\text{H}_4)\text{Cl}_2(\text{PMe}_3)_2$  is in equilibrium with  $\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_5)\text{Cl}_2(\text{PMe}_3)_2$  (see Chapter 2).

Finally, both  $\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_4)(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$  and  $\text{Ta}(\text{CHCMe}_3)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  react with ethylene to give -2 equivalents per Ta of 4,4-dimethyl-1-pentene (the expected rearrangement product formed from an intermediate metallacyclobutane complex) with  $\text{Ta}(\text{C}_2\text{H}_4)_2\text{Bu}^n(\text{PMe}_3)_2$  as the major organometallic product formed (see Chapter 5).

Synthesis and Characterization of  $\text{M}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$ ; M = Ta and Nb

Reacting  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  in ether at  $-30^\circ$  with 1.5 equivalents of  $\text{Mg}(\text{C}_2\text{H}_5)_2$  dioxane gives  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  (51a), isolated as red crystals in moderate yield. 51a is somewhat thermally sensitive and gives satisfactory elemental analysis. 51a is a monomer in cyclohexane (mol. wt. found 372).

Since  $\text{Nb}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  is unknown, alternate methods were sought for the preparation of  $\text{Nb}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  (51b). Several successful methods were attempted, first with tantalum and later applied to niobium. Typically, higher yields were observed in the tantalum systems than in the similar niobium system. Table VIII lists the reaction and yields for four different syntheses used to prepare  $\text{M}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$ .

Reaction 1 was discussed in the previous section. Presumably reactions 2 and 3 are simple  $\beta$ -elimination reactions<sup>6</sup> and need no further discussion. Reaction 4, however, is mechanistically unique since both  $\text{M}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  and  $\text{M}(\text{CHCMe}_3)(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  are formed from the pentacoordinate alkyl  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{C}_2\text{H}_5)_3$ .

$\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{C}_2\text{H}_5)_3$  (52) can be prepared by reacting  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$  with 1.5 equivalents of  $\text{Mg}(\text{C}_2\text{H}_5)_2$  dioxane in ether at  $-30^\circ$ . 52 can be isolated as an unstable yellow oil which is stable in ether but decomposes rapidly (~1 h) in hydrocarbon solvents. Typically, 52 was not isolated but instead was used in situ.

Standing 52 in ether or pentane with about two equivalents of  $\text{PMe}_3$  for 3 h at  $25^\circ$  gives a red solution from which  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  (51a) can be isolated in 48% yield. Examining the original reaction mixture by  $^{13}\text{C}$  NMR shows only 51a and 50a present in a 3:1 ratio.

Since analogous alkylidene and olefin complexes are generally found to be structurally similar, the structure of  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  (51a) is expected to be analogous to  $\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  (50a), a trigonal bipyramid containing axial  $\text{PMe}_3$  ligands. The obvious difference between 50a and 51a is that the neopentylidene ligand is

Table VIII. Preparation of  $M(C_2H_4)_2(C_2H_5)(PMe_3)_2$ ; Reactions and Yields

Reaction <sup>a</sup>	$M(C_2H_4)_2(C_2H_5)(PMe_3)_2$		$M(CHCMe_3)(C_2H_4)(C_2H_5)(PMe_3)_2$	
	Ta	a	Nb	b
$M(CHCMe_3)Cl_3(PMe_3)_2 + 1.5 Mg(C_2H_5)_2$ dioxane <sup>b</sup>	30		40	
$Ta(C_2H_4)Cl_3(PMe_3)_2 + 1.5 Mg(C_2H_5)_2$ dioxane <sup>c</sup>	50		--	
$MCl_5 + 2PMe_3 + 2.5 Mg(C_2H_5)_2$ dioxane <sup>c</sup>	40		7	
$M(CH_2CMe_3)_2(C_2H_5)_3 + 2PMe_3$ <sup>b</sup>	75		10	
				d

<sup>a</sup>Reactions were performed at  $-30^\circ$  or  $-78^\circ$  in ether.

<sup>b</sup>Yields based on  $^1H$  and  $^{13}C$  NMR spectra of the reaction mixture.

<sup>c</sup>Isolated yield.

<sup>d</sup>Data not available.

replaced by ethylene with both olefins orthogonal to the equatorial plane (see Figure 4). NMR spectroscopy supports this postulate (see Experimental).  $\text{Nb}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  (51b) is believed to be structurally similar to 51a.

Experimental

Selective proton decoupled  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR were recorded at 67.89 and 109.3 MHz (Brüker HFX-270), respectively.

Preparation of  $\text{Mg}(\text{C}_2\text{H}_5)_2$  dioxane (III, 73)

$\text{EtBr}$  (55 g, 0.5 mol) was slowly added to 500 mL of  $\text{Et}_2\text{O}$  containing  $\text{Mg}$  turnings (13 g, 0.52 mmol) and stirred overnight. Dioxane (170 mL, ~2 mol, excess) was slowly added (exothermic) then refluxed for 4 h. The gelatinous reaction mixture was filtered and stripped to an oily solid. Addition of pentane gave a white precipitate which was filtered off and extracted with  $\text{Et}_2\text{O}$  (~200 mL), and refiltered. The filtrate, reduced in vacuo to ~50 mL, gave ~25 g of white pyrophoric crystals which were isolated by filtration, washed with pentane and dried in vacuo (28% yield).

Preparation of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{C}_2\text{H}_5)_3$  (V, 10)

$\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$  (1.04 g, 2.42 mmol) was dissolved in  $\text{Et}_2\text{O}$  (~10 mL) and cooled to  $-30^\circ$ .  $\text{Mg}(\text{C}_2\text{H}_5)_2$  dioxane (0.62 g, 3.63 mmol), dissolved in  $\text{Et}_2\text{O}$  (10 mL) and cooled to  $-30^\circ$ , was added rapidly to the stirring Ta solution, then warmed to  $25^\circ$  and stirred for 5 min. The solvent was removed in vacuo. The oily residue was extracted with pentane (15 mL) and filtered. Removal of the solvent gave an orange oil (0.91 g) which rapidly darkened at  $25^\circ$ . The product was more stable in  $\text{Et}_2\text{O}$  than in pentane (92% yield).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 15 MHz; V, 21-1A, 2A;  $\{^1\text{H}\}$  and gated  $\{^1\text{H}\}$ ;  $-30^\circ$ ):  
119.7 (t,  $^1\text{J}_{\text{CH}} = 106$  Hz,  $\text{CH}_2\text{CMe}_3$ ); 92.9 (t,  $^1\text{J}_{\text{CH}} = 116$  Hz,  $\text{CH}_2\text{CH}_3$ );  
36.0 (s,  $\text{CH}_2\text{CMe}_3$ ); 34.9 (q,  $^1\text{J}_{\text{CH}} = 126$  Hz,  $\text{CH}_2\text{CMe}_3$ ); 15.7 (q,  $^1\text{J}_{\text{CH}} = 126$  Hz,  $(\text{CH}_2\text{CH}_3)$ ).

Preparation of Ta(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (V, 43)

Ta(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> was prepared in the same manner as

Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> and was only used in a reaction with PMe<sub>3</sub> (see below).

Preparation of Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (IV, 24)

Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub> (0.91 g, 1.96 mmol) dissolved in Et<sub>2</sub>O (30 mL), was

rapidly mixed with an Et<sub>2</sub>O solution containing Mg(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> dioxane

(0.35 g, 1.96 mmol) at -30°, then warmed to 25° and stirred for 5 min.

The reaction mixture was filtered, and the solvent was removed in vacuo.

The residue was extracted with 25 mL of pentane, filtered and stripped

to a yellow oil which rapidly darkened at 25°. Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>

decomposes rapidly (t<sub>1/2</sub> ≈ 3 min) in C<sub>6</sub>H<sub>6</sub>, at 25°, giving neopentane,

by <sup>1</sup>H NMR (IV, 24-1B, 2B).

<sup>13</sup>C NMR (δ; C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 15 MHz; IV, 27-1B through 4B; {<sup>1</sup>H} and gated {<sup>1</sup>H};

-20°): 119.2 (t, <sup>1</sup>J<sub>CH</sub> = 110 Hz, CH<sub>2</sub>CMe<sub>3</sub>); 91.1 (t, <sup>1</sup>J<sub>CH</sub> = 116 Hz,

CH<sub>2</sub>CH<sub>3</sub>); 36.6 (s, CH<sub>2</sub>CMe<sub>3</sub>); 35.1 (q, <sup>1</sup>J<sub>CH</sub> = 125 Hz, CH<sub>2</sub>CMe<sub>3</sub>);

15.8 (q, <sup>1</sup>J<sub>CH</sub> = 126 Hz, CH<sub>2</sub>CH<sub>3</sub>).

Reacting Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> with ca. 2 equivalents of PMe<sub>3</sub>, in pentane

for 2 h (25°), gave a red oil which was a complex mixture, containing

~20% Ta(CHCMe<sub>3</sub>)(C<sub>2</sub>H<sub>4</sub>)(C<sub>2</sub>H<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>, identified by <sup>13</sup>C NMR (IV, 27-1C).

<sup>13</sup>C NMR Data for Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>x</sub>Cl<sub>5-x</sub>; x = 1, 2, 3

<sup>13</sup>C NMR spectra were obtained for Ta(CH<sub>2</sub>CMe<sub>3</sub>)Cl<sub>4</sub>, Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub>

and Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub> in C<sub>6</sub>D<sub>6</sub> at 25°. These compounds were prepared

by published methods.<sup>10b, 15b</sup>

Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>x</sub>Cl<sub>5-x</sub>: (δ; C<sub>6</sub>D<sub>6</sub>; {<sup>1</sup>H} and gated {<sup>1</sup>H}; 25°):

x = 1: Ta(CH<sub>2</sub>CMe<sub>3</sub>)Cl<sub>4</sub> (22.5 MHz; VII, 40-1B, 2B): 132 (t, <sup>1</sup>J<sub>CH</sub> = 110 Hz,

CH<sub>2</sub>CMe<sub>3</sub>); 40.0 (s, CH<sub>2</sub>CMe<sub>3</sub>); 33.8 (q, <sup>1</sup>J<sub>CH</sub> = 126 Hz, CH<sub>2</sub>CMe<sub>3</sub>).

x = 2: Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub> (15.0 MHz; V, 63-1B, 2B): 123 (t, <sup>1</sup>J<sub>CH</sub> = 116 Hz, CH<sub>2</sub>CMe<sub>3</sub>); 37.2 (s, CH<sub>2</sub>CMe<sub>3</sub>); 35.1 (q, <sup>1</sup>J<sub>CH</sub> = 125 Hz, CH<sub>2</sub>CMe<sub>3</sub>).

x = 3: Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub> (15.0 MHz; V, 43-1A, 2A): 115 (t, <sup>1</sup>J<sub>CH</sub> = 119 Hz, CH<sub>2</sub>CMe<sub>3</sub>); 35.0 (q, <sup>1</sup>J<sub>CH</sub> = 125 Hz, CH<sub>2</sub>CMe<sub>3</sub>); 34.7 (s, CH<sub>2</sub>CMe<sub>3</sub>).

### Preparation of Ta(CHCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub>

#### 1. From Ta(CHCMe<sub>3</sub>)(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub> (IV, 34, 45)

Ta(CHCMe<sub>3</sub>)(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub> (4.0 g, 8.61 mmol) was dissolved in 100 mL of toluene and cooled to -78°. 1.88 mL of HCl in Et<sub>2</sub>O (4.58 M, 8.61 mmol), diluted with 10 mL of Et<sub>2</sub>O, was slowly added to the cold Ta solution, forming yellow Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>4</sub>Cl (see Chapter 1). It is important to use freshly titrated HCl in Et<sub>2</sub>O since any excess acid will further react to give Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>, which is difficult to separate from the product. After stirring for 2 min, PMe<sub>3</sub> (1.5 g, 19.7 mmol, excess) dissolved in toluene (5 mL), was added and the reaction mixture was warmed to room temperature and stirred for 4 h. In 20 min, a color change from yellow to red occurred. After 2 h, the solution slowly turned yellow, indicating a complete reaction. Removal of the solvent (in vacuo) gave 4.28 g of crude Ta(CHCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub>, which was recrystallized from a concentrated pentane solution at -30°. 3.90 g of large octahedral crystals were isolated by filtration and dried in vacuo (89% yield). Ta(CHCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub> can be sublimed, with some decomposition at 70° and 0.05 μ. Work-up of a similar reaction during the red color stage gave Ta(CHCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub> in 35% yield (II, 55).

2. From Ta(CHCMe<sub>3</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub> (III, 18)

Ta(CHCMe<sub>3</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub> (5.10 g, 10.0 mmol) was dissolved in Et<sub>2</sub>O (70 mL) and cooled to -25°. An ether solution (50 mL) of Mg(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>dioxane (2.65 g, 10.4 mmol) was added dropwise over 1 h, then slowly warmed to 25° and stirred for 1 h. The magnesium salts (2.0 g) were filtered from the red solution. The filtrate was stripped to an oily orange solid which was extracted with pentane (50 mL), filtered and concentrated to 15 mL. Standing at -30° gave 1.15 g of orange powder. Two additional crops (1.62 g) were obtained by concentrating then standing the mother liquor at -30°. The product obtained above was recrystallized from a saturated ether solution at -30° (54% yield).

Ta(CHCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub> can also be prepared from Ta(CHCMe<sub>3</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub> and 2 equivalents of Mg(CH<sub>2</sub>CMe<sub>3</sub>)Cl in Et<sub>2</sub>O at -30°, in 34% yield (III, 58).

Ta(CHCMe<sub>3</sub>)(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub> is formed in the above reactions if the alkylating agents are added too rapidly or at higher temperatures. Using LiCH<sub>2</sub>CMe<sub>3</sub>, at low temperature in toluene, gave Ta(CHCMe<sub>3</sub>)(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub> in >90% yield (III, 26; II, 75).

Ta(CHCMe<sub>3</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub> reacts slowly with Zn(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub> in toluene. After 24 h, the reaction mixture was stripped, extracted with pentane and concentrated. Cooling to -30° gave a small yield of a red powder which appeared to be a pure compound, by <sup>1</sup>H NMR (II, 71-3B). No further investigation of this product was made.

Molecular Weight (cyclohexane, II, 69): Calculated: 509. Found: 550.

Anal. (II, 53; IV, 34; I, 26-1): Calcd. for TaC<sub>16</sub>H<sub>38</sub>ClP<sub>2</sub>: C, 37.78; H, 7.52; Cl, 6.97; P, 12.17. Found: C, 39.15; H, 6.85; Cl, 7.08; P, 11.82. Found: C, 39.16; H, 6.88.

Mass Spec. (I, 31): Calcd. ( $M^+$ ): 508.16176. Found: 508.16044.

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 270 and 60 MHz; I, 35-1B through 3B; III, 49-1 and subsequent spectra;  $-75^\circ$  to  $110^\circ$ ):

(270 MHz;  $-30^\circ$ ): 8.200 (s, 1,  $\underline{\text{CHCMe}_3}$ ); 1.207 (s, 9,  $\text{CHCMe}_3$ ); 1.199 (s, 9,  $\text{CHCMe}_3'$ ); 1.158 (t, 18,  $^2J_{\text{PH}} = 3.13$  Hz,  $\text{PMe}_3$ ); 0.446 (s, 1,  $\underline{\text{CHCMe}_3'}$ ).

(60 MHz;  $0^\circ$ ): coalescence of neopentylidene  $\text{H}_\alpha$  resonances.

(60 MHz;  $110^\circ$ ): 4.74 (br,  $\underline{\text{CHCMe}_3}$ ); 1.31 (t,  $^2J_{\text{PH}} = 3.3$  Hz,  $\text{PMe}_3$ ); 1.23 (s,  $\text{CHCMe}_3$ ).  $T_c = 0 \pm 10^\circ$ ,  $\Delta\nu = 480 \pm 10$  Hz,  $\Delta G^\ddagger = 12.2 \pm 0.5$  kcal mol $^{-1}$ .

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 67.89, 22.5 and 15.0 MHz; I, 35-1 through 3; I, 32-2 through 4; III, 48-1A through 8A;  $\{^1\text{H}\}$  and gated  $\{^1\text{H}\}$ ;  $-40^\circ$  to  $95^\circ$ ):

(67.89 MHz;  $-30^\circ$ ): 273.4 (dt,  $^2J_{\text{PC}} = 5.5$  Hz,  $^1J_{\text{CH}} = 97.7$  Hz,  $\underline{\text{CHCMe}_3}$ ); 240.9 (dt,  $^2J_{\text{PC}} = 7.5$  Hz,  $^1J_{\text{CH}} = 85.5$  Hz,  $\underline{\text{CHCMe}_3'}$ ); 47.8 (s,  $\underline{\text{CHCMe}_3'}$ ); 44.2 (s,  $\text{CHCMe}_3$ ); 35.0 (q,  $^1J_{\text{CH}} = 125$  Hz,  $\text{CHCMe}_3$ ); 34.5 (q,  $^1J_{\text{CH}} = 130$  Hz,  $\text{CHCMe}_3'$ ); 17.2 (qt,  $^1J_{\text{PC}} = 12.5$  Hz,  $^1J_{\text{CH}} = 128$  Hz,  $\text{PMe}_3$ ). (22.5 MHz;  $25^\circ$ ): coalescence of  $\text{C}_\alpha$  of neopentylidene resonances.

(15.0 MHz;  $95^\circ$ ): 258.0 (br d,  $^1J_{\text{CH}} = 91$  Hz,  $\underline{\text{CHCMe}_3}$ ); 45.9 (s,  $\underline{\text{CHCMe}_3}$ ); 35.0 (q,  $^1J_{\text{CH}} = 125$  Hz,  $\text{CHCMe}_3$ ); 17.7 (qt,  $^1J_{\text{PC}} = 11.7$  Hz,  $^1J_{\text{CH}} \approx 125$  Hz,  $\text{PMe}_3$ ).

$T_c = 25 \pm 10^\circ$ ,  $\Delta\nu = 732 \pm 20$  Hz,  $\Delta G^\ddagger = 13.2 \pm 0.8$  kcal mol $^{-1}$ .

$^{31}\text{P}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 36.4 MHz; V, 59-61;  $\{^1\text{H}\}$ ;  $30^\circ$ ): 2.8 (s).

IR ( $\text{cm}^{-1}$ ; Nujol, Fluorolube/NaCl; I, 26-1,2): 2670, w ( $\nu_{\text{C-H}}$ ).

Preparation of Ta(CHCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>2</sub>Ph)<sub>2</sub> (II, 25)

Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>4</sub>Cl (1 mmol) was prepared in pentane, at -78°, using gaseous HCl (see Chapter 1). PMe<sub>2</sub>Ph (0.42 g, 3 mmol, 50% excess) was added to the cold solution. The reaction mixture was warmed to 25°, stirred for 30 min and filtered. The filtrate was treated with darco and the volume was reduced to ~1 mL. After cooling to -30° for 24 h, the solution was stripped to a yellow oil which contained >60% Ta(CHCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>2</sub>Ph)<sub>2</sub>, by <sup>1</sup>H NMR (II, 25-1B).

<sup>1</sup>H NMR (δ; C<sub>6</sub>H<sub>6</sub>; 60 MHz, II, 25-1B; 25°): 1.8 (t, 13, <sup>2</sup>J<sub>PH</sub> ≈ 3 Hz, PMe<sub>2</sub>Ph); 1.4 (s, 18, CHCMe<sub>3</sub>).

Preparation of Nb(CHCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub>

1. From Nb(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub> (I, 58)

Nb(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub> (0.75 g, 2.0 mmol) was dissolved in pentane (20 mL) and cooled to -78°. A pentane solution (20 mL) of LiCH<sub>2</sub>CMe<sub>3</sub> (0.31 g, 4.0 mmol), added slowly (dropwise) to the Nb solution, reacted at -78°, giving a cloudy brown solution. The solution was warmed to room temperature, stirred for 10 min, then cooled to -78°. Gaseous HCl (45 mL, 2.0 mmol) was added, via syringe, by slowly bubbling the acid under the surface of the solvent. Excess PMe<sub>3</sub> (0.5 mL, 5.3 mmol) was added at -78°, then warmed to room temperature for 5 min. The reaction mixture was cooled to 0°, stirred for 1 h, then filtered. The resulting green-brown filtrate was stripped leaving a tacky brown solid. The residue was extracted with pentane (10 mL), filtered, and concentrated to ~2 mL. Standing at -30° for 6 h gave 0.32 g of a yellow powder, pure by <sup>1</sup>H NMR (38% yield).

2. From Nb(CHCMe<sub>3</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub> (VII, 59)

A stirred solution of Nb(CHCMe<sub>3</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub> (3.17 g, 7.52 mmol) in 30 mL of Et<sub>2</sub>O at -30°, was treated dropwise with a solution of Mg(CHCMe<sub>3</sub>)<sub>2</sub>dioxane (1.92 g, 7.52 mmol) in 20 mL of Et<sub>2</sub>O. The magnesium salts were filtered from the yellow-brown solution after warming to 25° for 1.5 h. The crude product remained after removing all the volatiles in vacuo. The residue was extracted with pentane (50 mL), filtered and stripped to a tacky yellow solid. A saturated Et<sub>2</sub>O solution containing crude Nb(CHCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub>, cooled to -30° for 12 h, gave 2.07 g of pure product isolated as an amorphous powder. Crystalline Nb(CHCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub> can be obtained after multiple recrystallizations from concentrated pentane solutions, containing PMe<sub>3</sub>, at -30° (66% yield).

<sup>1</sup>H NMR (δ; C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 270 MHz; I, 58-1 through 3; -30°): 10.483 (br t, 1, <sup>3</sup>J<sub>PH</sub> = 2.4 Hz, CHCMe<sub>3</sub>); 1.491 (br s, 1, CHCMe<sub>3</sub>'); 1.208 (s, 9, CHCMe<sub>3</sub>); 1.182 (s, 9, CHCMe<sub>3</sub>'); 1.088 (t, 18, <sup>2</sup>J<sub>PH</sub> = 2.93 Hz, PMe<sub>3</sub>).

<sup>13</sup>C NMR (δ; C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 67.89 MHz; V, 34-1,2; {<sup>1</sup>H} and gated {<sup>1</sup>H}: -40°): 284 (bd, <sup>1</sup>J<sub>CH</sub> = 105 Hz, CHCMe<sub>3</sub>); 240 (br d, <sup>1</sup>J<sub>CH</sub> = 96 Hz, CHCMe<sub>3</sub>'); 45.8 (s, CHCMe<sub>3</sub>'); 43.1 (s, CHCMe<sub>3</sub>); 34.0 (q, <sup>1</sup>J<sub>CH</sub> = 126 Hz, CHCMe<sub>3</sub>); 33.6 (q, <sup>1</sup>J<sub>CH</sub> = 124 Hz; CHCMe<sub>3</sub>'); 16.8 (br q, <sup>1</sup>J<sub>CH</sub> = 129 Hz, PMe<sub>3</sub>).

<sup>31</sup>P NMR (δ; C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 36.4 MHz; V, 59-96; {<sup>1</sup>H}; -60°): -16 (br s).

Preparation of Ta(CHCMe<sub>3</sub>)<sub>2</sub>Me(PMe<sub>3</sub>)<sub>2</sub> (III, 22)

1.29 mL of LiMe·LiBr complex in Et<sub>2</sub>O (1.69 M, 2.12 mmol) diluted with 10 mL of ether, was added dropwise to an ether solution (15 mL) of Ta(CHCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub> cooled to -78°. The reaction was warmed to 25°

and stirred for 30 min. The solvent was removed in vacuo leaving a solid yellow residue. Pentane (20 mL) was added and the solution was filtered, treated with darco and stripped. Sublimation of the crude product at 70° and 1  $\mu$  gave 0.76 g of pure material (73% yield).

Anal. (III, 22; III, 22-1): Calcd. for TaC<sub>17</sub>H<sub>41</sub>P<sub>2</sub>: C, 41.81; H, 8.46. Found: C, 40.53; H, 8.18. Found: C, 35.66; H, 7.05.

<sup>1</sup>H NMR ( $\delta$ ; C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 60 MHz; III, 48-1C through 19C; 3° to 143°): (143°): 4.42 (br CHCMe<sub>3</sub>); 1.17 (br, PMe<sub>3</sub>); 1.06 (br, CHCMe<sub>3</sub>); -0.3 (br t, <sup>3</sup>J<sub>PH</sub>  $\approx$  30 Hz, Me). (72°): coalescence of neopentylidene H <sub>$\alpha$</sub>  resonances. (3°): 6.69 (br t, 1, <sup>3</sup>J<sub>PH</sub>  $\approx$  1 Hz, CHCMe<sub>3</sub>); 2.04 (s, 1, CHCMe<sub>3</sub>'); 1.10 (m, 36, <sup>1</sup>J<sub>PH</sub>  $\approx$  6 Hz, PMe<sub>3</sub> and CHCMe<sub>3</sub> overlapping); -0.2 (t, 3, <sup>3</sup>J<sub>PH</sub> = 31 Hz, Me). 279 Hz separation between the H <sub>$\alpha$</sub>  neopentylidene resonances. T<sub>c</sub> = 345  $\pm$  10 K,  $\Delta\nu$  = 279  $\pm$  5 Hz,  $\Delta G^\ddagger$  = 16.0  $\pm$  0.5 kcal mol<sup>-1</sup>.

<sup>13</sup>C NMR ( $\delta$ ; C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 15 MHz; III, 48-1B through 3B; {<sup>1</sup>H} and gated {<sup>1</sup>H}); 25°): 273.3 (br d, <sup>1</sup>J<sub>CH</sub> = 92 Hz, CHCMe<sub>3</sub>); 246.4 (br d, <sup>1</sup>J<sub>CH</sub> = 90 Hz, CHCMe<sub>3</sub>'); 47.3 (s, CHCMe<sub>3</sub>'); 44.6 (s, CHCMe<sub>3</sub>); 35.5 (q, <sup>1</sup>J<sub>CH</sub> = 126 Hz, CHCMe<sub>3</sub>); 18.7 (qt, <sup>1</sup>J<sub>PC</sub> = 11.7 Hz, <sup>1</sup>J<sub>CH</sub> = 127 Hz, PMe<sub>3</sub>).

#### Preparation of Ta(CHCMe<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub> (III, 71)

Ta(CHCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub> (0.32 g, 0.63 mmol) was dissolved in Et<sub>2</sub>O (7 mL) and cooled to -78°. 0.58 mL (0.63 mmol) of LiC<sub>2</sub>H<sub>5</sub> in benzene (1.08 M) was added dropwise. The reaction mixture was warmed to 25° and stirred for 30 min. The solvent was removed in vacuo and the residue was extracted with 20 mL of pentane. The solution was filtered and the

filtrate was concentrated to 1 mL. Cooling to  $-30^{\circ}$  for 16 h yielded 0.24 g of yellow needles (76% yield).

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 270 and 200 MHz; IV, 55-1B through 4B;  $25^{\circ}$ ): 6.92 (br s, 1,  $\text{CHCMe}_3$ ); 3.32 (br s, 1,  $\text{CHCMe}_3'$ ); 1.30 (s, 9,  $\text{CHCMe}_3$ ); 1.27 (s, 9,  $\text{CHCMe}_3'$ ); 1.18 (t, 18,  $^2\text{J}_{\text{PH}} = 6.6$  Hz,  $\text{PMe}_3$ ); 0.915 (t, 3,  $^3\text{J}_{\text{HAHB}} = 8$  Hz,  $\text{CH}_2\text{CH}_3$ ); 0.538 (qt, 2,  $^3\text{J}_{\text{HAHB}} = 8$  Hz,  $^2\text{J}_{\text{PH}} = 20.2$  Hz,  $\text{CH}_2\text{CH}_3$ ).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 15.0 MHz; III, 71-1B through 3B;  $\{^1\text{H}\}$  and gated  $\{^1\text{H}\}$ ;  $25^{\circ}$ ): 271.4 (dt,  $^2\text{J}_{\text{PC}} = 6$  Hz,  $^1\text{J}_{\text{CH}} = 97$  Hz,  $\text{CHCMe}_3$ ); 244.4 (dt,  $^2\text{J}_{\text{PC}} = 8$  Hz,  $^1\text{J}_{\text{CH}} = 92$  Hz,  $\text{CHCMe}_3'$ ); 46.2 (s,  $\text{CHCMe}_3'$ ); 44.1 (s,  $\text{CHCMe}_3$ ); 39.1 (qt,  $^2\text{J}_{\text{PC}} \approx 4$  Hz,  $^1\text{J}_{\text{CH}} \approx 125$  Hz,  $\text{CH}_2\text{CH}_3$ ); 35.0 (q,  $^1\text{J}_{\text{CH}} = 123$  Hz,  $\text{CHCMe}_3$ ); 34.5 (q,  $^1\text{J}_{\text{CH}} = 123$  Hz,  $\text{CHCMe}_3'$ ); 18.8 (qt,  $^1\text{J}_{\text{PC}} = 11$  Hz,  $^1\text{J}_{\text{CH}} = 130$  Hz,  $\text{PMe}_3$ ); 5.6 (q,  $^1\text{J}_{\text{CH}} \approx 125$  Hz,  $\text{CH}_2\text{CH}_3$ ).

$^{31}\text{P}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 36.4 MHz; V, 59-62;  $\{^1\text{H}\}$ ;  $30^{\circ}$ ): -2.4 (s).

IR ( $\text{cm}^{-1}$ ; Nujol/NaCl; III, 71-1): 2660, w ( $\nu_{\text{C-H}}$ ).

#### Preparation of $\text{Ta}(\text{CHCMe}_3)_2\text{Bu}^n(\text{PMe}_3)_2$ (V, 32)

$\text{Ta}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  (1.58 g, 3.11 mmol) was dissolved in pentane (20 mL) and cooled to  $-30^{\circ}$ . 1.24 mL (3.15 mmol, excess) of  $\text{LiBu}^n$  in hexane (2.54 mL) was diluted with 5 mL of pentane, cooled to  $-30^{\circ}$ , and added dropwise to the stirring Ta solution. The reaction mixture was warmed to room temperature. After 25 min, the solution was filtered through celite and stripped to yellow crystals. The crude product was dissolved in a minimal amount of pentane and cooled to  $-30^{\circ}$ . Two crops (0.69 g) of yellow crystals were collected (42% yield).

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 270 MHz; V, 32-5,6;  $30^{\circ}$ ): 6.858 (br s,  $\text{CHCMe}_3$ ); 2.822 (br s,  $\text{CHCMe}_3'$ ); 1.593 (br m,  $\text{J}_{\text{HH}} = 6.9$  Hz); 1.292 (s,  $\text{CHCMe}_3$ ); 1.265 (s,  $\text{CHCMe}_3'$ ); 1.116 (br m,  $\text{J}_{\text{HH}} = 6.4$  Hz); 0.588 (br m).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 67.89 MHz; V, 32-1 through 3;  $\{^1\text{H}\}$  and gated  $\{^1\text{H}\}$ ;  $30^\circ$ ): 272.7 (br d,  $^1J_{\text{CH}} = 92.4$  Hz,  $\text{CHCMe}_3$ ); 245.6 (br d,  $^1J_{\text{CH}} = 89.1$  Hz,  $\text{CHCMe}_3'$ ); 51.2 (t,  $^1J_{\text{CH}} = 113.4$  Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ); 46.4 (s,  $\text{CHCMe}_3'$ ); 44.0 (s,  $\text{CHCMe}_3$ ); 35.1 (q,  $^1J_{\text{CH}} = 124$  Hz,  $\text{CHCMe}_3$ ); 34.4 (q,  $^1J_{\text{CH}} = 124$  Hz,  $\text{CHCMe}_3'$ ); 30.1 (t,  $^1J_{\text{CH}} = 122$  Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ); 27.7 (t,  $^1J_{\text{CH}} = 123$  Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ); 19.0 (br q,  $^1J_{\text{CH}} = 129$  Hz,  $\text{PMe}_3$ ); 14.4 (q,  $^1J_{\text{CH}} = 124$  Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ).

$^{31}\text{P}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 36.4 MHz; V, 59-63;  $\{^1\text{H}\}$ ;  $30^\circ$ ): -1.9 (s).

Preparation of  $\text{Ta}(\text{CHCMe}_3)_2(\text{Mes})(\text{PMe}_3)_2$  (III, 42)

$\text{Ta}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  (0.76 g, 1.5 mmol) was dissolved in  $\text{Et}_2\text{O}$  (25 mL) and reacted with  $\text{LiMes}$  (0.20 g, 1.6 mmol, 7% excess) at  $-30^\circ$ .

The solution was warmed to room temperature and stirred for 1 h.

The solvent was removed in vacuo leaving a yellow solid. The residue was extracted with 25 mL of pentane and filtered. The filtrate was stripped to a crude product (0.76 g) which was dissolved in a minimal amount  $\text{Et}_2\text{O}$  and cooled to  $-30^\circ$  for 16 h. 0.67 g of yellow crystals were isolated and dried in vacuo. Crystals suitable for x-ray analysis were obtained by fractional crystallization from concentrated  $\text{Et}_2\text{O}$ /hexane solutions at  $-30^\circ$  (75% yield).

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 60 MHz; III, 42-1B, 2B;  $30^\circ$ ): 6.72 (br s, 1,  $\text{CHCMe}_3$ ); 2.74 (br s, 3, para-Me); 2.26 (br s, 6, ortho-Me); 2.0 (s, 1,  $\text{CHCMe}_3'$ ); 1.42 (s, 9,  $\text{CHCMe}_3$ ); 1.39 (s, 9,  $\text{CHCMe}_3'$ ); 1.15 (t, 18,  $^2J_{\text{PH}} = 3.2$  Hz,  $\text{PMe}_3$ ).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 15.0 MHz, III, 60-1A through 3A;  $\{^1\text{H}\}$  and gated  $\{^1\text{H}\}$ ; 25°): 275 (dt,  $^2\text{J}_{\text{PC}} = 6.6$  Hz,  $^1\text{J}_{\text{CH}} = 104$  Hz,  $\underline{\text{CHCMe}_3}$ ); 243 (dt,  $^2\text{J}_{\text{PC}} = 9.9$  Hz,  $^1\text{J}_{\text{CH}} = 90.6$  Hz,  $\underline{\text{CHCMe}_3'}$ ); 196 (s, phenyl- $\text{C}_\alpha$ ); 141 (br d,  $^3\text{J}_{\text{PC}} = 34$  Hz, phenyl-ortho); 133 (s, phenyl-para); 128 (d,  $^1\text{J}_{\text{CH}} = 157$  Hz, phenyl-meta); 48.2 (s,  $\underline{\text{CHCMe}_3'}$ ); 45.0 (s,  $\underline{\text{CHCMe}_3}$ ); 35.0 (q,  $^1\text{J}_{\text{CH}} = 124$  Hz,  $\underline{\text{CHCMe}_3}$ ); 30.0 (q,  $^1\text{J}_{\text{CH}} \approx 121$  Hz, para-methyl); 21.5 (q,  $^1\text{J}_{\text{CH}} = 125$  Hz, ortho-methyl); 19.1 (qt,  $^1\text{J}_{\text{PC}} = 11.7$  Hz,  $^1\text{J}_{\text{CH}} = 130$  Hz,  $\text{PMe}_3$ ).

$^{31}\text{P}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 36.4 MHz; V, 59-64;  $\{^1\text{H}\}$ ; 30°): 0.9 (s); -1.0 (s).

Preparation of  $\text{Ta}(\text{CHCMe}_3)_2(\text{CD}_2\text{CMe}_3)(\text{PMe}_3)_2$  (II, 60)

$\text{Ta}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  (2.21 g, 4.34 mmol) was dissolved in 15 mL of pentane.  $\text{LiCD}_2\text{CMe}_3$  (0.35 g, 4.34 mmol) was added slowly as a solid. The reaction was immediate, causing the solution to reflux. The reaction mixture was stirred for 1 h and filtered through celite. The filtrate was treated with darco, concentrated and cooled to  $-30^\circ$  for 16 h. The solvent was decanted and 0.86 g of crystals were isolated and dried in vacuo. Concentrating and cooling the mother liquor to  $-30^\circ$  gave an additional 0.9 g of pure product (74% yield).

Preparation of  $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)(\text{CHCMe}_3)_2(\text{PMe}_3)_2$  (II, 67)

$\text{Ta}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  (0.5 g, 1.0 mmol) was dissolved in 15 mL of a 10:1  $\text{Et}_2\text{O}/\text{THF}$  solution and cooled to  $-30^\circ$ . Solid  $\text{NaC}_5\text{H}_5$  (0.10 g, 1.14 mmol) was added and the reaction mixture was warmed to  $25^\circ$  and stirred for 16 h. The solvent was removed in vacuo. The residue,

a yellow solid, was extracted with pentane (15 mL) and filtered. The filtrate was concentrated to ~1 mL and cooled to  $-30^{\circ}$  for 12 hr. The crystallized product, isolated by decanting the mother liquor, was repeatedly crystallized from concentrated pentane solutions at  $-30^{\circ}$ ; 0.23 g (50% yield).

Molecular Weight (cyclohexane; II, 69): Calculated: 462. Found:  $482 \pm 40$ .

The spectroscopic data for  $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)(\text{CHCMe}_3)_2(\text{PMe}_3)$  has been previously reported.<sup>32</sup> Variable temperature  $^1\text{H}$  NMR (60 MHz, II, 67-4B through 16B) from  $-60^{\circ}$  to  $80^{\circ}$  was used to calculate  $\Delta G^{\ddagger}$ . It was found that at  $T_c = 0^{\circ} \pm 10^{\circ}\text{C}$ ,  $\Delta\nu = 375 \pm 20$  Hz and  $\Delta G^{\ddagger} = 12.4 \pm 0.5$  kcal mol $^{-1}$ .

Preparation of  $\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_4)(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$  (III, 62; IV, 66)

$\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  (1.5 g, 3.22 mmol) was dissolved in  $\text{Et}_2\text{O}$  (60 mL) and cooled to  $-30^{\circ}$ . Solid  $\text{Mg}(\text{CH}_2\text{CMe}_3)_2$  dioxane (1.25 g, 4.91 mmol, 2% excess) was added to the cold Ta solution, warmed to  $25^{\circ}$  and stirred for 30 min. The reaction mixture was filtered and the solvent was removed in vacuo. The oily residue was extracted with pentane and filtered. The filtrate was concentrated to ~3 mL and cooled to  $-30^{\circ}$ . Two crops of crude product were collected, and recrystallized from a saturated pentane solution at  $-30^{\circ}$  to give 1.0 g of large, yellow cubic crystals (59% yield).

$\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_4)(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$  is indefinitely stable at  $-30^{\circ}$  in the solid state, but in aromatic solvents it rapidly decomposes (hours) at  $>40^{\circ}$ .

Molecular Weight (cyclohexane; V, 25): Calcd: 502. Found: 632.

Anal. (V, 25; III, 62-1A): Calcd. for  $\text{TaC}_{18}\text{H}_{43}\text{P}_2$ ; C, 43.02; H, 8.62.

Found: C, 34.04; H, 6.77.

Chlorine Analysis (III, 68): Calcd. for  $\text{TaC}_{18}\text{H}_{43}\text{P}_2$ : Cl, 0.00. Found: Cl, 2.12.

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 250 MHz; IX, 17-1B, 2B;  $30^\circ$  and  $-30^\circ$ ): 1.431 (t, 18,  $^2\text{J}_{\text{PH}} = 2.75$  Hz,  $\text{PMe}_3$ ); 1.268 (m, 2,  $\text{CH}_1\text{H}_1' = \text{CH}_2\text{H}_2'$ ); 1.051 (s, 9,  $\text{CH}_2\text{CMe}_3$ ); 0.872 (s, 9,  $\text{CHCMe}_3$ ); 0.816 (br s, 1,  $\text{CHCMe}_3$ ); 0.399 (t, 2,  $^3\text{J}_{\text{PH}} = 21.06$  Hz,  $\text{CH}_2\text{CMe}_3$ ); -0.152 (m, 2,  $\text{CH}_1\text{H}_1' = \text{CH}_2\text{H}_2'$ ).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 67.89 and 15 MHz; III, 66-1B; V, 28-1A through 9A;  $\{^1\text{H}\}$  and gated  $\{^1\text{H}\}$ ;  $-40^\circ$  to  $30^\circ$ ): ( $-20^\circ$ ): 247.1 (dt,  $^2\text{J}_{\text{PC}} = 11.3$  Hz,  $^1\text{J}_{\text{CH}} = 93$  Hz,  $\text{CHCMe}_3$ ); 75.2 (br t,  $^2\text{J}_{\text{PC}} \approx 3$  Hz,  $^1\text{J}_{\text{CH}} = 108$  Hz,  $\text{CH}_2\text{CMe}_3$ ); 47.0 (s,  $\text{CHCMe}_3$ ); 36.2 (q,  $^1\text{J}_{\text{CH}} = 125$  Hz,  $\text{CH}_2\text{CMe}_3$ ); 35.8 (s,  $\text{CH}_2\text{CMe}_3$ ); 34.6 (q,  $^1\text{J}_{\text{CH}} = 125$  Hz,  $\text{CHCMe}_3$ ); 33.6 (tt,  $^2\text{J}_{\text{PC}} = 6.6$  Hz,  $^1\text{J}_{\text{CH}} = 145$  Hz,  $\text{C}_2\text{H}_4$ ); 18.5 (qt,  $^1\text{J}_{\text{PC}} = 9.5$  Hz,  $^1\text{J}_{\text{CH}} = 126$  Hz,  $\text{PMe}_3$ ).

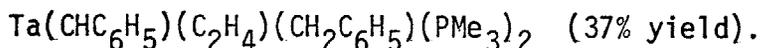
$^{31}\text{P}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 36.2 MHz; V, 59-82;  $\{^1\text{H}\}$ ;  $0^\circ$ ): -1.9 (s).

$\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_4)(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$  reacts with 1 equivalent of HCl in  $\text{Et}_2\text{O}$  at  $-78^\circ$ . Warming to room temperature and evaporation of the solvent gave a red oil which was a 7:3 mixture of  $\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_4)(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$  and  $[\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_5)\text{Cl}_2(\text{PMe}_3)_2 \rightleftharpoons \text{Ta}(\text{CH}_2\text{CMe}_3)(\text{C}_2\text{H}_4)\text{Cl}_2(\text{PMe}_3)_2]$ , by  $^1\text{H}$  NMR (VI, 25).

Reaction of  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  with  $\text{Mg}(\text{CH}_2\text{C}_6\text{H}_5)_2$  dioxane (IV, 70)

$\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  (0.47 g, 1.0 mmol) was dissolved in  $\text{Et}_2\text{O}$  (10 mL) and cooled to  $-30^\circ$ . Solid  $\text{Mg}(\text{CH}_2\text{C}_6\text{H}_5)_2$  dioxane (0.44 g, 1.5 mmol) was added to the cold solution. The reaction mixture was warmed to  $25^\circ$  and

stirred for 30 min. The yellow suspension was filtered, stripped, extracted with 25 mL of pentane, filtered and stripped again. The oily residue was dissolved in 8 mL of pentane. Cooling to  $-30^{\circ}$  for 12 h gave 0.2 g of yellow crystals, tentatively identified as



$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{H}_6$ ; 60 MHz; IV, 70-1A;  $25^{\circ}$ ): 2.80 (br m, olefinic H); 1.77 (t,  $^3\text{J}_{\text{PH}} \approx 13$  Hz,  $\text{CH}_2\text{C}_6\text{H}_5$ ); 1.15 (t,  $^2\text{J}_{\text{PH}} \approx 2.5$  Hz,  $\text{PMe}_3$ ); 0.30 (br m, olefinic H).

Preparation of  $\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  (IV, 19)

$\text{Ta}(\text{CHCMe}_3)\text{Cl}_3(\text{PMe}_3)_2$  (2.04 g, 4.00 mmol) dissolved in  $\text{Et}_2\text{O}$  (50 mL) and cooled to  $-30^{\circ}$  was mixed with an  $\text{Et}_2\text{O}$  solution of  $\text{Mg}(\text{C}_2\text{H}_5)_2$  dioxane (1.02 g, 6.00 mmol) at  $-30^{\circ}$ . The reaction mixture was warmed to  $25^{\circ}$  and stirred for 20 min, then filtered. The filtrate was stripped to an oil, extracted with 40 mL of pentane and filtered. Treating 3 times with darco gave, after filtering and evaporation of the solvent, 1.44 g of a red oil which was a 7:3 mixture of  $\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  and  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$ , by  $^1\text{H}$  and  $^{13}\text{C}$  NMR. (81% yield based on  $\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_4)(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ .)

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 60 MHz; IV, 12-1A;  $25^{\circ}$ ): 1.35 (t,  $^2\text{J}_{\text{PH}} \approx 3$  Hz,  $\text{PMe}_3$ ); 1.10 (s,  $\text{CHCMe}_3$ ); 0.0 (br q,  $^2\text{J}_{\text{H}_B\text{H}_A} \approx 9$  Hz,  $\text{CH}_2\text{CH}_3$ ); -0.90 (t,  $^2\text{J}_{\text{H}_A\text{H}_B} \approx 9$  Hz,  $\text{CH}_2\text{CH}_3$ ).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 67.89 and 15.0 MHz; IV, 17-1 through 4; IV, 20-1 through 18;  $\{^1\text{H}\}$  and gated  $\{^1\text{H}\}$ ;  $-50^{\circ}$  to  $60^{\circ}$ ): ( $-50^{\circ}$ ): Major isomer: 238.2 (dt,  $^2\text{J}_{\text{PC}} = 10.3$  Hz,  $^1\text{J}_{\text{CH}} = 92$  Hz,  $\text{CHCMe}_3$ ); 47.1 (s,  $\text{CHCMe}_3$ );

40.3 (br t,  $^1J_{CH} = 123$  Hz,  $\underline{CH_2CH_3}$ ); 34.5 (q,  $^1J_{CH} = 127$  Hz,  $\underline{CHCMe_3}$ );  
 28.8 (tt,  $^2J_{PC} \approx 7$  Hz,  $^1J_{CH} = 147$  Hz,  $\underline{C_2H_4}$ ); 16.73 (qt,  $^1J_{PC} = 11.6$  Hz,  
 $^1J_{CH} = 127$  Hz,  $PMe_3$ ); -2.41 (br q,  $^1J_{CH} = 124$  Hz).  
 minor isomer: 260.2 (dt,  $^2J_{PC} = 10.2$  Hz,  $^1J_{CH} = 80$  Hz,  $\underline{CHCMe_3}$ );  
 46.5 (s,  $\underline{CHCMe_3}$ ); 30.3 (br t,  $^1J_{CH} = 122$  Hz,  $\underline{CH_2CH_3}$ ); 34.0 (q,  $^1J_{CH} \approx$   
 127 Hz,  $\underline{CHCMe_3}$ ); 31.1 (bt,  $^1J_{CH} \approx 147$  Hz,  $\underline{C_2H_4}$ ); 16.6 (qt,  $^1J_{PC} = 11.7$  Hz,  
 $^1J_{CH} \approx 127$  Hz,  $PMe_3$ ); 1.34 (bq,  $^1J_{CH} = 126$  Hz,  $\underline{CH_2CH_3}$ ).  
 ( $5^\circ$ ): coalescence of  $C_\alpha$  of neopentylidene;  $\Delta\nu = 330 \pm 20$  Hz;  $\Delta G^\ddagger \approx$   
 13 kcal mol $^{-1}$ .

$^{31}P$  NMR ( $\delta$ ;  $C_6D_5CD_3$ ; 36.2 MHz; V, 59-92; { $^1H$ };  $-60^\circ$ ):

major isomer: 0.0 (s).

minor isomer: -7.8 (s).

Preparation of  $Nb(CHCMe_3)(C_2H_4)(C_2H_5)(PMe_3)_2$  (IV, 12)

$Nb(CHCMe_3)(C_2H_4)(C_2H_5)(PMe_3)_2$  was prepared from  $Nb(CHCMe_3)Cl_3(PMe_3)_2$ ,  
 using  $Mg(C_2H_5)_2$  dioxane, in the same manner as its Ta analog (see above).

The product, isolated as a red oil, was a 3:2 mixture of  
 $Nb(CHCMe_3)(C_2H_4)(C_2H_5)(PMe_3)_2$  and  $Nb(C_2H_4)_2(C_2H_5)(PMe_3)_2$ , by  $^{13}C$  and  
 $^1H$  NMR.

$^1H$  NMR ( $\delta$ ;  $C_6H_6$ ; 60 MHz; IV, 12-1B;  $25^\circ$ ): 3.95 (br s,  $\underline{CHCMe_3}$ );  
 1.23 (t,  $^2J_{PH} \approx 2.2$  Hz,  $PMe_3$ ); 1.10 (s,  $\underline{CHCMe_3}$ ); 0.75 (br m, olefinic  
 H); -0.28 (t,  $^2J_{H_AH_B} \approx 9$  Hz,  $\underline{CH_2CH_3}$ ).

$^{13}C$  NMR ( $\delta$ ;  $C_6H_6$ ; 15 MHz; IV, 12-2B; { $^1H$ };  $30^\circ$ ): 250 (br,  $\underline{CHCMe_3}$ );  
 44.5 (s,  $\underline{CHCMe_3}$ ); 33.0 (s,  $\underline{CHCMe_3}$ ); 30.0 (br m,  $\underline{C_2H_4}$ ); 16.43 (t,  
 $^1J_{PC} = 8.1$  Hz,  $PMe_3$ ); -0.25 (br s,  $\underline{CH_2CH_3}$ ).

Preparation of  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$

1. From  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  (IV, 3, 32)

$\text{Ta}(\text{C}_2\text{H}_4)(\text{Cl}_3)(\text{PMe}_3)_2$  (2.0 g, 4.3 mmol) was dissolved in  $\text{Et}_2\text{O}$  (50 mL) and cooled to  $-30^\circ$ .  $\text{Mg}(\text{C}_2\text{H}_5)_2$ dioxane (1.2 g, 7.03 mmol, 10% excess) dissolved in  $\text{Et}_2\text{O}$  (10 mL) and cooled to  $-30^\circ$ , was mixed with the Ta solution, warmed to  $25^\circ$  and stirred for 30 min. Gas evolution (presumably  $\text{C}_2\text{H}_6$ ) and a color change from blue to orange occurred at  $\sim 0^\circ$ . The reaction mixture was stripped, extracted with pentane ( $\sim 50$  mL) and filtered leaving 1.51 g of brown insolubles. Fractional crystallization from pentane gave 0.97 g of orange irregular crystals. Yields up to 65% have been obtained (54% yield).

$\text{Ta}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  can be prepared in 50% yield from  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  and 3 equivalents of  $\text{Mg}(\text{C}_2\text{H}_5)\text{Br}$  in  $\text{Et}_2\text{O}$  (IV, 30).

2. From  $\text{TaCl}_5$  (IV, 18)

$\text{TaCl}_5$  (0.72 g, 2.0 mmol) was reacted with  $\text{PMe}_3$  (0.4 mL, excess) in 30 mL  $\text{Et}_2\text{O}$  at  $-30^\circ$ , immediately precipitating the orange phosphine adduct. The reaction mixture was cooled to  $-78^\circ$  and reacted with  $\text{Mg}(\text{C}_2\text{H}_5)_2$ dioxane (0.85 g, 5.0 mmol) in 20 mL of  $\text{Et}_2\text{O}$ , which was added dropwise. After stirring for 45 min at  $-78^\circ$ , the solution was warmed to  $25^\circ$  for 20 min and filtered. Removal of the solvent left a brown solid which was extracted with 25 mL of pentane, filtered and stripped. The crude product was dissolved in 5 mL of a 3:2  $\text{Et}_2\text{O}$ /pentane solution and cooled to  $-30^\circ$  for 12 h. 0.34 g of pure product was isolated by decanting the mother liquor and drying in vacuo (40% yield). Larger scale reactions gave poorer yields.

3. From Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (IV, 72)

Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (1 mmol) dissolved in 5 mL of Et<sub>2</sub>O or pentane reacts with PMe<sub>3</sub> (2 mmol) in 3 h to give 0.2 g of Ta(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>, isolated by crystallization from Et<sub>2</sub>O (see above) (48% yield).

Molecular Weight (cyclohexane; IV, 47): Calcd. 418. Found: 372.

Anal. (IV, 47; IV, 3-1): Calcd. for TaC<sub>12</sub>H<sub>31</sub>P<sub>2</sub>: C, 34.46; H, 7.46.

Found: C, 34.58; H, 7.68.

<sup>1</sup>H NMR (δ; C<sub>6</sub>D<sub>6</sub>; 270 MHz; VI, 3-6, 7; 25°): 1.150 (t, 18, <sup>2</sup>J<sub>PH</sub> = 2.44 Hz, PMe<sub>3</sub>); 0.870 (qt, 2, <sup>2</sup>J<sub>PH</sub> = 23.8 Hz, <sup>3</sup>J<sub>H<sub>A</sub>H<sub>B</sub></sub> = 8.14 Hz, CH<sub>2</sub>CH<sub>3</sub>); 0.530 (m, 2, CH<sub>1</sub>H<sub>2</sub> = CH'<sub>1</sub>H'<sub>2</sub>); -0.294 (m, 2, CH<sub>1</sub>H<sub>2</sub> = CH'<sub>1</sub>H'<sub>2</sub>); -0.999 (t, 3, <sup>3</sup>J<sub>H<sub>A</sub>H<sub>B</sub></sub> = 7.94 Hz, CH<sub>2</sub>CH<sub>3</sub>).

<sup>1</sup>H{<sup>31</sup>P} (90 MHz; IV, 3-8; f<sub>1</sub> = 3635065 MHz): 1.15 (s, PMe<sub>3</sub>); 0.87 (q, <sup>3</sup>J<sub>H<sub>A</sub>H<sub>B</sub></sub> ≈ 8 Hz, CH<sub>2</sub>CH<sub>3</sub>); 0.53, -0.29 (br, olefinic H); -1.00 (t, <sup>3</sup>J<sub>H<sub>A</sub>H<sub>B</sub></sub> ≈ 8 Hz, CH<sub>2</sub>CH<sub>3</sub>).

<sup>13</sup>C NMR (δ; C<sub>6</sub>D<sub>6</sub>; 67.89 and 15.0 MHz; IV, 3-2, 1; {<sup>1</sup>H} and gated {<sup>1</sup>H}; 10° and -20°): 36.89 (t, <sup>1</sup>J<sub>CH</sub> = 128 Hz, CH<sub>2</sub>CH<sub>3</sub>); 36.41 (tt, <sup>2</sup>J<sub>PC</sub> = 7.3 Hz, <sup>1</sup>J<sub>CH</sub> = 150 Hz, C<sub>2</sub>H<sub>4</sub>); 14.04 (qt, <sup>1</sup>J<sub>PC</sub> = 9.53 Hz, <sup>1</sup>J<sub>CH</sub> = 128 Hz, PMe<sub>3</sub>); -2.28 (q, <sup>1</sup>J<sub>CH</sub> = 123 Hz, CH<sub>2</sub>CH<sub>3</sub>).

<sup>31</sup>P NMR (δ; C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 36.4 MHz; V, 59-83; {<sup>1</sup>H}; 0°): 1.1 (s)

IR (cm<sup>-1</sup>; Nujol/NaCl; IV, 3-1): 940, s (ν<sub>P-C</sub>).

Preparation of  $\text{Nb}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$

1. From  $\text{Nb}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$  (V, 5)

$\text{Nb}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$  (1.71 g, 5.0 mmol) was dissolved in  $\text{Et}_2\text{O}$  (25 mL) and cooled to  $-78^\circ$ .  $\text{Mg}(\text{CH}_2\text{CH}_3)_2$  dioxane (1.28 g, 7.50 mmol), dissolved in  $\text{Et}_2\text{O}$  (20 mL), was added dropwise to the Nb solution. The solution turned brown and clouded after 30 min at  $-78^\circ$ .  $\text{PMe}_3$  (~0.8 g, excess) was then added. The reaction mixture was brought slowly to ambient temperature (ca. 30 min), stirred for an additional 30 min, filtered and stripped to a brown residue. The crude product was extracted with pentane (25 mL), filtered, treated with darco, and filtered. The solvent was removed in vacuo yielding a gummy brown solid which dissolved in 2 mL of  $\text{Et}_2\text{O}$ . Cooling to  $-30^\circ$  for 16 h gave 0.17 g of soft deep red crystals isolated by decanting the mother liquor and drying in vacuo. A second crop (50 mg) was obtained by evaporating the mother liquor to 1 mL and cooling for 12 h at  $-30^\circ$  (10% yield).

2. From  $\text{NbCl}_5$  (IV, 21)

$\text{NbCl}_5$  (2.0 mmol) was reacted with  $\text{PMe}_3$  (2.1 mmol) in  $\text{Et}_2\text{O}$  (40 mL) at  $-78^\circ$ .  $\text{Mg}(\text{C}_2\text{H}_5)_2$  dioxane (0.85 g, 5.0 mmol) dissolved in  $\text{Et}_2\text{O}$  (15 mL), was slowly added to the cold Nb solution, and stirred for 20 min. The reaction mixture was warmed to  $25^\circ$  and stirred for 5 min. Following the same procedure used above, a tacky brown residue was obtained. Crystallization from 1-2 mL of  $\text{Et}_2\text{O}$  at  $-30^\circ$  (18 h) gave 45 mg of soft red crystals (7% yield).

3. From  $\text{Nb}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$  (IX, 38)

$\text{Nb}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$  (0.200 g, 0.438 mmol) was dissolved in pentane (~8 mL) and pressurized with  $\text{C}_2\text{H}_4$  (30 psi).  $\text{C}_2\text{H}_4$  reacted

immediately giving a deep red solution. After 2 h at 25°, the reaction mixture was filtered and stripped to soft red crystals. The product was dissolved in 20 mL of pentane, treated with darco and filtered. Removal of the solvent, in vacuo, gave 0.13 g of  $\text{Nb}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$ , pure by  $^1\text{H}$  NMR (IX, 38-1) (83% yield).

Anal. (V, 5; V, 5-1): Calcd. for  $\text{NbC}_{12}\text{H}_{31}\text{P}_2$ : C, 43.65; H, 9.46.

Found: C, 45.80; H, 9.44.

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{H}_6$ ; 60 MHz; V, 5-1A, 2A; IX, 38-1; 30°): 1.37 (br m, 3, olefinic H); 1.13 (t, 20,  $^2\text{J}_{\text{PH}} = 2.4$  Hz,  $\text{PMe}_3$ ); 0.81 (br m,  $\text{CH}_2\text{CH}_3$ ); 0.11 (br m, 3, olefinic H); -0.96 (t, 3,  $^2\text{J}_{\text{H}_A\text{H}_B} = 8$  Hz,  $\text{CH}_2\text{CH}_3$ ).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 15 MHz; VI, 14-1 through 5;  $\{^1\text{H}\}$  and gated  $\{^1\text{H}\}$ ; -10°): 35.09 (tt,  $^2\text{J}_{\text{PC}} = 7.33$  Hz,  $^1\text{J}_{\text{CH}} = 149$  Hz,  $\text{C}_2\text{H}_4$ ); 30.8 (br t,  $^1\text{J}_{\text{CH}} = 134$  Hz,  $\text{CH}_2\text{CH}_3$ ); 14.23 (qt,  $^2\text{J}_{\text{PC}} = 7.33$  Hz,  $^1\text{J}_{\text{CH}} = 127$  Hz,  $\text{PMe}_3$ ); -0.97 (q,  $^1\text{J}_{\text{CH}} = 121$  Hz,  $\text{CH}_2\text{CH}_3$ ).

$^{31}\text{P}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 36.2 MHz; V, 59-94;  $\{^1\text{H}\}$ ; -60°): 0.1 (br s).

IR ( $\text{cm}^{-1}$ ; Nujol/NaCl; IX, 38-1): 955, s ( $\nu_{\text{P-C}}$ ).

Reaction of  $\text{Ta}(\text{CH}_2\text{XMe}_3)_2(\text{C}_2\text{H}_5)_3$ ; X = C, Si with  $\text{PMe}_3$  (V, 43, 45)

$\text{Ta}(\text{CH}_2\text{XMe}_3)_2(\text{C}_2\text{H}_5)_3$  (0.5 mmol) (X = C, Si) was prepared in  $\text{Et}_2\text{O}$  (see above).  $\text{PMe}_3$  (0.1 g, excess) was added to the reaction mixture. After 5 min at -30°, the solution was warmed to 25° and stirred for 2.5 h. The red solution was filtered and the solvent was removed in vacuo. The residue was extracted with pentane (25 mL), filtered and stripped to oily red crystals. The product(s) was dissolved in  $d_8$ -toluene (~0.8 mL) and a  $^{13}\text{C}$   $\{^1\text{H}\}$  (15 MHz) spectrum was recorded at -20°. Unreacted  $\text{Ta}(\text{CH}_2\text{XMe}_3)_2(\text{C}_2\text{H}_5)_3$  (~20%) was present

in the NMR spectra. For  $X = C$ , the remaining components were  $Ta(C_2H_4)_2(C_2H_5)(PMe_3)_2$  (~60%) and  $Ta(CHCMe_3)(C_2H_4)(C_2H_5)(PMe_3)_2$  (~20%). The NMR spectrum was considerably more complex for the silicon analog. However,  $Ta(C_2H_4)_2(C_2H_5)(PMe_3)_2$  (ca. 30%) was present in the reaction mixture (V, 43-1A, 2A, 1B, 2B).

Exchange Temperature of 5-Coordinate Complexes with Free  $PMe_3$

Determined by  $^{31}P$  NMR (V, 59)

In a typical experiment,  $Ta(CHCMe_3)_2Cl(PMe_3)_2$  was dissolved in ~0.7 mL of toluene containing ~2 equivalents of free  $PMe_3$ . Variable temperature  $^{31}P$  { $^1H$ } NMR (36.4 MHz) was used to determine the approximate exchange temperature of the metal complex with free  $PMe_3$ . The exchange temperature was found to be  $\sim 20 \pm 5^\circ$  lower than the coalescence temperature ( $T_c$ ).<sup>36</sup> The exchange temperature ( $T_\epsilon$ ) was defined as the temperature when the peak height of  $PMe_3$  equaled twice its peak width.  $T_\epsilon$  was used because it was easier to measure (than  $T_c$ ) and judged more reliable, since it occurs at a temperature when most metal complexes are stable. The results obtained are tabulated below.

	$T_{\epsilon}$ (K)
$\text{Ta}(\text{CHCMe}_3)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$	352
$\text{Ta}(\text{CHCMe}_3)_2(\text{Bu}^n)(\text{PMe}_3)_2$	342
$\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$	337
$\text{Ta}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$	342
$\text{Nb}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$	$\sim 212^a$
$\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$	$> 357$
$\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_4)(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$	302
$\text{Ta}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$	304
$\text{Nb}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$	$\sim 262^a$

$^a T_{\epsilon}$ , determined in the same manner used for the Ta complexes, was assumed to be unaffected by any quadrupolar effects arising from the  $^{93}\text{Nb}$  ( $I = 9/2$ , 100% abundant) nucleus.

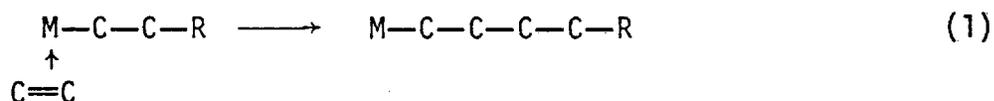
Chapter 4

Synthesis and Characterization of Reduced Tantalum Halide  
and Alkylidene Complexes:

Evidence for an  $\alpha$ -Hydrogen Elimination Reaction

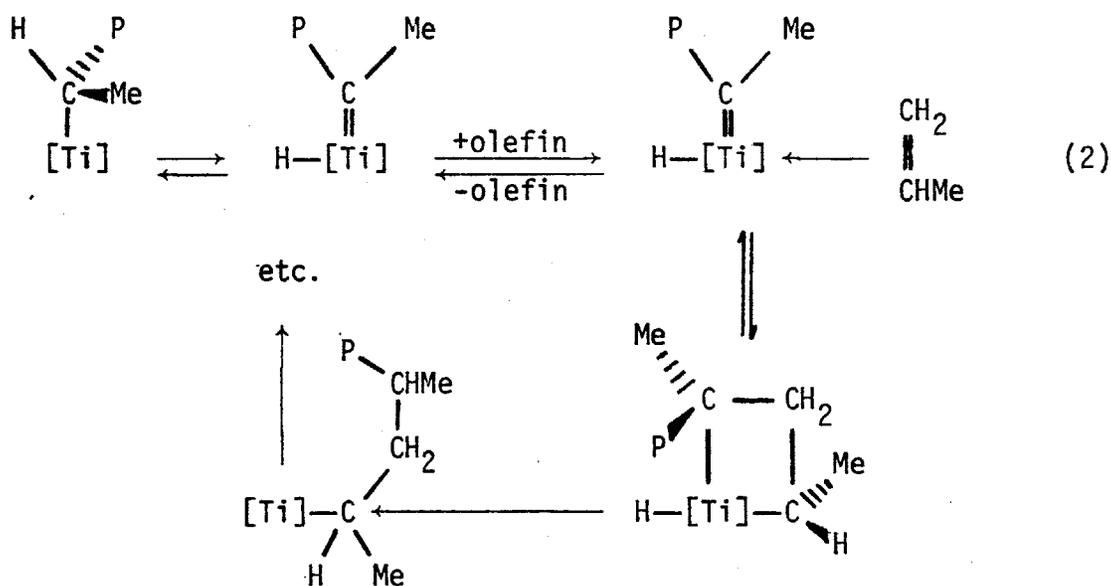
Introduction

The dimerization, oligomerization and Ziegler-Natta polymerization of olefins is usually catalyzed by transition metal compounds in various oxidation states with or without an alkyl-aluminum co-catalyst.<sup>16</sup> There is little direct evidence for the detailed nature of the catalytic sites but it has been generally proposed that a key step in the mechanism is insertion of a coordinated olefin into a metal-carbon chain (equation 1, where R = polymer



chain). Unfortunately, there are few (if any) unambiguous examples where a characterized metal-alkyl-olefin compound may be induced to react giving the expected insertion product.<sup>50</sup>

Recently, Rooney and Green have reported an alternate mechanism involving a reversible  $\alpha$ -hydrogen elimination step to account for the stereospecific polymerization of propylene (equation 2).<sup>51</sup>

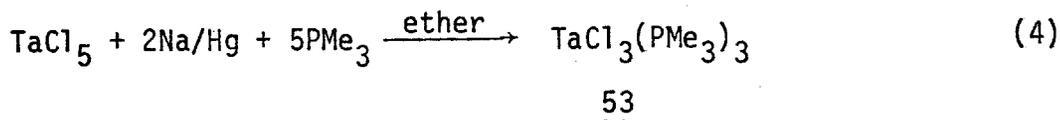




## Results and Discussion

### Ta(III) Halide Complexes; Synthesis and Characterization

The reduction of  $\text{TaCl}_5$  with two equivalents of 0.4% sodium amalgam in ether with five equivalents of  $\text{PMe}_3$  under  $\text{N}_2$  or Ar gives a good yield of a product which analyzes as  $\text{TaCl}_3(\text{PMe}_3)_3$  (53; equation 4). The molecular weight of 53 in benzene gives a value



which is low for a monomer (mol. wt. calcd., 550; found, 440).

This is not unusual since  $\text{PMe}_3$  dissociation in octahedral complexes often gives molecular weights lower than expected.<sup>26</sup>

53 shows a single featureless  $^1\text{H}$  NMR resonance at -6 ppm which broadens in the presence of added  $\text{PMe}_3$ . The high field chemical shift shown by 53 can be attributed to 53 being weakly paramagnetic. Although it shows no EPR signal at room temperature an eight line pattern ( $g = 1.92$ ) is observed at 77 K.<sup>55</sup>

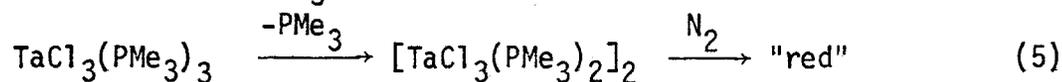
53 can be further characterized by its reaction with ethylene at  $50^\circ$  to give a nearly quantitative yield of  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  and one equivalent per Ta of  $\text{PMe}_3$  ( $^1\text{H}$  NMR).

Reducing  $\text{TaCl}_5$  in toluene by two electrons in the presence of four equivalents of  $\text{PMe}_3$  gives a 1:1 mixture of  $\text{TaCl}_3(\text{PMe}_3)_3$  (53) and a complex tentatively identified as  $[\text{TaCl}_3(\text{PMe}_3)_2]_2$  (54).<sup>56</sup> Adding  $\text{PMe}_3$  to a solution containing a mixture of 53 and 54 does not give pure 53. Similar results were observed in an analogous reduction of  $\text{TaBr}_5$  (see Experimental).

Unlike 53, 54 is diamagnetic and gives an  $^1\text{H}$  NMR spectrum consistent with the above formulation (a virtual coupled triplet at

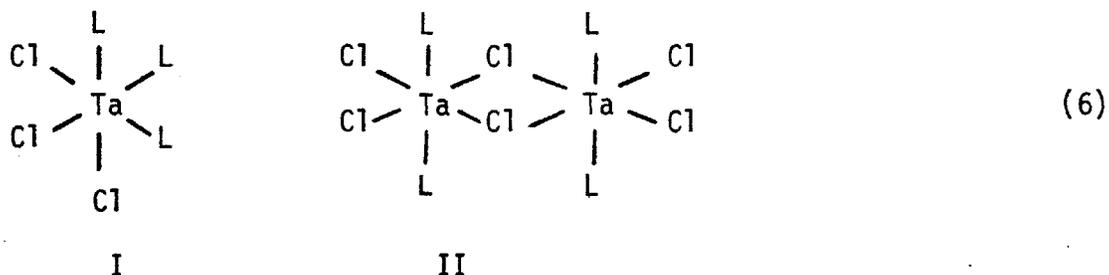
1.25 ppm). Reacting ethylene with a mixture of 53 and 54 gives only  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  and free  $\text{PMe}_3$ .

Pure 53 is indefinitely stable under  $\text{N}_2$  or Ar as a solid. In solution under Ar 53 loses  $\text{PMe}_3$  to give mostly 54 and free  $\text{PMe}_3$  (equation 2), by  $^1\text{H}$  NMR.<sup>57</sup> Standing 53 in benzene under  $\text{N}_2$  gives, after 48 h, an unidentified insoluble red crystalline product. However, 53 is stable (~1 week) in solution under  $\text{N}_2$  in the presence of small amounts of  $\text{PMe}_3$  (equation 5). Standing a solution



containing a mixture of 53 and 54 under  $\text{N}_2$  also gives insoluble red crystals. At this time there is no way to characterize this insoluble product since it appears to be a mixture of at least two different species. However, this product is believed to contain coordinated  $\text{N}_2$  since it is not formed in the absence of  $\text{N}_2$ .

The structures for 53 and 54 are unknown, however, two reasonable possibilities are shown below (equation 6, I and II, respectively).<sup>58</sup>

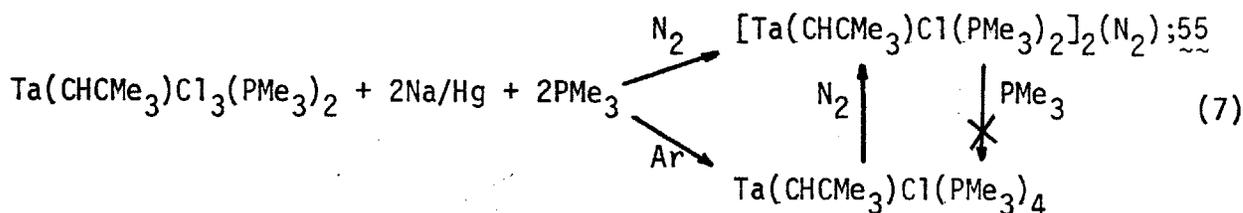


Little reaction chemistry of 53 was investigated. Attempts to alkylate 53 with  $\text{Mg}(\text{CH}_2\text{CMe}_3)_2$  gave  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$  as the only isolable diamagnetic complex.

Neopentylidene-Dinitrogen Complexes of Tantalum; Synthesis and Characterization

Ta(CHCMe<sub>3</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub> in an ether/THF solution containing PMe<sub>3</sub>, reacts with two equivalents of sodium amalgam to give a pyrophoric yellow powder with the formulation [Ta(CHCMe<sub>3</sub>)Cl(PMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(N<sub>2</sub>) (55). Although 55 analyzes low for nitrogen it is a dimer in cyclohexane (mol. wt. found 1080).<sup>59</sup>

The presence of nitrogen in 55 is supported by recent studies by H. Turner. Reducing Ta(CHCMe<sub>3</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub> in the presence of PMe<sub>3</sub> under Ar gives Ta(CHCMe<sub>3</sub>)Cl(PMe<sub>3</sub>)<sub>4</sub>. Purging pentane solutions containing Ta(CHCMe<sub>3</sub>)Cl(PMe<sub>3</sub>)<sub>4</sub> with N<sub>2</sub> gives 55 in good yield. The reverse reaction (i.e. adding PMe<sub>3</sub> to 55) does not occur, even under forced conditions (equation 7). In all cases reducing



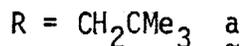
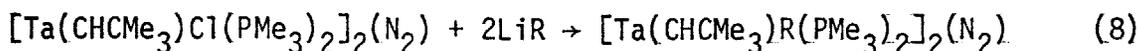
Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub> under similar conditions gives results similar to the reduction of Ta(CHCMe<sub>3</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>.

The infrared spectrum of 55 shows a weak band at 2590 cm<sup>-1</sup> which is assigned to the neopentylidene ν<sub>CH<sub>α</sub></sub> stretch. In addition, no absorbance attributable to a terminally bound N<sub>2</sub> ligand could be found. Therefore, it seems likely that N<sub>2</sub> acts as a bridging ligand.<sup>60</sup>

NMR spectroscopy shows that 55 contains equivalent PMe<sub>3</sub> ligands and the neopentylidene resonances are typical of alkylidene complexes with less than 18 electrons (see Experimental).

Alkylations of 55 with lithium reagents yield the corresponding alkyl derivatives. For example, LiCH<sub>2</sub>CMe<sub>3</sub> reacts with 55 to yield

pentane soluble crystals of  $[\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2]_2(\text{N}_2)$  (56a), which gives a near satisfactory nitrogen analysis (calcd., 2.87; found, 2.52).<sup>59</sup> Turner has also prepared the methyl analogue  $[\text{Ta}(\text{CHCMe}_3)\text{Me}(\text{PMe}_3)_2]_2(\text{N}_2)$  (56b, equation 8).

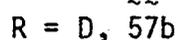
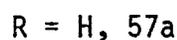
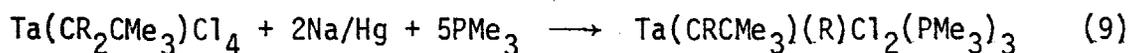


The  $^1\text{H}$  NMR spectrum (250 MHz) of 56a shows a 1:2:1 triplet ( $J_{\text{HP}} = 16.6$  Hz) at 0.63 ppm for the  $\alpha$ -hydrogen atoms of the neopentyl ligands. In addition, the remaining resonances are similar to those found for 55.

Since the NMR and infrared spectroscopy for 55, 56a and 56b<sup>59</sup> are similar, it is likely that the structures would also be analogous. Unfortunately, recent attempts to solve the structure of 56a showed it to be disordered. However, new derivatives are being prepared in an effort to obtain an insight into the nature of the bonding of  $\text{N}_2$  in these species.

#### Neopentylidene-Hydride Complexes of Tantalum; Synthesis and Characterization

Reduction of  $\text{Ta}(\text{CH}_2\text{CMe}_3)\text{Cl}_4$  under  $\text{N}_2$  or Ar, with two equivalents of sodium amalgam in ether and five equivalents of  $\text{PMe}_3$  gives  $\text{Ta}(\text{CHCMe}_3)(\text{H})\text{Cl}_2(\text{PMe}_3)_3$  (57a) in 57% yield. An analogous reduction of  $\text{Ta}(\text{CD}_2\text{CMe}_3)\text{Cl}_4$  gives  $\text{Ta}(\text{CDCMe}_3)(\text{D})\text{Cl}_2(\text{PMe}_3)_3$  (57b, equation 9).



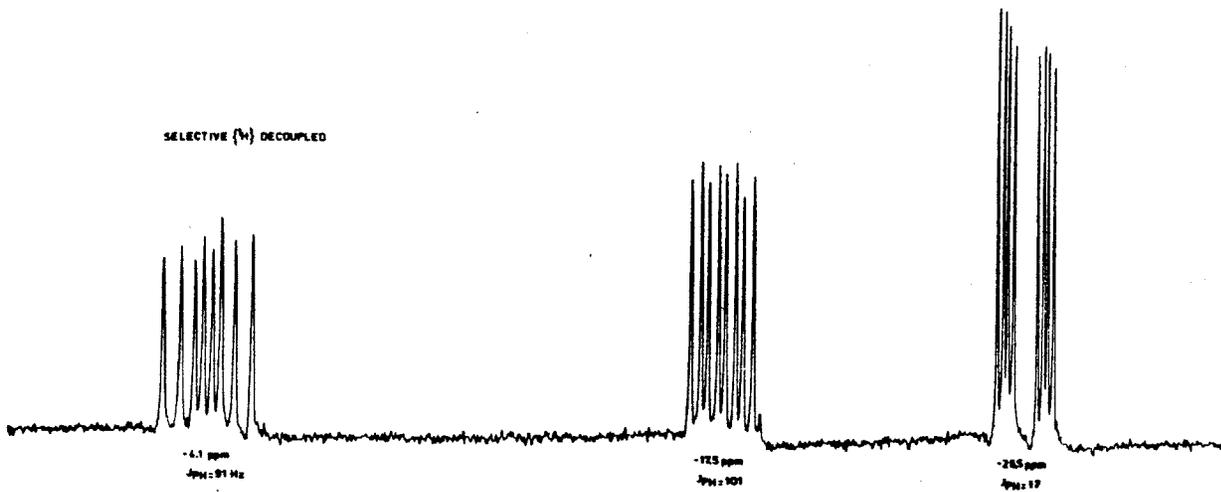
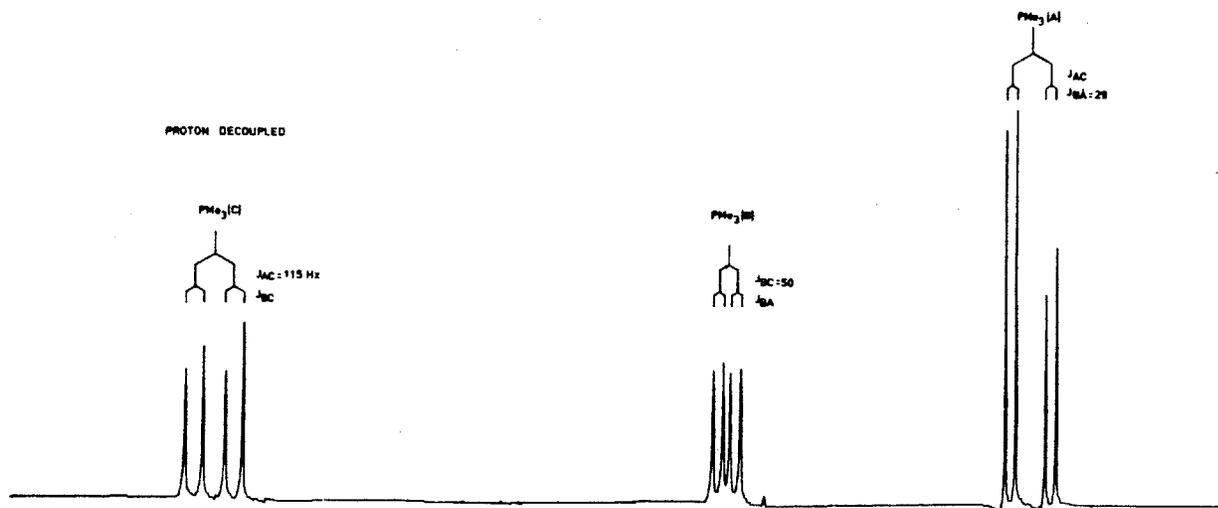
The infrared spectrum of 57a shows two medium strength absorbances at 2440 and 1730  $\text{cm}^{-1}$  which shift to 1805 and 1270  $\text{cm}^{-1}$ , respectively, for 57b. The former peak is assigned to the  $\nu_{\text{CH}\alpha}$  stretch of a neopentylidene ligand. The latter, stronger intensity band is assigned as  $\nu_{\text{TaH}}$ , and is in the range commonly expected for terminally bound hydrides.<sup>61</sup>

The  $^1\text{H}$  NMR spectrum (250 MHz,  $-30^\circ$ ) of 57a shows a double-double-doublet hydride resonance at 10.00 ppm ( $J_{\text{HPA}} = 17.7$  Hz,  $J_{\text{HPB}} = 101.9$  Hz,  $J_{\text{HPC}} = 91.0$  Hz), which is further coupled ( $J_{\text{HH}\alpha} = 1.5$  Hz) to the neopentylidene  $\alpha$ -hydrogen atom. The signal for the neopentylidene  $\alpha$ -hydrogen atom, a broadened doublet ( $J_{\text{H}\alpha\text{H}} = 1.5$  Hz) is found at 0.24 ppm. Both of these resonances are absent in 57b. The remaining resonances are in complete agreement with the  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR data mentioned below.

The  $^{13}\text{C}$  NMR spectrum of 57a shows a neopentylidene  $\alpha$ -carbon resonance, at 216 ppm ( $^1J_{\text{CH}} = 72$  Hz), as an eight-line multiplet with an average phosphorous coupling ( $J_{\text{CP}}$ ) of 6.4 Hz. This is consistent with the three distinct  $\text{PMe}_3$  doublets observed at 22.8 ( $J_{\text{CP}} = 24.8$  Hz), 18.8 ( $J_{\text{CP}} = 26.9$  Hz), and 16.3 ppm ( $J_{\text{CP}} = 20.7$  Hz).

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (109.3 MHz) for 57a shows three inequivalent  $\text{PMe}_3$  ligands coupled to give a pattern typical of an ABX spin system (Figure 1, top spectrum).<sup>79</sup> First-order analysis gave the magnitudes of the phosphorous-phosphorous coupling as  $J_{\text{PA}^{\text{P}}\text{B}} = 29.2$  Hz,  $J_{\text{PA}^{\text{P}}\text{C}} = 115$  Hz, and  $J_{\text{PB}^{\text{P}}\text{C}} = 51$  Hz. Selective  $^1\text{H}$  decoupling of the  $\text{PMe}_3$  protons shows only hydride coupling to each phosphorous nucleus (Figure 1, lower spectrum). These data agree with the  $^1\text{H}$  NMR data mentioned previously.

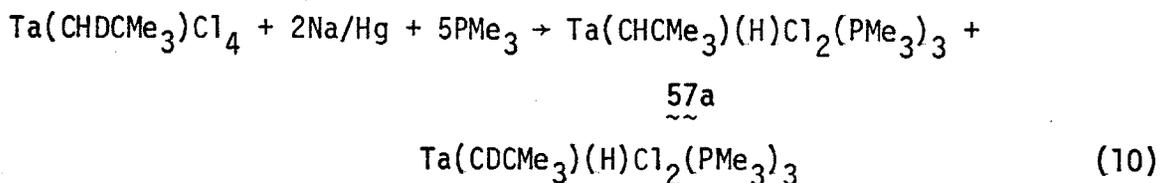
Figure 1. The 109 MHz  $^{31}\text{P}$  NMR Spectra of  $\text{Ta}(\text{CHCMe}_3)(\text{H})\text{Cl}_2(\text{PMe}_3)_3$   
(a)  $\{^1\text{H}\}$ ; (b) selective  $^1\text{H}$  decoupled at 1.38 ppm.



Since  $\text{Ta}(\text{CHCMe}_3)(\text{H})\text{Cl}_2(\text{PMe}_3)_3$  is seven coordinate and is obviously of low symmetry, there are several structures which could adequately fit these data. In order to assign a reasonable structure to 57a further work is needed.

Reducing  $\text{Ta}(\text{CD}_2\text{CMe}_3)\text{Cl}_4$  in the presence of  $\text{PMe}_3$  demonstrates that the hydride which is formed originates from the  $\alpha$ -carbon atom of the neopentyl ligand. However, there is no evidence supporting an intramolecular hydride transfer in the formation of  $\text{Ta}(\text{CDCMe}_3)(\text{D})\text{Cl}_2(\text{PMe}_3)_3$ .

Reducing  $\text{Ta}(\text{CHDCMe}_3)\text{Cl}_4$  in the presence of  $\text{PMe}_3$  shows that H/D scrambling occurs since  $\text{Ta}(\text{CHCMe}_3)(\text{H})\text{Cl}_2(\text{PMe}_3)_3$  and  $\text{Ta}(\text{CDCMe}_3)\text{HCl}_2(\text{PMe}_3)_3$  are present in about a 1:2 ratio, by  $^1\text{H}$  NMR (equation 10). Also present

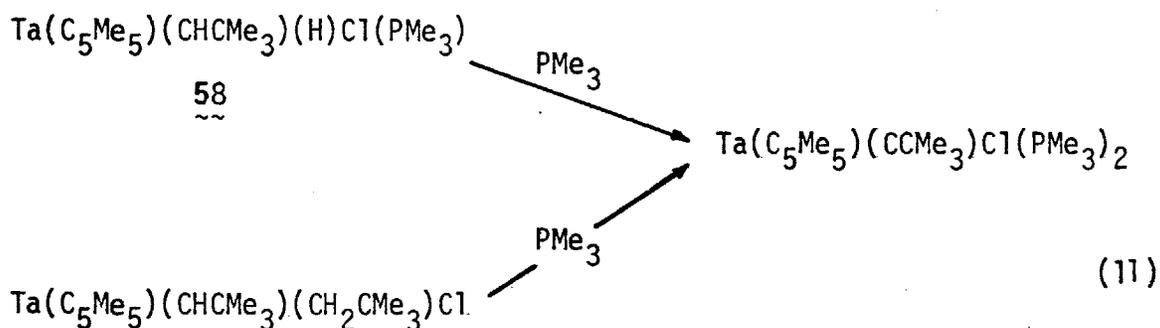


but not observed by this technique must be the analogous deuteride complexes  $\text{Ta}(\text{CDCMe}_3)(\text{D})\text{Cl}_2(\text{PMe}_3)_3$  and  $\text{Ta}(\text{CHCMe}_3)(\text{D})\text{Cl}_2(\text{PMe}_3)_3$ .<sup>62</sup> Scrambling of the hydride and deuterium atoms must occur prior to the formation of the alkylidene-hydride (or deuteride) complex since mixing equal amounts of  $\text{Ta}(\text{CHCMe}_3)(\text{H})\text{Cl}_2(\text{PMe}_3)_3$  and  $\text{Ta}(\text{CDCMe}_3)(\text{D})\text{Cl}_2(\text{PMe}_3)_3$  gave no  $\text{Ta}(\text{CDCMe}_3)(\text{H})\text{Cl}_2(\text{PMe}_3)_3$ . These data suggest that a bimolecular intermediate is present at some point in the  $\alpha$ -hydrogen elimination reaction. Further work is needed to understand the nature of the intermediate(s) and what factors influence the course of the  $\alpha$ -hydrogen elimination reaction.

Another alkylidene hydride complex can also be prepared using this technique. The sodium amalgam reduction of  $\text{Ta}(\text{C}_5\text{Me}_5)(\text{CH}_2\text{CMe}_3)\text{Cl}_3$  in the presence of two equivalents of  $\text{PMe}_3$  gives  $\text{Ta}(\text{C}_5\text{Me}_5)(\text{CHCMe}_3)(\text{H})\text{Cl}(\text{PMe}_3)$  58 in high yield (>90%) by  $^1\text{H}$  NMR. It is extremely soluble in pentane but can be isolated as flat yellow crystals in 30% yield.

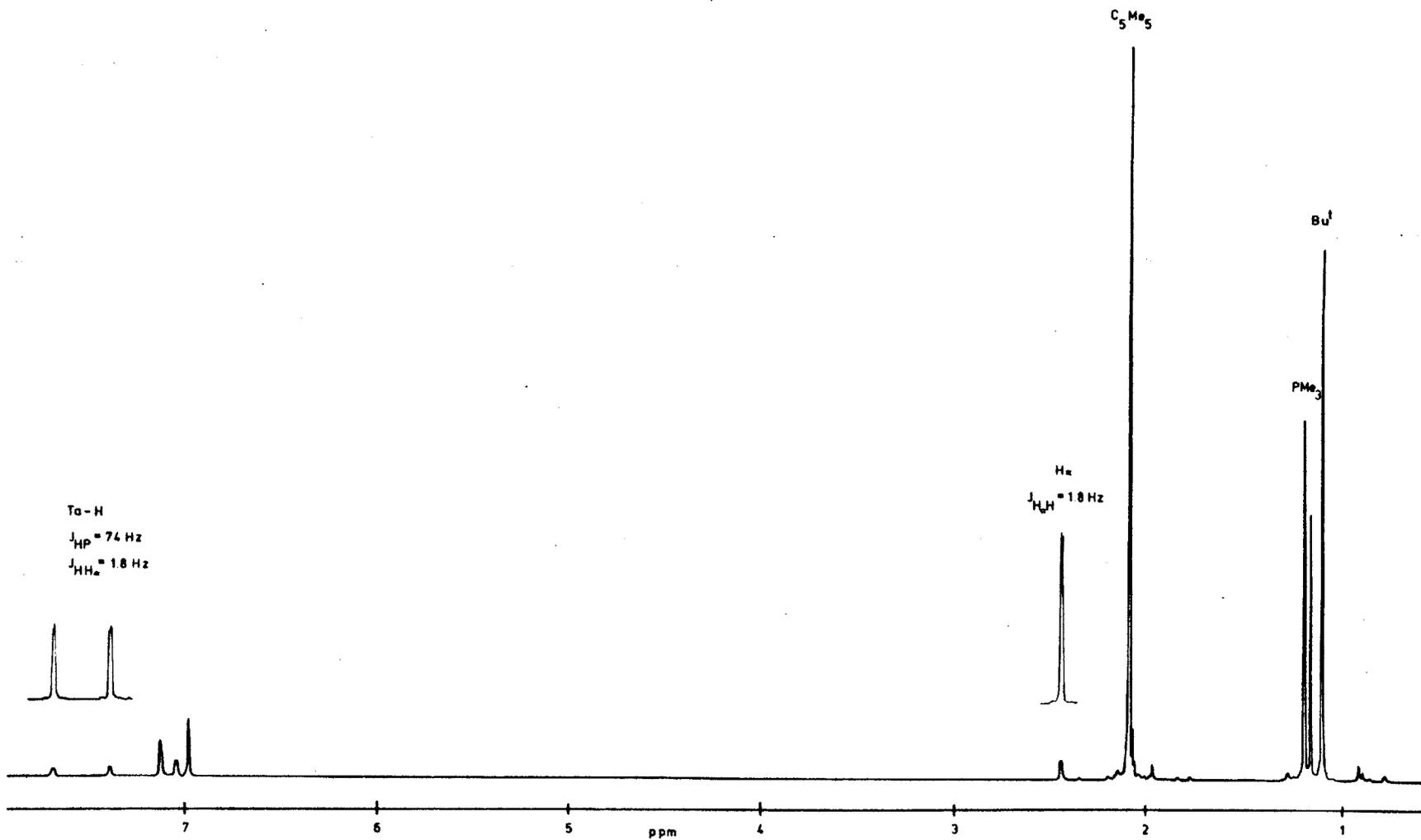
The 250 MHz  $^1\text{H}$  NMR spectrum for 58 is shown in Figure 2 and is in complete accord with its formulation. The low field hydride resonance (7.53 ppm) shows phosphorous coupling ( $J_{\text{HP}} = 74$  Hz) similar to that found for  $\text{Ta}(\text{C}_5\text{Me}_5)(\text{CCMe}_3)(\text{H})(\text{PMe}_3)_2$  ( $J_{\text{HP}} = 86$  Hz).<sup>32</sup> The infrared spectrum of 58 shows stretches for  $\nu_{\text{CH}_\alpha}$  at  $2525\text{ cm}^{-1}$  and  $\nu_{\text{TaH}}$  at  $1730\text{ cm}^{-1}$ .

58 is indefinitely stable in the solid state at  $-30^\circ$ . It decomposes in solution when heated ( $60^\circ$ ) in the presence of  $\text{PMe}_3$  to give  $\text{Ta}(\text{C}_5\text{Me}_5)(\text{CCMe}_3)\text{Cl}(\text{PMe}_3)_2$  in high yield, by  $^1\text{H}$  NMR (equation 11).  $\text{Ta}(\text{C}_5\text{Me}_5)(\text{CCMe}_3)\text{Cl}(\text{PMe}_3)_2$  has been isolated in



moderate yield on a preparative scale by H. Turner.  $\text{Ta}(\text{C}_5\text{Me}_5)(\text{CCMe}_3)\text{Cl}(\text{PMe}_3)_2$  has previously been prepared by Wood by reacting  $\text{Ta}(\text{C}_5\text{Me}_5)(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)\text{Cl}$  with  $\text{PMe}_3$ . The reaction has been proposed to occur by an  $\alpha$ -hydrogen abstraction process.<sup>32</sup> There is no way to tell at this time whether 58 decomposes by an analogous process, where  $\text{H}^\cdot$  abstracts the  $\alpha$ -hydrogen atom of the neopentylidene

Figure 2. The 250 MHz  $^1\text{H}$  NMR Spectrum of  $\text{Ta}(\text{C}_5\text{Me}_5)(\text{CHCMe}_3)(\text{H})\text{Cl}(\text{PMe}_3)$



ligand to form  $\text{Ta}(\text{C}_5\text{Me}_5)(\text{CCMe}_3)\text{Cl}(\text{PMe}_3)_2$  and  $\text{H}_2$ . However, the reverse process, addition of  $\text{H}_2$  to an alkylidyne complex [in this case  $\text{Ta}(\text{C}_5\text{Me}_5)(\text{CCPh})\text{Cl}(\text{PMe}_3)_2$ ] has been observed by L. Messerle to give  $\text{Ta}(\text{C}_5\text{Me}_5)(\text{CHCPh})\text{HCl}(\text{PMe}_3)_x$ , which further reacts with  $\text{H}_2$  to ultimately give  $[\text{Ta}(\text{C}_5\text{Me}_5)\text{HCl}(\text{PMe}_3)_2]_x$ .<sup>30</sup>

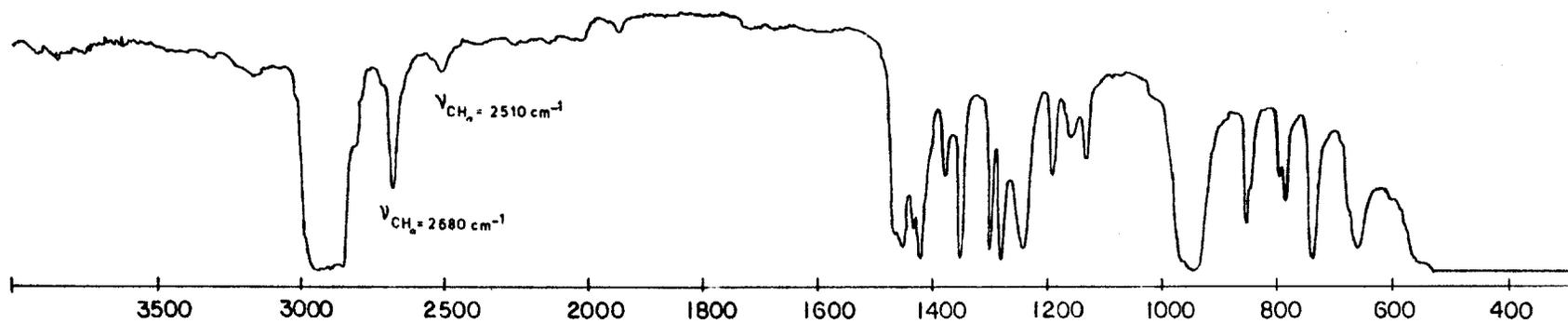
More complex versions of  $\alpha$ -elimination are possible. For example,  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$  is reduced, in an ether/THF solution containing  $\text{PMe}_3$ , by two equivalents of sodium amalgam (under  $\text{N}_2$  or Ar) to give a red oil. A low yield of a complex tentatively identified as  $[\text{Ta}(\text{CHCMe}_3)_2\text{H}(\text{PMe}_3)_2]_x$  (59) can be isolated from the reaction mixture.

The infrared spectrum of 59 shows  $\nu_{\text{CH}_\alpha}$  stretches for the two different neopentylidene ligands, but no assignable hydride stretch (see Figure 3).

The  $^1\text{H}$  NMR spectrum of 59 at  $-30^\circ$  shows two neopentylidene  $\alpha$ -hydrogen atom resonances at 8.24 (1 H) and 0.46 ppm (1 H), but no resonance attributable to a hydride. Two inequivalent t-butyl resonances and a virtual triplet for the  $\text{PMe}_3$  ligands are also present. The  $^{31}\text{P}$  ( $^1\text{H}$  coupled) NMR spectrum shows only one resonance (a singlet) with no observable proton-phosphorous coupling.

The  $^{13}\text{C}$  NMR spectrum of 59 is consistent with the  $^1\text{H}$  NMR data and with other complexes of the type  $\text{Ta}(\text{CHCMe}_3)_2\text{R}(\text{PMe}_3)_2$  (see Chapter 3). 59 also shows a temperature dependence due to the interconversion of two neopentylidene ligands. Although the exact  $\Delta G^\ddagger$  for this process is presently unknown, the temperature required to "freeze-out" interconversion is approximately the same as that

Figure 3. The Infrared Spectrum of "[Ta(CHCMe<sub>3</sub>)<sub>2</sub>H(PMe<sub>3</sub>)<sub>2</sub>]<sub>x</sub>"



found for  $\text{Ta}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  (ca.  $-30^\circ$ ). For complexes of the type  $\text{Ta}(\text{CHCMe}_3)_2\text{R}(\text{PMe}_3)_2$  the free energy of activation for neopentylidene interconversion increases as the steric bulk of R increases in the following order:  $\text{Cl} < \text{Me} < \text{CH}_2\text{CMe}_3$  (see Chapter 3). Therefore, the low temperature required in order to observe the low temperature limit spectrum of 59 is consistent with it being a bisneopentylidene hydride complex.

Molecular weight measurements and labeling experiments are in progress in order to more fully characterize 59.

The major product(s) formed in the reduction of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$  is(are) presently unknown. Recent results show that the same product is formed in the absence of  $\text{PMe}_3$ , but cannot be formed without THF.<sup>59</sup> The reaction of THF with reduced species (i.e. low oxidation state metal complexes) is known to give as products, after hydrolysis, a complex mixture most of which are alcohols.<sup>63</sup> It seems possible then, that the major product formed in the reduction of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$  is an alkoxide complex.  $^{13}\text{C}$  and  $^1\text{H}$  NMR support this view, but due to the complexity of the data no identification can yet be made. Hydrolysis experiments are in progress.

Attempts to prepare a methylene-hydride complex from the reduction of  $\text{TaMeCl}_4(\text{PMe}_3)_2$  in the presence of  $\text{PMe}_3$  were unsuccessful. In all cases large quantities of an unidentified gas were released throughout the course of the reduction. Examination of the residue by  $^{13}\text{C}$  NMR spectroscopy showed that a complicated mixture of products were present.

### Conclusion

The formation of alkylidene-hydride complexes from the rearrangement of lower oxidation state alkyl complexes is one of the two main requirements of the Rooney/Green mechanism. The fact that Ta(III) neopentyl complexes rearrange to form Ta(V) neopentylidene-hydrides is believed due to the thermodynamic stability of tantalum in the +5 oxidation state.<sup>20</sup> Therefore, if a catalyst is to operate in this fashion, a similar driving force must also be present. The other requirement in the Rooney/Green postulate is that any  $\beta$ -elimination reactions must be slower than both  $\alpha$ -hydrogen elimination and reductive elimination in order to form the new alkyl chain. Recent studies of the reaction of ethylene with Ta(CHCMe<sub>3</sub>)(H)Cl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> shows that ethylene is oligomerized to give olefins of the type C<sub>5+2n</sub>H<sub>10+4n</sub> where n = 1,2,3,4... The actual identity of these products are as yet unknown, however, work is continuing in this area. These facts do indicate the credibility of the Rooney/Green mechanism.

Experimental

$\text{Ta}(\text{CHCMe}_3)\text{Cl}(\text{PMe}_3)_4$  was obtained from H. Turner.

Preparation of  $\text{TaCl}_3(\text{PMe}_3)_3$  (VIII, 5)

50 mL of  $\text{Et}_2\text{O}$ , containing  $\text{PMe}_3$  (5 mL, 52.6 mmol, excess) and 0.41% Na/Hg (112 Hg, 20 mmol), was cooled to  $-30^\circ$ . Solid  $\text{TaCl}_5$  (3.6 g, 10 mmol) was added. The reaction mixture was warmed to  $25^\circ$  and vigorously stirred for 1h. In 40 min, the color of solution changed from green to red. The insolubles were filtered through celite and the solvent was removed in vacuo leaving red crystals. The crude product was extracted with 25 mL of  $\text{Et}_2\text{O}$  and filtered. Pentane (2 mL) and  $\text{PMe}_3$  (~0.1 mL) were added to the filtrate. Cooling the solution to  $-30^\circ$  for 12 h gave 2.76 g of irregular deep red crystals, isolated by filtration and dried in vacuo. Concentrating and cooling the mother liquor to  $-30^\circ$  gave an additional 1.26 g of pure product. An analytically pure sample was obtained after repeated crystallizations from concentrated ether solutions, containing free  $\text{PMe}_3$ , at  $-30^\circ$  (78% yield).

Using less than 4 eq.  $\text{Ta}^{-1}$  of  $\text{PMe}_3$  in a similar Na/Hg reduction of  $\text{TaCl}_5$  gave  $\text{TaCl}_3(\text{PMe}_3)_3$  and several unidentified diamagnetic complexes, in low yield, by  $^1\text{H}$  NMR (IV, 59, 61, 62). Heating a sealed benzene solution of  $[\text{TaCl}_3(\text{THT})_2](\text{THT})$  containing excess  $\text{PMe}_3$  at  $60^\circ$  for 24 h, gave  $\text{TaCl}_3(\text{PMe}_3)_3$  in ~50% yield by  $^1\text{H}$  NMR (V, 22).

Anal. (VIII, 12; VIII, 12-4): Calcd. for  $\text{TaC}_9\text{H}_{27}\text{Cl}_3\text{P}_3$ :

C, 20.97; H, 5.28. Found: C, 20.69; H, 5.21.

Molecular Weight (benzene; VIII, 8): Calculated: 516. Found: 440.

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{H}_6$ ; 60 MHz; VII, 65-3;  $25^\circ$ ): -6.0 (s).

IR ( $\text{cm}^{-1}$ ; Nujol/NaCl; VIII, 5-1): 940, s ( $\nu_{\text{P-C}}$ ).

Decomposition of  $\text{TaCl}_3(\text{PMe}_3)_3$  (VII, 65)

A toluene solution (4 mL) of freshly recrystallized  $\text{TaCl}_3(\text{PMe}_3)_3$  (2.0 g, 3.9 mmol) was left to stand undisturbed for 2 d at 25°. The violet crystals (0.75 g) which slowly formed on the walls of the reaction vessel were isolated by filtration then dried in vacuo. Standing the filtrate for another 2 d gave an additional 0.31 g. The crude product was dissolved in boiling toluene (~90 mL), filtered and cooled to -30°. NMR analysis ( $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$ ) of this product showed it to be a mixture of at least two phosphorous containing compounds. No further characterization of this product has been made. In a separate experiment, 1 equivalent  $\text{Ta}^{-1}$  of  $\text{PMe}_3$  was present in the mother liquor, after 2 d at 25° (VIII, 9).

Reaction of  $\text{TaCl}_3(\text{PMe}_3)_3$  with  $\text{C}_2\text{H}_4$  (VIII, 9)

$\text{TaCl}_3(\text{PMe}_3)_3$  (0.516 g, 1.000 mmol) was dissolved in benzene (6 mL) which contained toluene (0.276 g, 3.000 g) as an internal NMR standard. 3 mL of the solution was pressurized with  $\text{C}_2\text{H}_4$  (30 psi) and heated to 50°. After 1.5 h, the volatiles were trap-to-trap distilled leaving 0.22 g of  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  (95%) as a residue. The isolated solution contained 1 eq.  $\text{Ta}^{-1}$  of  $\text{PMe}_3$ , determined by integrating  $\text{PMe}_3$  vs. the toluene methyl resonance.

Reaction of  $\text{TaCl}_3(\text{PMe}_3)_3$  with  $\text{Mg}(\text{CH}_2\text{CMe}_3)_2$  (VIII, 49,53)

$\text{TaCl}_3(\text{PMe}_3)_3$  (0.80 g, 1.55 mmol) was dissolved in toluene (~5 mL) and cooled to -30°. A toluene solution (~2 mL) of  $\text{Mg}(\text{CH}_2\text{CMe}_3)_2$  (0.39 g, 2.33 mmol) was added dropwise to the cold Ta solution. The reaction

mixture was warmed to room temperature and stirred. After 1 h, the solution changed from red to orange while precipitating the magnesium salts. Filtration and removal of the volatiles in vacuo gave an orange oil which contained  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$  as the only identifiable component by  $^1\text{H}$  NMR (VIII, 53-1A).  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$  (70 mg) was isolated by sublimation at  $50^\circ$  and  $1\ \mu$ . The non-volatile residue (0.62 g) gave a complicated  $^1\text{H}$  NMR spectrum and was not further characterized (VIII, 53-2A).

Preparation of  $\text{TaBr}_3(\text{PMe}_3)_3$  (V, 9)

$\text{TaBr}_5$  (2.7 g, 5.0 mmol) was stirred for 1 h at  $25^\circ$  with Na/Hg (0.41%, 33.3 g, 10.0 mmol) in a toluene solution (15 mL) containing  $\text{PMe}_3$  (1.9 mL, 20 mmol, excess). The resulting green solution was filtered through celite and the volatiles were removed in vacuo leaving 1.4 g of red crystals. The crude product was ~50%  $\text{TaBr}_3(\text{PMe}_3)_3$  and an uncharacterized insoluble red compound which is believed to be analogous to the decomposition product isolated from  $\text{TaCl}_3(\text{PMe}_3)_3$  (see above).

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{H}_6$ ; 60 MHz; V, 9-1;  $25^\circ$ ): -4.3 (br s,  $\text{PMe}_3$ ).

Preparation of  $\text{Ta}(\text{CHCMe}_3)(\text{H})\text{Cl}_2(\text{PMe}_3)_3$  (IX, 6)

Freshly recrystallized  $\text{Ta}(\text{CH}_2\text{CMe}_3)\text{Cl}_4$  (1.97 g, 5.00 mmol) was added as a solid to an  $\text{Et}_2\text{O}$  solution (~40 mL), cooled to  $-30^\circ$ , containing Na/Hg (0.41%, 56.1 g, 10.0 mmol) and  $\text{PMe}_3$  (2.4 mL, 25 mmol). The solution which turned immediately deep red, was warmed to  $25^\circ$  and

vigorously stirred. A color change from red to green, then finally to beige, occurred after 20 min. The reaction mixture was stirred for 12 h, filtered through celite and the solvent was removed in vacuo. The residue was extracted with Et<sub>2</sub>O (~150 mL), filtered and concentrated in vacuo to ~20 mL. Filtration gave 1.38 g of pure product, after washing with cold Et<sub>2</sub>O and drying in vacuo. The filtrate was reduced in vacuo to ~10 mL and cooled to -30° for 48 h. The mother liquor was decanted and 0.2 g of Ta(CHCMe<sub>3</sub>)(H)Cl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> was isolated after drying in vacuo (57% yield).

Ta(CHCMe<sub>3</sub>)(H)Cl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> was also prepared in 48% yield under argon (VIII, 23).

Anal. (VIII, 12; VIII, 12-1): Calcd. for TaC<sub>14</sub>H<sub>38</sub>Cl<sub>2</sub>P<sub>3</sub>: C, 30.51; H, 6.95. Found: C, 30.37; H, 7.01. Found: C, 29.77; H, 6.53.

<sup>1</sup>H NMR (δ; C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 270 and 250 MHz; VII, 41-1C through 4C; VIII, 67-1, 5,9; 30° to -30°):

(250 MHz; -30°): 10.000 (dddd, 1, <sup>3</sup>J<sub>HH<sub>α</sub></sub> = 1.47 Hz, <sup>2</sup>J<sub>HP<sub>A</sub></sub> = 17.7 Hz, <sup>2</sup>J<sub>HP<sub>B</sub></sub> = 101.9 Hz, <sup>2</sup>J<sub>HP<sub>C</sub></sub> = 91.0 Hz, Ta-H); 1.521 (d, 9, <sup>2</sup>J<sub>PH</sub> = 8.53 Hz, PMe<sub>3</sub>(C)); 1.379 (d, 9, <sup>2</sup>J<sub>PH</sub> = 7.46 Hz, PMe<sub>3</sub>(B)); 1.256 (d, 9, <sup>2</sup>J<sub>PH</sub> = 6.82 Hz, PMe<sub>3</sub>(A)); 0.970 (s, 9, CHCMe<sub>3</sub>); 0.241 (br d, 1, <sup>3</sup>J<sub>HH<sub>α</sub></sub> = 1.5 Hz, CHCMe<sub>3</sub>).

<sup>13</sup>C NMR (δ; C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 67.89 MHz; VIII, 57-1B through 6B; {<sup>1</sup>H} and gated {<sup>1</sup>H}; -15°): 216.0 (d of octet, <sup>2</sup>J<sub>PC</sub> = 6.4 Hz, <sup>1</sup>J<sub>CH</sub> = 72 Hz, CHCMe<sub>3</sub>); 46.2 (s, CHCMe<sub>3</sub>); 34.1 (q, <sup>1</sup>J<sub>CH</sub> = 124 Hz, CHCMe<sub>3</sub>); 22.8 (qd, <sup>1</sup>J<sub>PC</sub> = 24.8 Hz, <sup>1</sup>J<sub>CH</sub> = 130.8 Hz, PMe<sub>3</sub>(C)); 18.8 (qd, <sup>1</sup>J<sub>PC</sub> = 26.9 Hz, <sup>1</sup>J<sub>CH</sub> = 130.8 Hz, PMe<sub>3</sub>(B)); 16.3 (qd, <sup>1</sup>J<sub>PC</sub> = 20.7 Hz, <sup>1</sup>J<sub>CH</sub> = 130.8 Hz, PMe<sub>3</sub>(A)).

$^{31}\text{P}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 109.3 and 36.4 MHz; VIII, 56-1B through 10B; 57-1A through 3A;  $\{^1\text{H}\}$  and selective  $\{^1\text{H}\}$  at 1.38 ppm;  $-30^\circ$  to  $105^\circ$ ): (109.3 MHz;  $-30^\circ$ ): -4.1 (8 line pattern,  $^2J_{\text{HP}_\text{C}} = 90.6$  Hz,  $^2J_{\text{P}_\text{A}\text{P}_\text{C}} = 114.9$  Hz,  $^2J_{\text{P}_\text{B}\text{P}_\text{C}} = 50$  Hz,  $\text{PMe}_3(\text{C})$ ); -17.5 (8 line pattern;  $^2J_{\text{HP}_\text{B}} = 101.0$  Hz,  $^2J_{\text{P}_\text{A}\text{P}_\text{B}} = 29.2$  Hz,  $^2J_{\text{P}_\text{C}\text{P}_\text{B}} = 51.1$  Hz,  $\text{PMe}_3(\text{B})$ ); -26.5 (8 line pattern,  $^2J_{\text{HP}_\text{A}} = 17.3$  Hz,  $^2J_{\text{P}_\text{B}\text{P}_\text{A}} = 29.3$  Hz,  $^2J_{\text{P}_\text{C}\text{P}_\text{A}} = 115.0$  Hz,  $\text{PMe}_3(\text{A})$ ).

IR ( $\text{cm}^{-1}$ ; Nujol/NaCl; VIII, 44-2): 2440, m ( $\nu_{\text{C-H}_\alpha}$ ); 1730, m ( $\nu_{\text{Ta-H}}$ ).

Reaction of  $\text{Ta}(\text{CHCMe}_3)\text{Cl}(\text{PMe}_3)_4$  with HCl (VIII, 41; IX, 29)

$\text{Ta}(\text{CHCMe}_3)\text{Cl}(\text{PMe}_3)_4$  (0.5 g, 0.85 mmol) was dissolved in pentane (~20 mL), under Ar, and cooled to  $-78^\circ$ . 0.94 mL of a 0.9 M HCl in  $\text{Et}_2\text{O}$  solution, slowly added to the cold solution, reacted immediately forming a brown precipitate. After stirring for 20 min at  $-78^\circ$ , the solution was filtered. The solid was washed with pentane (20 mL) and dried in vacuo. The residue was dissolved in toluene (20 mL) at  $-78^\circ$  and filtered. The filtrate was warmed to  $25^\circ$  and stirred for 1 h. Removal of the solvent in vacuo gave a red oil which was a complex mixture of products, one of which was  $\text{Ta}(\text{CHCMe}_3)(\text{H})\text{Cl}_2(\text{PMe}_3)_3$ , by  $^1\text{H}$  NMR (VIII, 41-1). In a separate experiment, the pentane suspension which formed at  $-78^\circ$  after all the HCl was added, was warmed to  $25^\circ$ . After 5 min, the solid dissolved and the orange solution became deep red. The solution was filtered and the solvent was removed in vacuo. The residue, a tacky solid, was dissolved in 2 mL of  $\text{Et}_2\text{O}$  and cooled to  $-30^\circ$ . After 12 h, ~50 mg of red crystals were isolated by decanting the mother liquor and drying in vacuo.  $^1\text{H}$  NMR analysis at 250 MHz showed it to be a

complex mixture of products, mostly paramagnetic with ~10% being  $\text{Ta}(\text{CHCMe}_3)(\text{H})\text{Cl}_2(\text{PMe}_3)_3$  (IX, 29-1).

Preparation of  $\text{Ta}(\text{CDCMe}_3)(\text{D})\text{Cl}_2(\text{PMe}_3)_3$  (VIII, 44)

$\text{Ta}(\text{CD}_2\text{CMe}_3)\text{Cl}_4$  (1.98 g, 5.00 mmol) was added as a solid to a cold  $\text{Et}_2\text{O}/\text{THF}$  (3:2) solution (~30 mL) containing Na/Hg (0.41%, 56.1 g, 10.0 mmol) and  $\text{PMe}_3$  (2.4 mL, 25 mmol). The reaction mixture was warmed to 25° and stirred for 1.5 h.  $\text{Ta}(\text{CDCMe}_3)(\text{D})\text{Cl}_2(\text{PMe}_3)_3$  (1.3 g) was isolated by the same procedure used for the protio complex (47% yield). IR ( $\text{cm}^{-1}$ ; Nujol/NaCl; VIII, 44-1): 1805, m ( $\nu_{\text{C-D}_\alpha}$ ); 1270, m ( $\nu_{\text{Ta-D}}$ ).

Preparation of  $\text{Ta}(\text{CXCMe}_3)(\text{X})\text{Cl}_2(\text{PMe}_3)_3$ ; X = H or D (VIII, 45)

$\text{Ta}(\text{CHDCMe}_3)\text{Cl}_4$  (1.98 g, 5.00 mmol) was stirred with Na/Hg (0.41%, 56.1 g, 10.0 mmol) and  $\text{PMe}_3$  (2.4 mL, 25 mmol) in an  $\text{Et}_2\text{O}/\text{THF}$  solution (~30 mL) for 1.5 h.  $\text{Ta}(\text{CXCMe}_3)(\text{X})\text{Cl}_2(\text{PMe}_3)_3$  (X = H or D) was isolated by the above procedure in 41% yield (1.14 g). IR ( $\text{cm}^{-1}$ ; Nujol/NaCl; VIII, 45-1): 2440, m ( $\nu_{\text{C-H}_\alpha}$ ); 1805, m ( $\nu_{\text{C-D}_\alpha}$ ); 1730, m ( $\nu_{\text{Ta-H}}$ ); 1270, m ( $\nu_{\text{Ta-D}}$ ).

Reaction of  $\text{Ta}(\text{CHCMe}_3)(\text{H})\text{Cl}_2(\text{PMe}_3)_3$  with  $\text{Ta}(\text{CDCMe}_3)(\text{D})\text{Cl}_2(\text{PMe}_3)_3$  (VIII, 51; IX, 5)

$\text{Ta}(\text{CHCMe}_3)(\text{H})\text{Cl}_2(\text{PMe}_3)_3$  (30 mg) and  $\text{Ta}(\text{CDCMe}_3)(\text{D})\text{Cl}_2(\text{PMe}_3)_3$  (30 mg) were stirred for 1.5 h in 2 mL of a 1:1  $\text{Et}_2\text{O}/\text{THF}$  solution. The volatiles were removed in vacuo. The residue was dissolved in 10 mL of  $\text{Et}_2\text{O}$ , filtered and stripped. The product, dissolved in toluene- $d_8$ , was analyzed by  $^1\text{H}$  NMR (250 MHz) at -30°. Inspection of the hydride

resonances showed no appreciable H/D exchange. In a separate experiment, equal amounts of the above complexes were dissolved in toluene-d<sub>8</sub> and stood for 15 d under nitrogen at room temperature. Analysis by <sup>1</sup>H NMR (250 MHz, -30°) gave the same result found above (VIII, 67).

Preparation of Ta(C<sub>5</sub>Me<sub>5</sub>)(CHCMe)(H)Cl(PMe<sub>3</sub>) (VII, 57)

Ta(C<sub>5</sub>Me<sub>5</sub>)(CH<sub>2</sub>CMe<sub>3</sub>)Cl<sub>3</sub> (3.0 g, 6.1 mmol) was added as a solid to 60 mL of a 1:1 Et<sub>2</sub>O/THF solution containing PMe<sub>3</sub> (0.7 mL, 7.3 mmol, excess), Na/Hg (0.41%, 68.2 g, 12.2 mmol) and 10 mg of Naphthalene. The reaction mixture was stirred vigorously for 3 h, filtered through celite and stripped. The residue was extracted with pentane (25 mL), filtered and treated with darco. Removal of the solvent in vacuo left a red oil which was >90% Ta(C<sub>5</sub>Me<sub>5</sub>)(CHCMe<sub>3</sub>)(H)Cl(PMe<sub>3</sub>), by <sup>1</sup>H NMR. The crude product was dissolved in a minimal amount of pentane (~3 mL) and left to stand at -30°. After 24 h, oily yellow plates (0.9 g) of pure Ta(C<sub>5</sub>Me<sub>5</sub>)(CHCMe<sub>3</sub>)(H)Cl(PMe<sub>3</sub>) were isolated by decanting the mother liquor, and dried in vacuo (30% yield).

Longer reaction times increased PMe<sub>3</sub> content and higher reaction temperatures increased the amount of Ta(C<sub>5</sub>Me<sub>5</sub>)(CCMe<sub>3</sub>)Cl(PMe<sub>3</sub>)<sub>2</sub> produced in the reduction of Ta(C<sub>5</sub>Me<sub>5</sub>)(CH<sub>2</sub>CMe<sub>3</sub>)Cl<sub>3</sub>. A separate experiment using toluene as the reaction solvent, gave a brown crystalline compound, tentatively characterized by EPR as the le reduction product Ta(C<sub>5</sub>Me<sub>5</sub>)(CH<sub>2</sub>CMe<sub>3</sub>)Cl<sub>2</sub>(PMe<sub>3</sub>)<sub>x</sub> (VI, 73).

<sup>1</sup>H NMR (δ; C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 250 MHz; IX, 17-1A; -30°): 7.531 (dd, 1, <sup>3</sup>J<sub>HH<sub>α</sub></sub> = 1.83 Hz, <sup>3</sup>J<sub>PH</sub> = 73.6 Hz, Ta-H); 2.438 (d, 1, J<sub>HH<sub>α</sub></sub> = 1.83 Hz, CHCMe<sub>3</sub>);

2.092 (s, 15,  $C_5Me_5$ ); 1.183 (d, 9,  ${}^2J_{PH} = 7.32$  Hz,  $PMe_3$ ); 1.107 (s, 9,  $CHCMe_3$ ).

${}^{13}C$  NMR ( $\delta$ ;  $C_6D_5CD_3$ ; 67.89 MHz; VII, 18-1A through 4A;  $\{^1H\}$  and gated  $\{^1H\}$ ;  $-30^\circ$ ): 232.4 (dd,  ${}^2J_{PC} = 6.5$  Hz,  ${}^1J_{CH} = 72$  Hz,  $CHCMe_3$ ); 112.1 (s,  $C_5Me_5$ ); 47.4 (s,  $CHCMe_3$ ); 33.4 (q,  ${}^1J_{CH} \approx 122$  Hz,  $CHCMe_3$ ); 18.4 (qd,  ${}^1J_{PC} = 25.6$  Hz,  ${}^1J_{CH} \approx 125$  Hz,  $PMe_3$ ); 13.0 (q,  ${}^1J_{CH} = 130$  Hz,  $C_5Me_5$ ).

${}^{31}P$  NMR ( $\delta$ ;  $C_6D_6$ ; 36.4 MHz; IX, 41-1D, 2D;  $30^\circ$ ): -14.9 (d,  ${}^2J_{H,P} = 71$  Hz).

IR ( $cm^{-1}$ ; Nujol/NaCl; VII, 18-1): 2525, w ( $\nu_{C-H}$ ); 1730, m ( $\nu_{Ta-H}$ ).

#### Reduction of $TaMeCl_4(PMe_3)_2$ with Na/Hg (VIII, 6)

$TaMeCl_4(PMe_3)_2$  (0.5 g, 1.02 mmol) was added as a solid to an  $Et_2O$  solution (20 mL) containing Na/Hg (0.41%, 11.5 g, 2.04 mmol) and  $PMe_3$  (0.4 mL, 4.08 mmol). The yellow solution slowly turned green in 30 min. After 4 h, the reaction mixture was filtered through celite and the solvent was removed in vacuo yielding red crystals which were paramagnetic by  ${}^1H$  NMR. In a separate experiment, a 1:1 THF/ $Et_2O$  solution was used as the reaction solvent. Following a similar procedure, a brown oil was isolated which gave an uninformative  ${}^1H$  NMR (VII, 49).

#### Preparation of $[Ta(CHCMe_3)Cl(PMe_3)_2]_2(N_2)$

##### 1. From $Ta(CHCMe_3)Cl_3(PMe_3)_2$ (VII, 34)

16.8 G (3.00 mmol) of 0.41% Na/Hg was placed in 20 mL of a 1:1  $Et_2O$ /THF solution, containing  $PMe_3$  (0.3 mL, 3 mmol), and cooled to  $-30^\circ$ .

$Ta(CHCMe_3)Cl_3(PMe_3)_2$  (0.76 g, 1.50 mmol) was added as a solid to the cold solution. The reaction mixture was warmed to  $25^\circ$  and vigorously

stirred for 4 h. The solution was filtered through celite and the solvent was removed in vacuo leaving an oily yellow solid. Et<sub>2</sub>O (~3 mL) was added to the residue. Filtration gave a yellow solid (0.3 g) which was washed twice with pentane (~2-3 mL) and dried in vacuo. Combining the filtrate and pentane washes gave an additional 0.1 g of product, after cooling to -30° for 12 h. The crude product was dissolved in a minimal amount of Et<sub>2</sub>O (~20 mL), and filtered. Removal of the solvent (in vacuo) gave pure [Ta(CHCMe<sub>3</sub>)Cl(PMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(N<sub>2</sub>), by <sup>1</sup>H NMR (59% yield).

2. From Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub> (VII, 25)

Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub> (2.15 g, 5 mmol) was added as a solid to a 1:1 Et<sub>2</sub>O/THF solution (~45 mL) containing Na/Hg (0.41%, 56.1 g, 10.0 mmol) and PMe<sub>3</sub> (2 mL, 20 mmol). The reaction mixture was vigorously stirred for 2 h and filtered with difficulty through celite. The solvent was removed in vacuo leaving an oily yellow solid. The residue was extracted with pentane (125 mL) and filtered. The pentane insolubles were extracted with Et<sub>2</sub>O (20 mL) and filtered. The pentane solution was reduced in vacuo to ~40 mL and 0.58 g of yellow [Ta(CHCMe<sub>3</sub>)Cl(PMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(N<sub>2</sub>) was isolated by filtration, washed with pentane and dried in vacuo. The Et<sub>2</sub>O filtrate from the above extraction, was reduced in vacuo to ~6 mL and combined with the pentane filtrate and cooled to -30°. After 16 h, an additional 0.35 g of product was collected by filtration and dried in vacuo (45% yield). [Ta(CHCMe<sub>3</sub>)Cl(PMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(N<sub>2</sub>) is very soluble in THF and can be recrystallized from a saturated THF solution at -30° to yield yellow crystals which disintegrate upon exposure to vacuum.

Anal.<sup>59</sup> Calcd. for  $\text{Ta}_2\text{C}_{22}\text{H}_{56}\text{Cl}_2\text{P}_4\text{N}_2$ :

C, 29.19; H, 6.24; N, 3.09. Found: C, 23.11; H, 5.08; N, 1.88.

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 270 MHz; VII, 40-1C, 2C; 25°): 8.79 (br s, 1,  $\text{CHCMe}_3$ ); 1.32 (t, 18,  $^2\text{J}_{\text{PH}} = 3.45$  Hz,  $\text{PMe}_3$ ); 1.29 (s, 9,  $\text{CHCMe}_3$ ).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 15.0 MHz; VII, 40-1B, 2B;  $\{^1\text{H}\}$  and gated  $\{^1\text{H}\}$ ; 25°): 274.5 (br d,  $^1\text{J}_{\text{CH}} = 90.6$  Hz,  $\text{CHCMe}_3$ ); 46.6 (s,  $\text{CHCMe}_3$ ); 35.0 (q,  $^1\text{J}_{\text{CH}} = 125$  Hz,  $\text{CHCMe}_3$ ); 15.2 (qt,  $^1\text{J}_{\text{PC}} = 12.0$  Hz,  $^1\text{J}_{\text{CH}} = 129$  Hz,  $\text{PMe}_3$ ).

$^{31}\text{P}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 109.3 MHz; VIII, 58-1B through 3B;  $\{^1\text{H}\}$ ; 30° and -30°):

(30°): -11.2 (s).

IR ( $\text{cm}^{-1}$ ; Nujol/NaCl; VII, 25-1): 2590, m ( $\nu_{\text{C-H}}$ ).

Preparation of  $[\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2]_2(\text{N}_2)$  (VII, 56)

An  $\text{Et}_2\text{O}$  solution (2 mL), cooled to -30°, containing  $\text{LiCH}_2\text{CMe}_3$  (0.045 g, 0.57 mmol) was added dropwise to an  $\text{Et}_2\text{O}$  solution (20 mL) of  $[\text{Ta}(\text{CHCMe}_3)\text{Cl}(\text{PMe}_3)_2](\text{N}_2)$  at -30°. The reaction mixture was warmed to 25°, stirred for 1.5 h, and filtered through celite. Removal of the solvent in vacuo gave yellow crystals which were extracted with pentane (15 mL) and filtered. Evaporation of the volatiles gave 0.24 g of crude product which was dissolved in a minimal amount of pentane and cooled to -30°. After 16 h, the mother liquor was decanted, and 0.20 g of yellow crystals were isolated after drying in vacuo (74% yield).

Anal.<sup>59</sup> Calcd. for  $\text{Ta}_2\text{C}_{32}\text{H}_{78}\text{P}_4\text{N}_2$ : C, 39.35; H, 8.05; N, 2.87.

Found: C, 37.49; H, 7.53; N, 2.52.

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 250 MHz; IX, 8-1;  $30^\circ$ ): 6.224 (br s, 1,  $\text{CHCMe}_3$ ); 1.367 (s, 9,  $\text{CH}_2\text{CMe}_3$ ); 1.346 (t, 18,  $^2J_{\text{PH}} = 2.94$  Hz,  $\text{PMe}_3$ ); 1.276 (s, 9,  $\text{CHCMe}_3$ ); 0.626 (t, 2,  $^3J_{\text{PH}} = 16.6$  Hz,  $\text{CH}_2\text{CMe}_3$ ).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 22.5 MHz; VIII, 54-1A through 4A;  $\{^1\text{H}\}$  and gated  $\{^1\text{H}\}$ ;  $25^\circ$ ): 270.5 (dt,  $^2J_{\text{PC}} = 6.6$  Hz,  $^1J_{\text{CH}} = 87.9$  Hz,  $\text{CHCMe}_3$ ); 71.5 (t,  $^1J_{\text{CH}} = 107.7$  Hz,  $\text{CH}_2\text{CMe}_3$ ); 47.7 (s,  $\text{CHCMe}_3$ ); 38.2 (q,  $^1J_{\text{CH}} = 123.1$  Hz,  $\text{CH}_2\text{CMe}_3$ ); 35.9 (s,  $\text{CH}_2\text{CMe}_3$ ); 35.2 (q,  $^1J_{\text{CH}} = 123.8$  Hz,  $\text{CHCMe}_3$ ); 16.8 (qt,  $^1J_{\text{PC}} = 11.0$  Hz,  $^1J_{\text{CH}} = 126.7$  Hz,  $\text{PMe}_3$ ).

$^{31}\text{P}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 36.4 MHz; IX, 36-1,2;  $\{^1\text{H}\}$ ;  $25^\circ$ ): -10.9 (s).

IR ( $\text{cm}^{-1}$ ; Nujol/NaCl; IX 42-1): 2600, w ( $\nu_{\text{C-H}}$ ).

Reduction of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$  with Na/Hg (VII, 35; VIII, 75)

In a typical experiment,  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$  (4.0 g, 8.6 mmol) was added as a solid to 70 mL of a 1:1  $\text{Et}_2\text{O}/\text{THF}$  solution containing Na/Hg (0.41%, 96.4 g, 17.2 mmol) and  $\text{PMe}_3$  (3.4 mL, 35.8 mmol, excess).

The yellow solution immediately turned turquoise upon vigorous stirring of the reaction mixture. After 4.5 h at  $25^\circ$ , a color change to red occurred. The solution was filtered through celite and the solvent was removed in vacuo. The residue, a red oil, was extracted with pentane (75 mL), filtered, and the volume was reduced (in vacuo) to 15 mL. Cooling to  $-30^\circ$  for 16 h gave a yellow solid, consisting of a pentane soluble and pentane insoluble fraction. The soluble fraction was extracted with 3 mL of pentane. Filtration gave a yellow powder which was not characterized. The powder can be recrystallized from ether. The above filtrate was cooled to  $-30^\circ$  for 16 h and gave 0.68 g

of yellow crystals of a compound tentatively characterized as  $\text{Ta}(\text{CHCMe}_3)_2\text{H}(\text{PMe}_3)_2$ . The major product formed in this reaction was isolated as a red oil which has not been characterized,

$[\text{Ta}(\text{CHCMe}_3)_2\text{H}(\text{PMe}_3)_2]_x$  was isolated in 16% yield.

$\text{Ta}(\text{CHCMe}_3)_2\text{H}(\text{PMe}_3)_2$ :

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 270 and 250 MHz; VIII, 3-1B, 55-1B, through 4B;  $-30^\circ$ ):

8.240 (br s, 1,  $\underline{\text{CHCMe}_3}$ ); 1.242 (s, 9,  $\text{CHCMe}_3$ ); 1.233 (s, 9,  $\text{CHCMe}_3'$ );

1.180 (t, 18,  $^2\text{J}_{\text{PH}} = 6.62$  Hz,  $\text{PMe}_3$ ); 0.476 (br s, 1,  $\underline{\text{CHCMe}_3'}$ ).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 67.89 MHz; VIII, 56-1A through 9A;  $\{^1\text{H}\}$  and gated

$\{^1\text{H}\}$ ;  $-30^\circ$ ): 272.9 (dt,  $^2\text{J}_{\text{PC}} = 5.8$  Hz,  $^1\text{J}_{\text{CH}} = 100.8$  Hz,  $\underline{\text{CHCMe}_3}$ );

240.3 (dt,  $^2\text{J}_{\text{PC}} = 7.2$  Hz,  $^1\text{J}_{\text{CH}} = 82.5$  Hz,  $\underline{\text{CHCMe}_3'}$ ); 47.6 (s,  $\text{CHCMe}_3'$ );

44.1 (s,  $\text{CHCMe}_3$ ); 34.9 (q,  $^1\text{J}_{\text{CH}} = 124.4$  Hz,  $\text{CHCMe}_3$ ); 34.4 (q,  $^1\text{J}_{\text{CH}} =$

124.9 Hz,  $\text{CHCMe}_3'$ ); 16.95 (qt,  $^1\text{J}_{\text{PC}} = 11.8$  Hz,  $^1\text{J}_{\text{CH}} = 130.6$  Hz,  $\text{PMe}_3$ ).

$^{31}\text{P}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 109.2 and 36.4 MHz, VIII, 5 - 1C through 5C;

$\{^1\text{H}\}$  and  $^1\text{H}$  coupled;  $-30^\circ$  and  $30^\circ$ ): 2 (s).

IR ( $\text{cm}^{-1}$ ; Nujol/NaCl; VIII, 55-1): 2680, s ( $\nu_{\text{C-H}_\alpha}$ ); 2510, w ( $\nu_{\text{C-H}_\alpha}$ ).

Reaction of  $\text{Ta}(\text{CHCMe}_3)(\text{H})\text{Cl}_2(\text{PMe}_3)_3$  with  $\text{C}_2\text{H}_4$  (IX, 9, 15)

$\text{Ta}(\text{CHCMe}_3)(\text{H})\text{Cl}_2(\text{PMe}_3)_3$  (0.165 g, 0.300 mmol) was dissolved in toluene (3 mL) containing 50  $\mu\text{L}$  of n-nonane (0.280 mmol) as an internal standard. Addition of  $\text{C}_2\text{H}_4$  at 30 psi gave an immediate reaction as indicated by the yellow-brown solution changing to green. After 1.5 h the solution, still taking up  $\text{C}_2\text{H}_4$ , became violet. A sample was withdrawn after 2h, quenched with air and analyzed on column A. The same sample, passed down a short column of  $\text{Al}_2\text{O}_3$  (~2 cm), was reanalyzed and gave similar results to the air quenched sample. The

organic products, determined using calculated response factors, were a complex mixture of  $C_{5+2n}$  ( $n = 1, 2, 3, \dots$ ) olefins:

[ $C_7$  (0.08 eq.  $Ta^{-1}$ ),  $C_9$  (0.10 eq.  $Ta^{-1}$ ),  $C_{11}$  (0.06 eq.  $Ta^{-1}$ ),  $C_{13}$  (0.03 eq.  $Ta^{-1}$ ) and  $C_{15}$  (0.05 eq.  $Ta^{-1}$ )].

In a separate experiment,  $C_2H_4$  (4 eq.  $Ta^{-1}$ ) was slowly added beneath the liquid surface of a toluene solution containing

$Ta(CHCMe_3)(H)Cl_2(PMe_3)_3$  (0.300 mmol) and n-nonane (0.280 mmol). After 1.5 h at  $25^\circ$ , an air quenched sample, analyzed on column A, showed a complex mixture of  $C_{5+2n}$  ( $n=1, 2, 3$ ) olefins, with  $C_7$  (0.10 eq.  $Ta^{-1}$ ),  $C_9$  (0.12 eq.  $Ta^{-1}$ ) and  $C_{11}$  (0.09 eq.  $Ta^{-1}$ ) being the most prominent products (IX, 15).

Reaction of  $Ta(CHCMe_3)_2H(PMe_3)_2$  with  $C_2H_4$

$Ta(CHCMe_3)_2H(PMe_3)_2$  (0.142 g, 0.300 mmol) was dissolved in toluene (5 mL) containing n-nonane (50  $\mu$ L, 0.280 mmol), and pressurized with  $C_2H_4$  (30 psi) at  $60^\circ$ . Two samples were withdrawn (2 h and 8 h), quenched with air, and analyzed on column A using calculated response factors. The products 4,4-dimethyl-1-pentene (1.03 eq.  $Ta^{-1}$ ), 4,4-dimethyl-trans-2-pentene (0.06 eq.  $Ta^{-1}$ ) and 2,2,5,5-tetramethyl-trans-2-hexene (0.13 eq.  $Ta^{-1}$ ), accounted for 1.35  $Bu^+$  per Ta. 1-Butene (1.3 eq.  $Ta^{-1}$ ) and 2-butene (0.03 eq.  $Ta^{-1}$ ) were also present. No attempt was made to determine the amount of neopentane present, if any.

Chapter 5

Ethylene Complexes of Tantalum(I) and  
Niobium(I) and Their Involvement in the  
Selective Catalytic Dimerization of Ethylene to 1-Butene

## Introduction

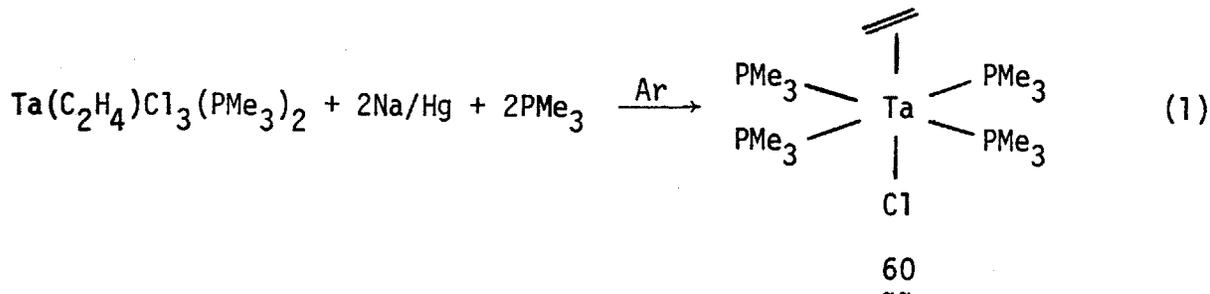
The number of known group V olefin complexes is relatively small. The earliest reported compounds were of the 18 electron variety  $M(C_5H_5)_2(C_2H_4)X$  ( $M = Nb$  or  $Ta$ ,  $X = Et, Me, H, I$ ).<sup>64</sup> Recently, 14 electron complexes of the type  $Ta(C_5Me_5)(olefin)X_2$  ( $X = Cl, Me$ ) have been reported.<sup>4a</sup> They function as reactants with  $\alpha$ -olefins to form tantalacyclopentane complexes which are highly selective catalysts for the dimerization of olefins.<sup>65,4b</sup> Other Ta(III) olefin complexes of the type  $Ta(olefin)X_3L_2$  ( $X = Cl, Br, alkoxide$ ;  $L = PMe_3, PMe_2Ph$ ) also exist, however, they do not function as dimerization catalysts.

Olefin complexes for Ta or Nb in the +1 oxidation state are rare. The only examples are  $Ta(C_5Me_5)(C_2H_4)(\eta\text{-butadiene})$ <sup>4b</sup> and  $Nb(C_2H_4)_2H(DMPE)_2$ .<sup>66</sup> Recently, we reported the preparation of compounds of the type  $M(C_2H_4)_2(C_2H_5)(PMe_3)_2$  (where  $M = Nb, Ta$ ).<sup>67</sup> In that communication it was shown that for  $M = Ta$ , this complex is an active catalyst for the selective dimerization of ethylene to 1-butene, whereas the niobium analogue does not.

This chapter discusses the catalytic reaction in more detail. In addition, the synthesis and characterization of a novel class of Ta(I) and Nb(I) ethylene complexes is presented.

Results and DiscussionSynthesis and Characterization of Ta(I) and Nb(I) Ethylene Complexes:Ta(C<sub>2</sub>H<sub>4</sub>)Cl(PMe<sub>3</sub>)<sub>4</sub>

Reducing Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub> in the presence of PMe<sub>3</sub> with two equivalents of sodium amalgam, under Ar, yields Ta(C<sub>2</sub>H<sub>4</sub>)Cl(PMe<sub>3</sub>)<sub>4</sub> (60) (equation 1). 60 is obtained as violet crystals containing ca. one



equivalent of occluded PMe<sub>3</sub>.

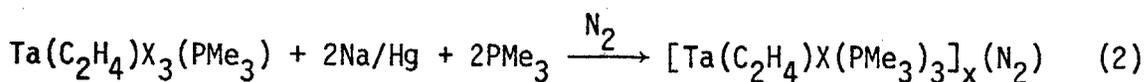
The <sup>1</sup>H NMR spectrum of 60 shows equivalent ethylene protons at 2.21 ppm which are coupled to the four equivalent phosphorous nuclei, (quintet, J<sub>HP</sub> = 3.68 Hz). The PMe<sub>3</sub> resonance is present as a "virtually-coupled" triplet similar to that found for Ta(CHCMe<sub>3</sub>)Cl(PMe<sub>3</sub>)<sub>4</sub><sup>59</sup>. Both carbons of the ethylene ligand in 60 are equivalent and are located at 35.4 ppm (J<sub>CH</sub> = 149 Hz) in the <sup>13</sup>C NMR spectrum.

The occluded PMe<sub>3</sub> shows a broad resonance at room temperature in both the <sup>1</sup>H and <sup>13</sup>C NMR spectrum. Lowering the temperature sharpens only the free PMe<sub>3</sub> resonance while leaving all others unaffected.

Variable temperature <sup>31</sup>P NMR confirms the presence of free PMe<sub>3</sub> with no other resonances being observed over the entire temperature range studied. Apparently, a second order paramagnetic effect is responsible for the absence of any signals attributable to 60. This uncommon effect has also been observed for ReCl<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub><sup>68</sup>.

### Dinitrogen-Ethylene Complexes

The two electron reduction of  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  under  $\text{N}_2$  does not give 60. Instead, orange crystals of  $[\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}(\text{PMe}_3)_3]_x(\text{N}_2)$  (61a) are isolated as a solvate from concentrated ether or THF solutions at  $-30^\circ$ . Careful integrations show (in the case of THF) that 0.25 equivalents per tantalum of solvent is occluded. The analogous bromide compound ( $[\text{Ta}(\text{C}_2\text{H}_4)\text{Br}(\text{PMe}_3)_3]_x(\text{N}_2)$ ; 61b) can also be prepared (equation 2).



X = Cl, 61a

X = Br, 61b

61a is believed to be a dimer containing a bridging  $\text{N}_2$  ligand by analogy to  $[\text{Ta}(\text{CHCMe}_3)\text{Cl}(\text{PMe}_3)_2]_2(\text{N}_2)$ . The lack of any assignable nitrogen stretch supports this contention. Furthermore, recent work by Rocklage has definitively shown that coordinated  $\text{N}_2$  is present.<sup>69</sup> Molecular weight measurements and nitrogen analysis are in progress.

The 109.3 MHz  $^{31}\text{P}$  NMR spectrum of 61a at  $-70^\circ$ , shows an  $\text{A}_2\text{B}$  pattern arising from the three  $\text{PMe}_3$  ligands, ( $J_{\text{pp}}$  = 10.2 Hz). The magnitude of the coupling constant indicates that the  $\text{PMe}_3$  ligands are meridional about each Ta atom (see Figure 1). Warming the sample to  $80^\circ$  shows loss of coupling to the two trans  $\text{PMe}_3$  ligands, while the cis- $\text{PMe}_3$  broadens and moves upfield toward free  $\text{PMe}_3$ . Only the cis-phosphine ligand shows exchange on the NMR time scale over the temperature range studied. The 270 MHz  $^1\text{H}$  NMR spectrum of 61a at  $0^\circ$  shows a triplet and a doublet for the two types of  $\text{PMe}_3$  ligands. This agrees with the  $^{31}\text{P}$  NMR results.

Warming to temperatures above room temperature, the sample shows the cis-PMe<sub>3</sub> to broaden while the other two remain as a triplet. Cooling the sample to -60° causes the cis PMe<sub>3</sub> to become a doublet while the trans PMe<sub>3</sub> ligands split into two broad resonances of equal area. The  $\Delta G^\ddagger$  for the interconversion is  $14 \pm 1$  kcal mol<sup>-1</sup>. <sup>13</sup>C NMR data agree with these results. Also, at this low temperature two olefinic carbons are observed which coalesce upon warming.

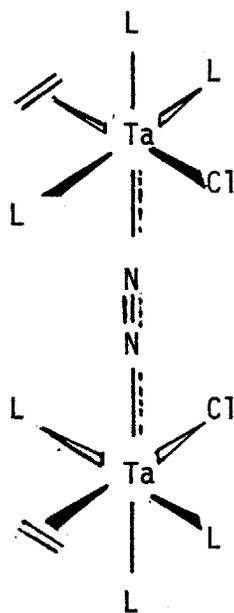


Figure 1

The structure shown in Figure 1 best fits the low temperature form of 61a. The temperature dependence shown by 61a probably arises from a restricted rotation between the two tantalum octahedra. The cause(s) for the observed barrier to rotation are unknown at this time.

The analogous niobium complex can be prepared in the following manner: Nb(CHCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub> reacts with ethylene in the presence of PMe<sub>3</sub> to give a homogeneous violet solution. Exposing the solution to nitrogen, followed by vacuum, causes the solution to become red and form an oil which separates from the solvent. Dissolving this oil in a

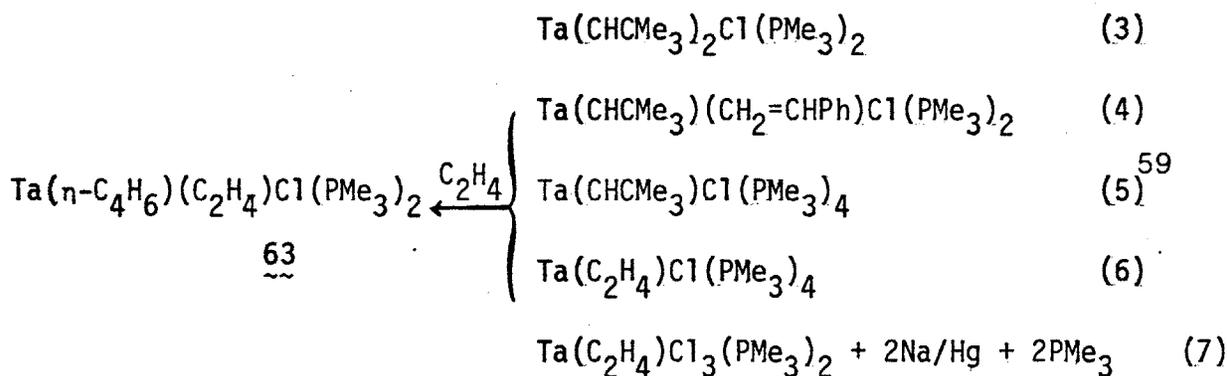
minimal amount of ether gives red crystals of

$[\text{Nb}(\text{C}_2\text{H}_4)\text{Cl}(\text{PMe}_3)_3]_x(\text{N}_2)$  (62). 62 crystallizes only in the presence of ethereal solvents.

Since all of these dinitrogen complexes (61a, 61b, and 62) show similar spectroscopy, they are believed to be of the same structure.

#### Butadiene-Ethylene Complexes; Preparation and Formation

The reaction of  $\text{Ta}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  with ethylene does not give 61a. Instead, red crystals of  $\text{Ta}(\eta\text{-C}_4\text{H}_6)(\text{C}_2\text{H}_4)\text{Cl}(\text{PMe}_3)_2$  (63) are isolated. 63 can be prepared by the different methods shown below (equations 3-7).



The ethyl derivative,  $\text{Ta}(\text{C}_4\text{H}_6)(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  (64) can be prepared by reacting EtLi with 63. Both 63 and 64 are soluble in ethereal and aromatic solvents.

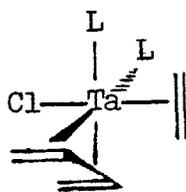
Low temperature  $^{31}\text{P}$  NMR studies show the presence of two isomers for both 63 and 64 where each isomer contains two separate noncoupled phosphorous nuclei. The  $^{13}\text{C}$  NMR shows the presence of two isomers for only 64. Apparently, the resonances for the major and minor isomers of  $\text{Ta}(\eta\text{-C}_4\text{H}_6)(\text{C}_2\text{H}_4)\text{Cl}(\text{PMe}_3)_2$  are coincident. All the observed isomers of 63 and 64 are asymmetric since separate resonances are observed for each olefinic carbon.

Variable temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR studies of 63 show a symmetric form at high temperature. Fluxional processes are rare in six-coordinate systems.<sup>70</sup> Since  $\text{Ta}(\text{C}_5\text{Me}_5)(\eta\text{-C}_4\text{H}_6)\text{Cl}_2$  shows no fluxional behavior,<sup>65</sup> it is reasonable to assume that ethylene rotation is responsible for the temperature dependence of 63.

$\Delta G^\ddagger$  was calculated for this process from both  $^1\text{H}$  and  $^{13}\text{C}$  NMR data and were found to be  $17 \pm 1$  and  $16 \pm 1$  kcal mol<sup>-1</sup>, respectively. These activation energies agree with the  $\Delta G^\ddagger$  found for another octahedral complex,  $\text{Ta}(\text{CH}_2=\text{CHPh})\text{Cl}_3(\text{PMe}_3)_2$  ( $\Delta G^\ddagger \geq 20$  kcal mol<sup>-1</sup>; see Chapter 2).

The  $^{13}\text{C}$  NMR data for the butadiene ligand in these complexes, are somewhat different but on the order of data found for  $\text{Fe}(\text{CO})_3(\eta^4\text{-butadiene})$ .<sup>71</sup> The structure of  $\text{Fe}(\text{CO})_3(\eta^4\text{-butadiene})$  has been determined by X-ray diffraction<sup>72</sup> and shows that the four carbon atoms are equidistant from Fe. Since the  $^{13}\text{C}$  NMR spectra of the Ta and Fe compounds are similar, 63 and 64 probably also contains an  $\eta^4$ -butadiene ligand rather than a metallacyclopentene.

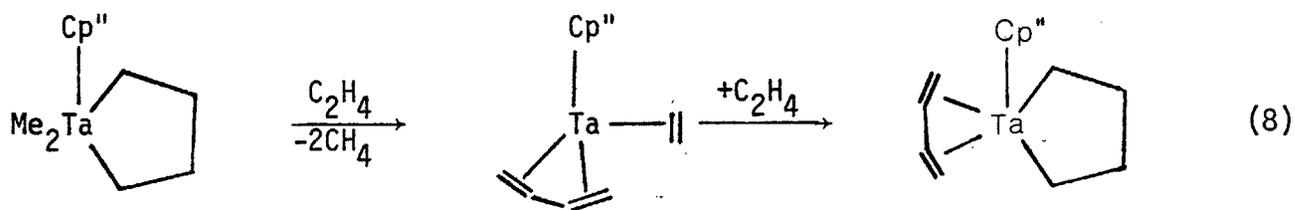
One possible structure is shown below. The freely rotating ethylene ligand would give a symmetric high temperature form. The "frozen" form for each isomer would be asymmetric with ethylene aligned along one of the two coordinate axes containing both  $\text{PMe}_3$  ligands. Figure 2 shows the structure for one of these isomers.



63

Figure 2

The formation of  $\text{Ta}(\eta\text{-C}_4\text{H}_6)(\text{C}_2\text{H}_4)\text{Cl}(\text{PMe}_3)_2$  (63), from  $\text{Ta}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  plus ethylene, resembles reactions which form a different class of butadiene complexes from methyl substituted tantallacyclopentane compounds. An example of this is the decomposition of  $\text{Me}_2(\text{C}_5\text{Me}_5)\overline{\text{TaCH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$  under ethylene which follows equation 8 (McLain and Schrock).<sup>65</sup> They postulate that the butadiene

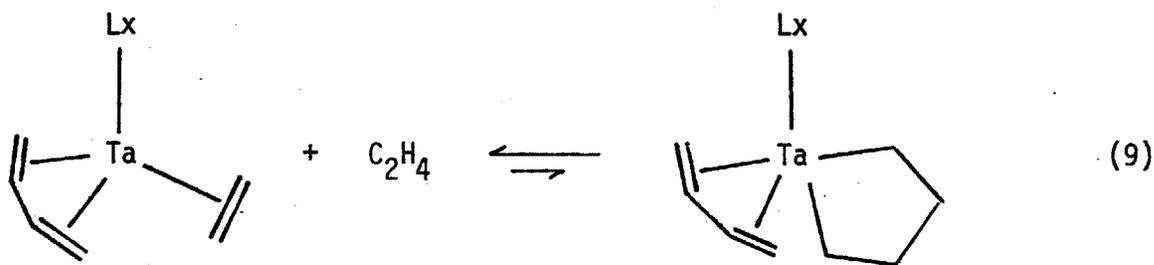


is formed from a four step mechanism involving two  $\beta$ -hydride elimination steps from the metallacycle each followed by a reductive elimination of methane.

The coordination sites left open by methane loss are filled by two ethylene molecules which couple to give the highly stable metallacycle ring. These complexes do not function as catalysts for the selective dimerization of ethylene to 1-butene.<sup>65</sup>

The organic products formed in the reaction between  $\text{Ta}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  and ethylene are two equivalents of the expected rearrangement products, and only a small amount of 1-butene which is formed late in the reaction.

The reaction of  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2=\text{CHPh})\text{Cl}(\text{PMe}_3)_2$  with ethylene also gives slow 1-butene formation and the expected rearrangement products. In fact,  $\text{Ta}(\eta\text{-C}_4\text{H}_6)(\text{C}_2\text{H}_4)\text{Cl}(\text{PMe}_3)_2$  reacts with ethylene to slowly form some 1-butene showing that the equilibrium lies to the left in equation 9, below.



The presence of metallacycles in the formation of 63 is further supported by the fact that  $\text{Nb}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  reacts with ethylene to give  $[\text{Nb}(\text{C}_2\text{H}_4)\text{Cl}(\text{PMe}_3)_3]_x(\text{N}_2)$ , instead of a butadiene complex. In addition, there is a considerable amount of evidence that niobacyclopentane complexes do not form nearly as readily as tantalacyclopentane complexes.<sup>15c</sup>

#### Catalytic Dimerization of Ethylene

Schrock first observed that  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$  in the presence of  $\text{PMe}_3$ , reacts with ethylene to form only 1-butene catalytically, at a rate of ca.  $\text{two Ta}^{-1} \text{ min}^{-1}$ . If any 2-butene isomers are present, the concentration of each isomer is below the limit of detection. Few higher oligomers are formed in this catalytic reaction. There are few catalytic systems which demonstrate such high selectivity as this system.<sup>1a</sup>

Similar high selectivity has been reported for  $\text{Cl}_2(\text{C}_5\text{H}_5)\overline{\text{TaCH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$ .<sup>73</sup> This tantalum catalyst converts ethylene to 1-butene efficiently but at a rate which is considerably slower than the above reaction. Also, it is less effective for dimerization of 1-butene and higher olefins than it is for ethylene. In the reaction of this system with

ethylene, higher olefins can form by co-dimerization however, slowly. This catalyst does not involve hydride intermediates that might catalyze double bond migrations, therefore, the terminal olefin products are stable in solution. Isomerization of the olefin products to a thermodynamic mixture is often encountered in later transition metal dimerization systems.<sup>74,1a</sup> Very effective catalysts for olefin dimerization which do not isomerize the olefins they form, also arise from reactions of alkyl aluminum reagents with nickel and titanium compounds.<sup>75</sup> However, the rate of dimerization versus the rate of oligomerization is very sensitive to reaction conditions.

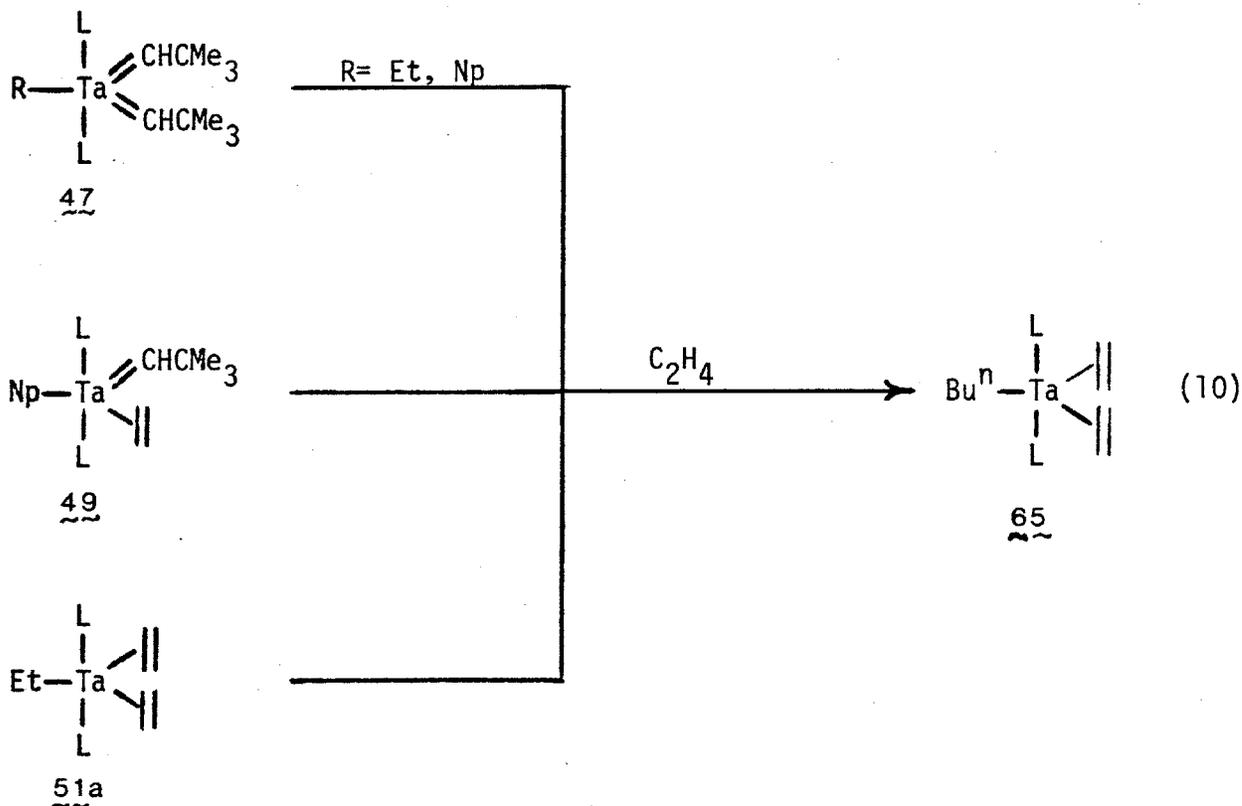
Rupprecht showed that the other major organic products formed in the reaction of ethylene with  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)_3$  in the presence of  $\text{PMe}_3$  was 4,4-dimethyl-1-pentane ( $\sim 2.9$  eq.  $\text{Ta}^{-1}$ ). He later found that  $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$  also gave 3 equivalents per Ta of 4,4-dimethyl-1-pentene and catalytically dimerized ethylene to 1-butene at a rate of about  $2.5 \text{ Ta}^{-1} \text{ min}^{-1}$  at  $25^\circ$ . This catalyst remains active for several days at  $25^\circ$  although the rate of 1-butene production decreases with time. The amount of  $\text{C}_6$  and  $\text{C}_8$  olefins present increased as the 1-butene formed became the major component of the total solution.

As previously indicated,  $\text{Ta}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  is a very poor dimerization catalyst in contrast to  $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ . Therefore, the reactions of ethylene with other bisneopentylidene complexes was studied in order to determine what effects (if any) the alkyl group has on the catalytic reactions.

$\text{Ta}(\text{CHCMe}_3)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  reacts rapidly with ethylene to give two equivalents  $\text{Ta}^{-1}$  of rearrangement products and an active dimerization catalyst. Whereas,  $\text{Ta}(\text{CHCMe}_3)_2\text{Me}(\text{PMe}_3)_2$  reacts slowly with ethylene to

give small amounts of 1-butene and nearly two equivalents of rearrangement products. In addition, no propylene or pentenes are observed which would arise from ethylene insertion into the Ta-Me bond. The mesityl complex  $\text{Ta}(\text{CHCMe}_3)_2(\text{mesityl})(\text{PMe}_3)_2$  did not react with ethylene at all, even at 50° (50 psi). Therefore, only the bisneopentylidene complexes which function as active catalysts are the ones where the alkyl group contains either  $\alpha$ - or  $\beta$ -abstractable hydrogen atoms.

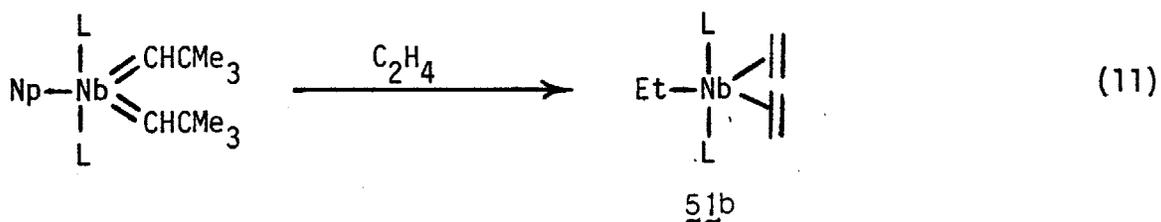
$\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_4)(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$  (49) and  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  (51a) show similar catalytic activity as in  $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$  (47d). All these systems react with ethylene to give  $\text{Ta}(\text{C}_2\text{H}_4)_2\text{Bu}^n(\text{PMe}_3)_2$  (65) as the major component (>75%) of a reaction mixture by  $^{13}\text{C}$  NMR (equation 10). 65 can also be identified under



catalytic conditions (see Experimental).

Assignment of the NMR resonances for the butyl ligands was made by analogy to  $\text{Ta}(\text{CHCMe}_3)_2\text{Bu}^n(\text{PMe}_3)_2$ . Only one type of ethylene carbon is present, therefore, 65 must be structurally analogous to  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$ . The minor component of the catalyst (~25%) can not be positively identified.

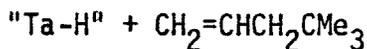
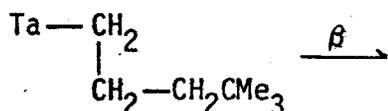
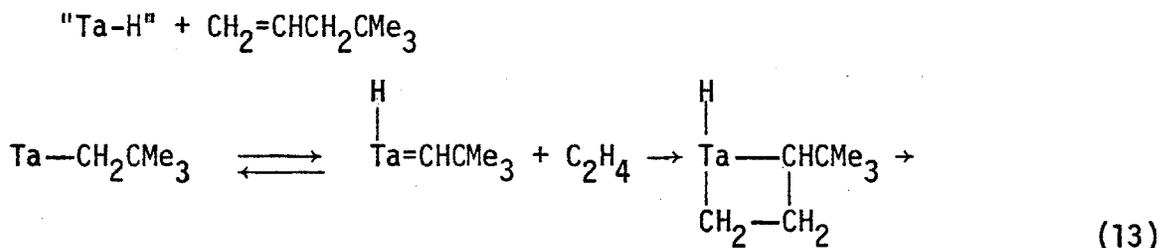
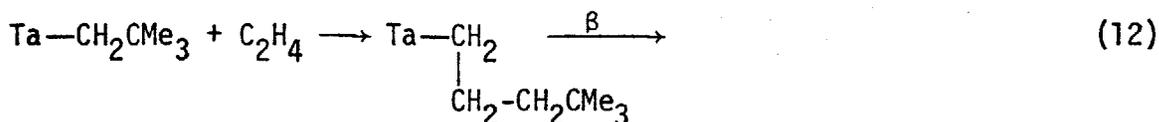
$\text{Nb}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$  reacts immediately with ethylene (under  $\text{N}_2$  or Ar) to give cleavage products <sup>18</sup> and a solution which is a poor catalyst for the dimerization of ethylene to 1-butene. The solution contains largely, if not solely,  $\text{Nb}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  (51b) by  $^1\text{H}$  and  $^{13}\text{C}$  NMR (equation 11). It can be isolated in high yield from



the reaction mixture and can also be prepared by other routes (see Chapter 3).

Since olefin insertion into a Ta-alkyl bond has not been demonstrated (for any system) and since 4,4-dimethyl-1-pentene is the only t-butyl containing olefin produced in the reaction between  $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ , the mechanism of this formation was studied in some detail. Two equivalents of the 4,4-dimethyl-1-pentene probably

arise from the decomposition of a tantalacyclobutane intermediate, formed by the reaction of ethylene with each neopentylidene ligand.<sup>15c,26</sup> The third equivalent of 4,4-dimethyl-1-pentene can form by one (or both) of the two possible pathways shown in equations 12 and 13.



Equation 12 shows ethylene insertion into the tantalum neopentyl bond.  $\beta$ -hydride elimination of the neopentyl intermediate gives 4,4-dimethyl-1-pentene and an incipient hydride. Alternatively a neopentyl ligand transfers an  $\text{H}_2$  to the metal giving a hydrido-alkylidene which reacts with ethylene to eventually give 4,4-dimethyl-1-pentene (equation 13).

Both mechanisms have been shown to occur in model systems. Bergman postulates that ethylene reacts with  $\text{Cp}_2\text{CoMe}$  to give propylene via equation 12.<sup>76</sup> Reversible  $\alpha$ -hydride elimination has been demonstrated to occur between octahedral  $\text{Ta}(\text{CH}_2\text{CMe}_3)(\text{C}_2\text{H}_4)\text{Cl}_2(\text{PMe}_3)_2$  and  $\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_5)\text{Cl}_2(\text{PMe}_3)_2$  (see Chapter 2).

In order to distinguish between these pathways the reaction of ethylene with  $\text{Ta}(\text{CHCMe}_3)_2(\text{CD}_2\text{CMe}_3)(\text{PMe}_3)_2$  was investigated.<sup>77</sup> Analysis shows the presence of three equivalents of a 1:1 mixture of 4,4-dimethyl-1-pentene- $\text{d}_0$  and  $\text{d}_1$  containing <5% (if any) 4,4-dimethyl-1-pentene- $\text{d}_2$ . The lack of any 4,4-dimethyl-1-pentene- $\text{d}_2$  is consistent with (but does not prove) the  $\alpha$ -hydride elimination pathway.

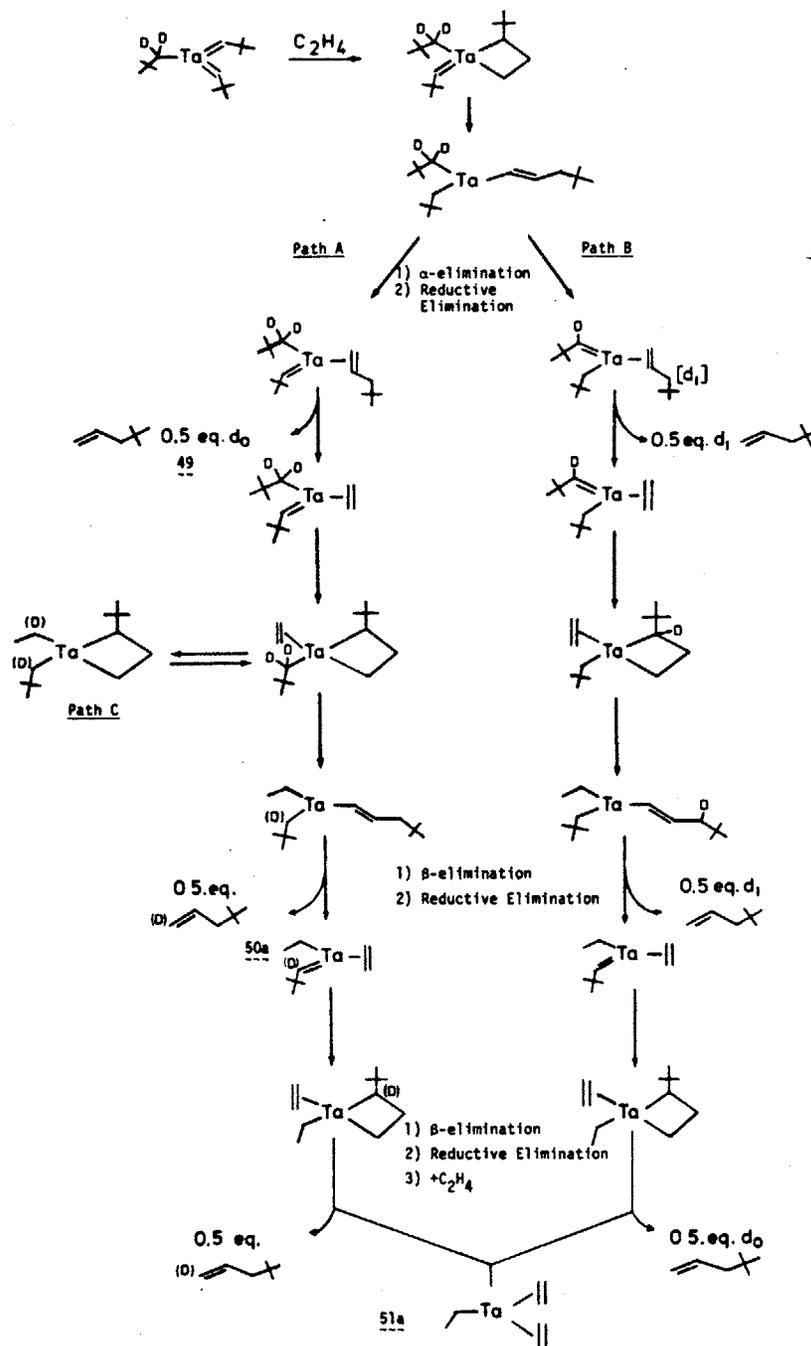
To account for H/D scrambling and the loss of 0.5 equivalents of deuterium, a possible mechanism is presented in Scheme IV. This simplified mechanism is attractive for several reasons. The initial metallacyclobutane formation is a known process. It is reasonable that the reaction with ethylene occurs stepwise since bis-neopentylidene complexes contain different neopentylidene ligands spectroscopically, and the intermediate complexes (49, 50a and 51a) are known, stable, complexes which also function as active catalysts. Secondly,  $\alpha$ -elimination is known to occur in Ta(III) neopentyl complexes (see Chapter 4). Thirdly, the H/D scrambling occurs by reversible hydrogen (or deuterium) transfer to an ethylene ligand similar to that found in  $\text{Ta}(\text{CH}_2\text{CMe}_3)(\text{C}_2\text{H}_4)\text{Cl}_2(\text{PMe}_3)_2$  (path C).

A plausible mechanism for the dimerization of ethylene is shown in Scheme V. A mechanism involving monophosphine intermediates is also possible but less likely. This is due to the fact that  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  exchanges on the NMR time scale with free  $\text{PMe}_3$  faster than more crowded five coordinate complexes of similar structure, implying that the exchange occurs by an associative mechanism.

One of two necessary conditions for forming a metallacyclopentane from two ethylene ligands is that the angle between their two coordination sites be small enough for cyclization to occur (e.g.

Scheme IV. A Reasonable Mechanism for the Reaction of Ethylene with  
 $\text{Ta}(\text{CHCMe}_3)_2(\text{CD}_2\text{CMe}_3)(\text{PMe}_3)_2$

Scheme IV. A Reasonable Mechanism for the Reaction of Ethylene with  
 $\text{Ta}(\text{CHCMe}_3)_2(\text{CD}_2\text{CMe}_3)(\text{PMe}_3)_2$



\* $\text{PMe}_3$  ligands have been excluded for clarity.

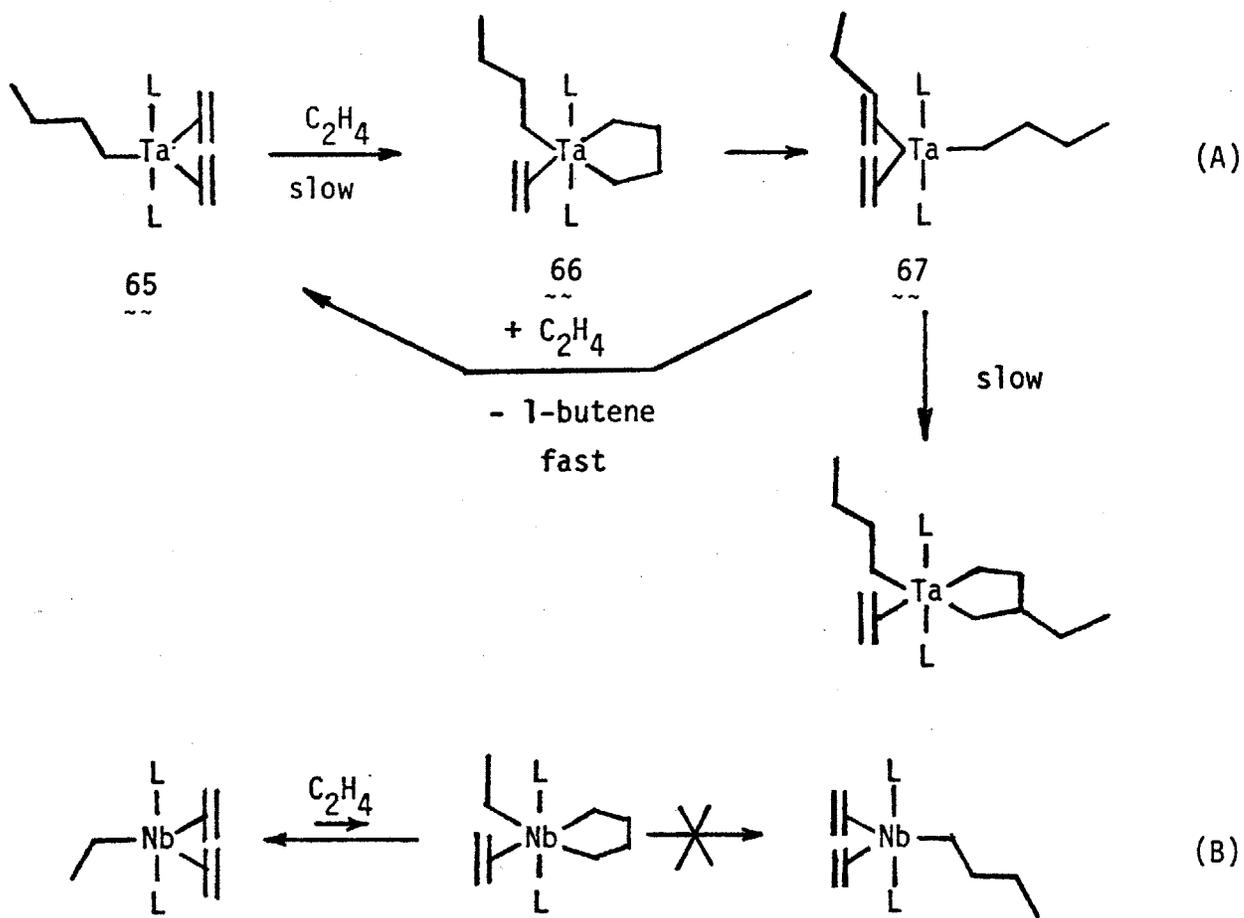
66, Scheme V <sup>78,4a</sup>). In addition, a metallacycle cannot readily form in  $\text{Ta}(\text{C}_2\text{H}_4)_2\text{Bu}^n(\text{PMe}_3)_2$  (65) unless one  $\text{PMe}_3$  and one ethylene exchange positions. The second requirement is that the metal can be readily oxidized (i.e. 65  $\rightarrow$  66), since metallacycle formation from olefins is formally an oxidative coupling reaction.

Stable relatives of 66 are known, for example,  $\text{Ta}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)\text{Cl}_2(\text{PMe}_3)_2$  and  $\text{Ta}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)_2\text{Cl}(\text{PMe}_3)_2$  (see Chapter 2). However,  $\text{Ta}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)_3(\text{PMe}_3)_2$  a reasonable intermediate in the formation of  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  from  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  decomposes readily. Therefore a  $\beta$ -hydrogen should transfer readily from the butyl ligand in 66 to one metallacycle  $\alpha$ -carbon. The alternative  $\beta$ -hydrogen transfer from the metallacycle to the butyl ligand (or ethylene ligand) should be slow. The rates of olefin dimerization reactions where  $\beta$ -hydrogen transfer from the metallacycle is the rate-determining step are in fact slow ( $k \approx 10^{-4} \text{ s}^{-1}$  at  $30^\circ$ ) compared to the rate of dimerization found in this system. <sup>73,4b</sup> Finally, ethylene can displace less strongly bound olefins without forming a metallacycle in complexes of the type  $\text{Ta}(\text{C}_5\text{Me}_5)(\text{olefin})\text{Cl}_2$ . <sup>4a</sup> In this case, 67 must react with ethylene to give 65. Since 65 is observed under catalytic conditions the step from 65  $\rightarrow$  66 must be slowest.

If 1-butene is not displaced, but forms a mixed metallacycle (1-butene-ethylene), then the next higher olefin ( $\text{C}_6$ ) can form. This is consistent with the observation that  $\text{C}_6$  and  $\text{C}_8$  olefins are found only when the concentration of 1-butene approaches that of the reaction solvent.

Scheme V. The Mechanism for the Dimerization of Ethylene to 1-Butene

Scheme V. Mechanism for the Dimerization of Ethylene to 1-Butene



Unlike  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  (51a),  $\text{Nb}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  (51b) is a poor ethylene dimerization catalyst for the following reasons. First of all, niobium does not become oxidized as readily as tantalum.<sup>20</sup> Secondly,  $^{31}\text{P}$  NMR studies show that niobium  $\text{PMe}_3$  compounds exchange with free  $\text{PMe}_3$  at faster rates (on the NMR time-scale) than the analogous tantalum species (see Chapter 3). Therefore, 51b must be a weaker Lewis acid (than 51a) and cannot effectively coordinate ethylene to obtain the necessary metallacycle 68, which is required in order for catalysis to occur.

Experimental

$\text{Ta}(\text{CHCMe}_3)(\text{CH}_2=\text{CPh})\text{Cl}(\text{PMe}_3)_2$  was obtained from H. Turner.

Reaction of  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  with  $\text{C}_2\text{H}_4$

1. By GLC (VI, 16)

$\text{Ta}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  (0.105 g, 0.250 mmol) was dissolved in  $\text{Et}_2\text{O}$  (4 mL), containing n-heptane (50  $\mu\text{L}$ , 0.340 mmol), and cooled to  $0^\circ$ . The reaction mixture was pressurized with  $\text{C}_2\text{H}_4$  (30 psi) and samples were periodically withdrawn with a cold syringe, and quenched with air. GLC analysis (column A) showed that 1-butene was produced at a rate of 0.5 turnovers  $\text{Ta}^{-1} \text{min}^{-1}$ . 2-Ethyl-1-butene (0.32 eq.  $\text{Ta}^{-1}$ ) and  $\text{C}_8$  olefin (assumed, 0.14 eq.  $\text{Ta}^{-1}$ ) were also present after 3 h at  $0^\circ$ .

2. By  $^{13}\text{C}$  NMR (IV, 14, 29; V, 8a, 13, 27, 33)

$\text{Ta}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  (0.11 g) was dissolved in toluene- $\text{d}_8$  (~0.7 mL) and cooled to  $-78^\circ$ . Gaseous  $\text{C}_2\text{H}_4$  (6 mL) was added slowly via syringe to the cold solution. The sample was placed in a NMR probe cooled to  $-25^\circ$  and a  $^{13}\text{C}\{^1\text{H}\}$  NMR (15.0 MHz) was recorded. The spectrum showed that 1-butene,  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  and  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{Bu}^n)(\text{PMe}_3)_2$  were present. Addition of more  $\text{C}_2\text{H}_4$  (~6 mL), added at  $25^\circ$ , followed by cooling to  $-25^\circ$ , showed a decrease in the amount of  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  with  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{Bu}^n)(\text{PMe}_3)_2$  and 1-butene increasing (IV, 14-1 through 7).

In a separate experiment,  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  dissolved in toluene- $\text{d}_8$  was reacted with  $\text{C}_2\text{H}_4$  (30 psi) at  $0^\circ$  for 3 h.  $^{13}\text{C}\{^1\text{H}\}$  NMR (15.0 and 67.89 MHz) at  $-20^\circ$ , showed  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{Bu}^n)(\text{PMe}_3)_2$ , 1-butene, and an unidentified minor component. Unreacted  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  was not observed (V, 8-1A, 2A; 33-1 through 4).

Mostly  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{Bu}^n)(\text{PMe}_3)_2$  was isolated, in low yield, from a concentrated pentane solution at  $-78^\circ$  (V, 13).  $^{13}\text{C}\{\text{H}\}$  and  $^{31}\text{P}\{\text{H}\}$  analysis, in agreement with the above in situ spectra, showed that  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{Bu}^n)(\text{PMe}_3)_2$  constituted ~75% of a two component mixture with each complex containing equivalent phosphines (V, 13-1 through 13).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 67.89 MHz; V, 33-1 through 4;  $\{\text{H}\}$  and gated  $\{\text{H}\}$ ;  $-20^\circ$ ):  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{Bu}^n)(\text{PMe}_3)_2$ : 52.6 (tt,  $^2\text{J}_{\text{PC}} = 4.4$  Hz,  $^1\text{J}_{\text{CH}} = 118$  Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ); 39.4 (tt,  $^2\text{J}_{\text{PC}} = 7.3$  Hz,  $^1\text{J}_{\text{CH}} = 145$  Hz,  $\text{C}_2\text{H}_4$ ); 33.5 (t,  $^1\text{J}_{\text{CH}} = 124$  Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ); 28.2 (t,  $^1\text{J}_{\text{CH}} = 124$  Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ); 14.7 (qt,  $^1\text{J}_{\text{PC}} \approx 11$  Hz,  $^1\text{J}_{\text{CH}} = 128$  Hz,  $\text{PMe}_3$ ); 12.7 (q,  $^1\text{J}_{\text{CH}} = 124$  Hz,  $\text{CH}_2\text{CH}_2\text{CHCH}_3$ ).

(minor component): 56.3 (br d,  $^1\text{J}_{\text{CH}} = 146$  Hz,  $\text{CH}_2=\text{CHCH}_2\text{CH}_3$ ); 54.3 (br t,  $^1\text{J}_{\text{CH}} = 147$  Hz,  $\text{CH}_2=\text{CHCH}_2\text{CH}_3$ ); 51.0 (br t,  $^1\text{J}_{\text{CH}} = 117$  Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ); 36.0 (br t,  $^1\text{J}_{\text{CH}} \approx 133$  Hz,  $-\text{CH}_2-$ ); 29.3 (t,  $^1\text{J}_{\text{CH}} \approx 120$  Hz,  $-\text{CH}_2-$ ); 28.8 (t,  $^1\text{J}_{\text{CH}} \approx 120$  Hz,  $-\text{CH}_2-$ ); 22.2 (q,  $^1\text{J}_{\text{CH}} \approx 120$  Hz,  $-\text{CH}_3$ ); 20.3 (t,  $^1\text{J}_{\text{CH}} \approx 120$  Hz,  $-\text{CH}_2-$ ); 15.9 (qt,  $^1\text{J}_{\text{PC}} \approx 11$  Hz,  $^1\text{J}_{\text{CH}} \approx 128$  Hz,  $\text{PMe}_3$ ); 8.8 (q,  $^1\text{J}_{\text{CH}} = 124$  Hz,  $-\text{CH}_3$ ).

$^{31}\text{P}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 36.4 MHz; V, 13-1,2;  $\{\text{H}\}$  and fully  $^1\text{H}$  coupled;  $-20^\circ$ ):  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{Bu}^n)(\text{PMe}_3)_2$ : 6.2 (s).

minor component: 7.5 (s).

Reaction of  $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$  with  $\text{C}_2\text{H}_4$  by NMR (V, 8)

$\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$  (0.20 g) was dissolved in toluene- $d_8$  (~0.7 mL) and cooled to  $0^\circ$ . The solution changed from yellow-orange

to deep red upon addition of  $C_2H_4$  (30 psi). After 3 h a sample was withdrawn and placed in a NMR tube chilled to  $-78^\circ$ . A  $^{13}C\{^1H\}$  NMR (15.0 MHz) was recorded for this sample at  $-20^\circ$ . The product was a mixture of compounds with  $Ta(C_2H_4)_2(Bu^N)(PMe_3)_2$  being present as ~75% of the organometallic mixture (V, 8-1B through 3B). The organic products, identified by  $^{13}C$  NMR, were 1-butene and 4,4-dimethyl-1-pentene. The amount of the organics produced in a similar reaction has appeared elsewhere.<sup>18</sup>

Reaction of  $Ta(CHCMe_3)(C_2H_4)(CH_2CMe_3)(PMe_3)_2$  with  $C_2H_4$  (III, 68)

1. By GLC (III, 68)

$Ta(CHCMe_3)(C_2H_4)(CH_2CMe_3)(PMe_3)_2$  (0.18 g, 0.36 mmol) in 2 mL of  $Et_2O$  with n-heptane as an internal standard was stirred under 30 psi of  $C_2H_4$ . The yellow solution immediately turned red upon introduction of  $C_2H_4$ . After 1 h, a sample was withdrawn at  $0^\circ$ , using a cold syringe, and quenched with air. GLC analysis (column A) showed the reaction to be 90% complete. The products found were 4,4-dimethyl-1-pentene (1.8 eq.  $Ta^{-1}$ ) and 1-butene (21.5 eq.  $Ta^{-1}$ ). The GLC relative responses were assumed to be proportional to the molecular weight.

2. By NMR (V, 11)

$Ta(CHCMe_3)(C_2H_4)(CH_2CMe_3)(PMe_3)_2$  (0.25 g) was dissolved in 8 mL of  $Et_2O$ , cooled to  $0^\circ$  and pressurized with  $C_2H_4$  (30 psi) for 3 h. The volatiles were removed in vacuo at  $0^\circ$ . The residue, a red oil, was dissolved in toluene- $d_8$  (~0.5 mL) and its  $^{13}C\{^1H\}$  NMR (15.0 MHz)

was recorded at  $-20^{\circ}$ . The product was a mixture of compounds with  $\text{Ta}(\text{C}_2\text{H}_4)_2(\text{Bu}^n)(\text{PMe}_3)_2$  being present as ~75% of this mixture (V, 11-1A, 2A).

Reaction of  $\text{Ta}(\text{CHCMe}_3)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  with  $\text{C}_2\text{H}_4$  by GLC (V, 29)

$\text{Ta}(\text{CHCMe}_3)_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  (0.100 g, 0.199 mmol) was dissolved in  $\text{Et}_2\text{O}$  (~3 mL) containing n-heptane (50  $\mu\text{L}$ , 0.340 mmol) and pressurized with  $\text{C}_2\text{H}_4$  (30 psi). After 1.5 h at  $25^{\circ}$ , a sample was withdrawn, quenched with air, and analyzed on column A. GLC analysis showed 1-butene (43.7 eq.  $\text{Ta}^{-1}$ ), cis-2-butene (0.012 eq.  $\text{Ta}^{-1}$ ), 4,4-dimethyl-1-pentene (1.6 eq.  $\text{Ta}^{-1}$ ) and 4,4-dimethyl-trans-2-pentene (0.031 eq.  $\text{Ta}^{-1}$ ). The relative GLC response was assumed to be proportional to the molecular weight.

Reaction of  $\text{Ta}(\text{CHCMe}_3)_2\text{Me}(\text{PMe}_3)_2$  with  $\text{C}_2\text{H}_4$  (III, 30)

$\text{Ta}(\text{CHCMe}_3)_2\text{Me}(\text{PMe}_3)_2$  (0.122 g, 0.250 mmol) in 3 mL of pentane with n-octane as an internal standard, was stirred under 50 psi of  $\text{C}_2\text{H}_4$ . The yellow solution slowly changed to red (hours) and some precipitate formed. Samples were withdrawn periodically at  $0^{\circ}$  using a cold syringe and quenched with air. After 48 h, GLC analysis (column A) showed the reaction to be 78% complete. The products found were 4,4-dimethyl-1-pentene (1.44 eq.  $\text{Ta}^{-1}$ ), 4,4-dimethyl-trans-2-pentene (0.11 eq.  $\text{Ta}^{-1}$ ), and 1-butene (6.8 eq.  $\text{Ta}^{-1}$ ). The GLC relative responses were assumed to be proportional to the molecular weight.

Reaction of Nb(CHCMe<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>CMe<sub>3</sub>)(PMe<sub>3</sub>)<sub>2</sub> with C<sub>2</sub>H<sub>4</sub> under Ar (IX, 38)

Nb(CHCMe<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>CMe<sub>3</sub>)(PMe<sub>3</sub>)<sub>2</sub> (0.200 g, 0.438 mmol) was dissolved in pentane (8 mL), containing n-heptane (100 μL, 0.682 mmol), and placed under Ar (4 freeze-pump-thaw cycles). Upon pressurization with C<sub>2</sub>H<sub>4</sub> (30 psi), the solution immediately changed from yellow to deep red. Samples were periodically withdrawn at 0° using a cold syringe, quenched with air, and analyzed on column A. GLC analysis showed that the amounts of the organic products were unchanged from that found under nitrogen.<sup>18</sup>

Reaction of Ta(CHCMe<sub>3</sub>)(CH<sub>2</sub>=CHPh)Cl(PMe<sub>3</sub>)<sub>2</sub> with C<sub>2</sub>H<sub>4</sub> (VII, 28)

Ta(CHCMe<sub>3</sub>)(CH<sub>2</sub>=CHPh)Cl(PMe<sub>3</sub>)<sub>2</sub> (0.163 g, 0.300 mmol) was dissolved in Et<sub>2</sub>O (6 mL), containing n-octane (50 μL, 0.308 mmol), and pressurized with C<sub>2</sub>H<sub>4</sub> (30 psi). GLC analysis (column A) showed that the amounts of 4,4-dimethyl-1-pentene (0.97 eq. Ta<sup>-1</sup>) and 4,4-dimethyl-trans-2-pentene (0.09 eq. Ta<sup>-1</sup>) did not change after 4 h at 25°. The other olefins present steadily increased with time. After 4 d, styrene (0.91 eq. Ta<sup>-1</sup>), 1-butene (6.78 eq. Ta<sup>-1</sup>), and 2-ethyl-1-butene (0.51 eq. Ta<sup>-1</sup>) were the only other observable products. The GLC relative responses were assumed proportional to the molecular weight or experimentally determined.

Reaction of Ta(CHCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub> with C<sub>2</sub>H<sub>4</sub> (VIII, 29)

Ta(CHCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub> (0.153 g, 0.300 mmol) was dissolved in Et<sub>2</sub>O (~6 mL) containing n-octane (100 μL, 0.616 mmol) and pressurized with C<sub>2</sub>H<sub>4</sub> (30 psi). The solution was heated to 40° for 1 h then cooled

to 25°. Samples were periodically withdrawn at 0° using a cold syringe and analyzed on column A. After 44 h, there was little change in the amount of tert-butyl containing olefins with 4,4-dimethyl-1-pentene (1.75 eq. Ta<sup>-1</sup>) and 4,4-dimethyl-trans-2-pentene (0.14 eq. Ta<sup>-1</sup>) being present. However, the amount of 1-butene increased steadily over a longer period. The amount of 1-butene was 6.5 eq. Ta<sup>-1</sup> after 4 d. 2-Ethyl-1-butene (0.34 eq. Ta<sup>-1</sup>) was also found and identified by coinjection with an authentic sample. The GLC relative responses were assumed to be proportional to the molecular weight.

Preparation of Ta(n-C<sub>4</sub>H<sub>9</sub>)(C<sub>2</sub>H<sub>4</sub>)Cl(PMe<sub>3</sub>)<sub>2</sub>

1. From Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub> (VII, 47)

Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub> (1.40 g, 3.00 mmol) and Na/Hg (0.41%, 33.6 g, 6.0 mmol) were placed in a pressure vessel and flushed with C<sub>2</sub>H<sub>4</sub>. A solution of Et<sub>2</sub>O/THF (1:1, 30 mL) containing PMe<sub>3</sub> (0.6 mL, 6.3 mmol, excess) was added by syringe. The reaction mixture was pressurized with C<sub>2</sub>H<sub>4</sub> (30 psi) and stirred for 16 h at 25°. The solution was filtered through celite and the solvent was removed in vacuo. The residue was extracted with pentane (50 mL) and filtered. The filtrate was stripped to red crystals which were dissolved in Et<sub>2</sub>O (~5 mL). Cooling to -30° for 12 h gave 0.9 g of irregular red crystals (67% yield).

2. From Ta(C<sub>2</sub>H<sub>4</sub>)Cl(PMe<sub>3</sub>)<sub>4</sub> (IX, 34)

Ta(C<sub>2</sub>H<sub>4</sub>)Cl(PMe<sub>3</sub>)<sub>4</sub> (0.3 g, 0.55 mmol) was dissolved in 6 mL of Et<sub>2</sub>O, under Ar, and pressurized with C<sub>2</sub>H<sub>4</sub> (30 psi). The reaction was immediate. The green solution turned deep red within 5 min at 25°. After 1 h, the solvent was removed in vacuo leaving red crystals. The residue was

extracted with pentane (20 mL) and filtered. The filtrate was stripped to 0.25 g of red crystals, which were pure by  $^1\text{H}$  NMR (100% yield).

3. From  $\text{Ta}(\text{CHCMe}_3)(\text{CH}_2=\text{CHPh})\text{Cl}(\text{PMe}_3)_2$  (VIII, 26)

$\text{Ta}(\text{CHCMe}_3)(\text{CH}_2=\text{CHPh})\text{Cl}(\text{PMe}_3)_2$  (0.26 g, 0.48 mmol) was dissolved in  $\text{Et}_2\text{O}$  (5 mL) and pressurized with  $\text{C}_2\text{H}_4$  (30 psi) for 36 h at  $25^\circ$ . The solvent was removed in vacuo and the residue, a red solid, was extracted with pentane (~35 mL) and filtered. Removal of the solvent in vacuo gave 0.17 g of  $\text{Ta}(\text{C}_4\text{H}_6)(\text{C}_2\text{H}_4)\text{Cl}(\text{PMe}_3)_2$ , pure by  $^1\text{H}$  NMR (77% yield).

4. From  $\text{Ta}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  (IV, 34)

$\text{Ta}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$  (4.28 g, 8.41 mmol) was dissolved in pentane (~40 mL) and pressurized with  $\text{C}_2\text{H}_4$  (35 psi) for 24 h at  $40^\circ$ . The yellow solution became deep red (~4 h) and a red powder precipitated from solution. The reaction mixture was cooled to  $25^\circ$ , 60 mL of pentane was added and the solution was filtered. Removal of the solvent in vacuo gave 3.37 g of red microcrystalline product, pure by  $^1\text{H}$  NMR. Multiple recrystallizations from concentrated  $\text{Et}_2\text{O}$  solutions did not give an analytically pure sample (see below) (89% yield).

Anal. (VII, 47; IV, 34-1): Calcd. for  $\text{TaC}_{12}\text{H}_{28}\text{ClP}_2$ : C, 31.98; H, 6.26.

Found: C, 30.73; H, 6.96.

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 270 and 60 MHz; III, 28-1A through 7A; III, 25-1A through 11A;  $-70^\circ$  to  $105^\circ$ ):

(270 MHz;  $-30^\circ$ ): 4.826 (m, 1,  $\text{CH}_2=\text{CH}_\text{A}-\text{CH}_\text{B}=\text{CH}_2$ ); 4.600 (m, 1,  $\text{CH}_2=\text{CH}_\text{A}-\text{CH}_\text{B}=\text{CH}_2$ ); 1.380 (d, 9,  $^2J_{\text{PH}} = 7.3$  Hz,  $\text{PMe}_3(\text{A})$ ); 0.957 (d, 9,  $^2J_{\text{PH}} = 6.71$  Hz,  $\text{PMe}_3(\text{B})$ ); 2.23, 1.44, 1.15, 1.00, 0.842, -0.161, -0.807, -0.919 (m, 1, olefinic resonances).

(270 MHz; 75°): coalescence of 4.826 and 4.600 resonances.

(60 MHz; 105°): 4.72 (br m,  $\text{CH}_2=\underline{\text{CH}}-\underline{\text{CH}}=\text{CH}_2$ ); 1.22 (br d,  ${}^2J_{\text{PH}} \approx 8$  Hz,

$\text{PMe}_3$ ). At 270 MHz,  $T_c = 75 \pm 10^\circ\text{C}$ ,  $\Delta\nu = 62 \pm 5$  Hz and

$\Delta G^\ddagger = 17 \pm 1$  kcal mol $^{-1}$ .

${}^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 67.89 and 15.0 MHz; III, 63-1A through 5A; III, 29-1A through 4A;  $\{^1\text{H}\}$  and gated  $\{^1\text{H}\}$ ;  $-30^\circ$  to  $100^\circ$ ):

(67.89 MHz;  $-30^\circ$ ): 94.87 (d,  ${}^1J_{\text{CH}} = 160$  Hz,  $\text{CH}_2=\underline{\text{CH}}-\underline{\text{CH}}=\text{CH}_2$ ); 92.57 (d,

${}^1J_{\text{CH}} = 163$  Hz,  $\text{CH}_2=\underline{\text{CH}}-\underline{\text{CH}}=\text{CH}_2$ ); 51.79 (tt,  ${}^2J_{\text{PC}} = 5.6$  Hz,  ${}^1J_{\text{CH}} = 147$  Hz,

$\underline{\text{CH}}_2=\underline{\text{CH}}_2$ ); 43.40 (ddd,  ${}^2J_{\text{PC}} = 5.7$  Hz,  ${}^1J_{\text{CH}} = 155.5$  and  $147.9$  Hz,  $\text{CH}_2=\underline{\text{CH}}_2$ );

34.75 (ddd,  ${}^2J_{\text{PC}} = 7.8$  Hz,  ${}^1J_{\text{CH}} = 141.3$  and  $149.0$  Hz,  $\underline{\text{CH}}_2=\underline{\text{CH}}-\underline{\text{CH}}=\text{CH}_2$ );

30.19 (tt,  ${}^2J_{\text{PC}} = 8.2$  Hz,  ${}^1J_{\text{CH}} \approx 150$  Hz,  $\text{CH}_2=\underline{\text{CH}}-\underline{\text{CH}}=\underline{\text{CH}}_2$ ); 14.92 (qd,

${}^1J_{\text{PC}} = 21.6$  Hz,  ${}^1J_{\text{CH}} = 130$  Hz,  $\text{PMe}_3(\text{A})$ ); 13.54 (qd,  ${}^1J_{\text{PC}} = 23.3$  Hz,

${}^1J_{\text{CH}} = 130$  Hz,  $\text{PMe}_3(\text{B})$ ).

(15.0 MHz;  $60^\circ$ ): coalescence of ethylene carbons.

(15.0 MHz;  $100^\circ$ ): 93.95 (s,  $\text{CH}_2=\underline{\text{CH}}-\underline{\text{CH}}=\text{CH}_2$ ); 47.8 (br s,  $\underline{\text{CH}}_2=\underline{\text{CH}}_2$ );

33.1 (s,  $\underline{\text{CH}}_2=\underline{\text{CH}}-\underline{\text{CH}}=\text{CH}_2$ ); 14.9 (d,  ${}^1J_{\text{PC}} \approx 12$  Hz,  $\text{PMe}_3$ ).

At 15.0 MHz,  $T_c = 60 \pm 10^\circ\text{C}$ ,  $\Delta\nu = 129 \pm 5$  Hz and  $\Delta G^\ddagger = 16 \pm 1$  kcal mol $^{-1}$ .

${}^{31}\text{P}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 109.3 MHz, IV, 25-2A;  $\{^1\text{H}\}$ ;  $-30^\circ$ ):

major isomer: 2.0 (s); -8.3 (s).

minor isomer: 2.5 (s); -7.8 (s).

The ratio of the major to minor isomer was 2:1 at  $-30^\circ$ .

IR ( $\text{cm}^{-1}$ ; Nujol/NaCl; III, 25-1A): 945, s ( $\nu_{\text{P-C}}$ ).

Preparation of  $\text{Ta}(\text{n-C}_4\text{H}_9)(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5)(\text{PMe}_3)_2$  (IV, 63)

$\text{Ta}(\text{C}_4\text{H}_9)(\text{C}_2\text{H}_4)\text{Cl}(\text{PMe}_3)_2$  (1.25 g, 2.77 mmol) was dissolved in  $\text{Et}_2\text{O}$  (25 mL) and cooled to  $-78^\circ$ . 4.7 mL of a 1.18 M  $\text{LiC}_2\text{H}_5$  (excess) in

benzene solution was added slowly by syringe to the cold Ta solution. The reaction mixture was warmed to 25°, stirred for 30 min, and filtered. The solvent was removed in vacuo. The residue was extracted with pentane (-20 mL) and filtered. The filtrate was concentrated (in vacuo) to ~5 mL, filtered and cooled to -30°. After 16 h the mother liquor was decanted and 0.6 g of red crystals were isolated after drying in vacuo. An analytically pure sample was obtained after repeated recrystallizations from concentrated pentane solutions at -30° (49% yield).

Anal. (IV, 63; IV, 52-1B): Calcd. for  $\text{TaC}_{14}\text{H}_{33}\text{P}_2$ : C, 37.84; H, 7.48.

Found: C, 37.23; H, 7.32.

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 270 and 200 MHz; IV, 75-1A through 3A; -40°):

4.92 (m,  $\text{CH}_2=\underline{\text{C}}\text{H}-\text{CH}=\text{CH}_2$ ); 3.46 (m,  $\text{CH}_2=\text{CH}-\underline{\text{C}}\text{H}=\text{CH}_2$ ); 1.30 (d,  $^2\text{J}_{\text{PH}} \approx 6$  Hz,  $\text{PMe}_3(\text{A})$ ); 0.87 (d,  $^2\text{J}_{\text{PH}} \approx 6$  Hz,  $\text{PMe}_3(\text{B})$ ); 1.55, 1.16, 0.76, -0.16 and -0.37 (m, olefinic resonances); -0.05 (t,  $^3\text{J}_{\text{HAHB}} = 7.7$  Hz,  $\text{CH}_2\text{CH}_3$ ).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 67.89 MHz; IV, 61-1A, 2A;  $\{^1\text{H}\}$  and gated  $\{^1\text{H}\}$ ; -40°):

major isomer: 102.3 (d,  $^1\text{J}_{\text{CH}} = 157$  Hz,  $\text{CH}_2=\underline{\text{C}}\text{H}-\text{CH}=\text{CH}_2$ ); 89.0 (d,  $^1\text{J}_{\text{CH}} = 163$  Hz,  $\text{CH}_2=\text{CH}-\underline{\text{C}}\text{H}=\text{CH}_2$ ); 48.6 (tt,  $^2\text{J}_{\text{PC}} = 5.7$  Hz,  $^1\text{J}_{\text{CH}} = 146$  Hz,  $\underline{\text{C}}\text{H}_2=\text{CH}_2$ ); 42.1 (td,  $^2\text{J}_{\text{PC}} = 4.8$  Hz,  $^1\text{J}_{\text{CH}} = 14.9$  Hz,  $\text{CH}_2=\underline{\text{C}}\text{H}_2$ ); 33.9 (td,  $^2\text{J}_{\text{PC}} = 5.8$  Hz,  $^1\text{J}_{\text{CH}} = 150$  Hz,  $\underline{\text{C}}\text{H}_2=\text{CH}-\text{CH}=\text{CH}_2$ ); 33.6 (t,  $^1\text{J}_{\text{CH}} = 116$  Hz,  $\underline{\text{C}}\text{H}_2\text{CH}_3$ ); 25.1 (td,  $^2\text{J}_{\text{PC}} = 9.0$  Hz,  $^1\text{J}_{\text{CH}} = 149$  Hz,  $\text{CH}_2=\text{CH}-\text{CH}=\underline{\text{C}}\text{H}_2$ ); 15.0 (qd,  $^1\text{J}_{\text{PC}} = 17.7$  Hz,  $^1\text{J}_{\text{CH}} \approx 130$  Hz,  $\text{PMe}_3(\text{A})$ ); 13.5 (qd,  $^1\text{J}_{\text{PC}} = 19.4$  Hz,  $^1\text{J}_{\text{CH}} \approx 130$  Hz,  $\text{PMe}_3(\text{B})$ ); 5.8 (q,  $^1\text{J}_{\text{CH}} = 123$  Hz,  $\text{CH}_2\text{CH}_3$ ).

minor isomer: 94.4 ( $\text{CH}_2=\underline{\text{C}}\text{H}-\text{CH}=\text{CH}_2$ ); 92.3 ( $\text{CH}_2=\text{CH}-\underline{\text{C}}\text{H}=\text{CH}_2$ ); 51.7 ( $\underline{\text{C}}\text{H}_2=\text{CH}_2$ ); 43.2 ( $\text{CH}_2=\underline{\text{C}}\text{H}_2$ ); 1.55 ( $\text{CH}_2\text{CH}_3$ ).

$^{31}\text{P}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 109.3 MHz; V, 36-1B, 2B;  $\{^1\text{H}\}$ ; -47° and 30°): (-47°):

major isomer: -6.4 (s); -11.4 (s).

minor isomer: -6.0 (s); -11.9 (s).

The ratio of the major to minor isomer was 1:1 at 30° and 3:1 at -47°.

Reaction of Ta(n-C<sub>4</sub>H<sub>9</sub>)(C<sub>2</sub>H<sub>4</sub>)Cl(PMe<sub>3</sub>)<sub>2</sub> with C<sub>2</sub>H<sub>4</sub> (VIII, 30)

Ta(C<sub>4</sub>H<sub>9</sub>)(C<sub>2</sub>H<sub>4</sub>)Cl(PMe<sub>3</sub>)<sub>2</sub> (0.180 g, 0.399 mmol) was dissolved in Et<sub>2</sub>O (6 mL), containing n-octane (50 μL, 0.308 mmol), and pressurized with C<sub>2</sub>H<sub>4</sub> (30 psi). After 20 h, a sample was withdrawn at 0°, using a cold syringe and analyzed on column A. GLC analysis showed 1-butene (0.61 eq. Ta<sup>-1</sup>), trans-2-butene (0.06 eq. Ta<sup>-1</sup>) and cis-2-butene (0.04 eq. Ta<sup>-1</sup>) to be present. Heating the reaction mixture to 45° for 6 h gave no increase in the amount of butenes initially formed.

Reaction of Nb(CHCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub> with C<sub>2</sub>H<sub>4</sub> (VI, 21)

Nb(CHCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub> (0.110 g, 0.261 mmol) was dissolved in Et<sub>2</sub>O (~5 mL), containing n-heptane (50 μL, 0.340 mmol), and pressurized with C<sub>2</sub>H<sub>4</sub> (30 psi). The reaction was immediate with a color change from yellow to red occurring. After ~5 min, a brown precipitate formed. Samples were periodically withdrawn at 0°, using a cold syringe, and analyzed on column A. GLC analysis showed 4,4-dimethyl-1-pentene (1.42 eq. Nb<sup>-1</sup>), 4,4-dimethyl-trans-2-pentene (0.24 eq. Nb<sup>-1</sup>), 2,2,5,5-tetramethyl-trans-3-hexene (0.06 eq. Nb<sup>-1</sup>), neopentane (0.09 eq. Nb<sup>-1</sup>) and 1-butene (0.18 eq. Nb<sup>-1</sup>) to be present after 16 h. The GLC relative responses were assumed to be proportional to the molecular weight.

Preparation of [Nb(C<sub>2</sub>H<sub>4</sub>)Cl(PMe<sub>3</sub>)<sub>3</sub>]<sub>x</sub>(N<sub>2</sub>) (VII, 51)

Nb(CHCMe<sub>3</sub>)<sub>2</sub>Cl(PMe<sub>3</sub>)<sub>2</sub> (1.81 g, 4.30 mmol) was suspended in pentane (~10 mL), containing PMe<sub>3</sub> (0.5 mL, 5.3 mmol, excess), and cooled to 0°. C<sub>2</sub>H<sub>4</sub>

(30 psi) was slowly reacted with the yellow solution causing a color change to red after ~2.5 h. The reaction mixture was slowly warmed to 25°. After 12 h, a color change from red to purple occurred. The reaction mixture was filtered. The homogeneous filtrate turned red and an oil came out of solution upon removal of the solvent in vacuo. The residue was dissolved in 20 mL of Et<sub>2</sub>O. Standing at 25° for 10 min gave 0.60 g of red crystals containing solvated Et<sub>2</sub>O, which were isolated by filtration and dried in vacuo. The filtrate was concentrated (in vacuo) and an additional 0.35 g of pure product was isolated by filtration (58% yield).

<sup>1</sup>H NMR (δ; C<sub>6</sub>H<sub>6</sub>; 60 MHz; VII, 51-1; 25°): 1.36 (t, 18, <sup>2</sup>J<sub>PH</sub> ≈ 3 Hz, PMe<sub>3</sub>(A)); 0.75 (d, 9, <sup>2</sup>J<sub>PH</sub> ≈ 4 Hz, PMe<sub>3</sub>(B)).

<sup>31</sup>P NMR (δ; C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 109.3 MHz; IX, 41-1E; {<sup>1</sup>H}; -70°): -8 (br s); -41 (s).

Preparation of [Ta(C<sub>2</sub>H<sub>4</sub>)Cl(PMe<sub>3</sub>)<sub>3</sub>]<sub>x</sub>(N<sub>2</sub>) (VII, 52)

Ta(C<sub>2</sub>H<sub>4</sub>)Cl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub> (2.0 g, 4.3 mmol) was added as a solid to a 1:1 Et<sub>2</sub>O/THF solution (50 mL) containing Na/Hg (0.41%, 48.2 g, 8.6 mmol) and PMe<sub>3</sub> (0.8 mL, 8.6 mmol). A color change from blue to red occurred after 2 h with vigorous stirring. The solution was filtered through celite and the solvent was removed in vacuo leaving a red-brown solid. The residue was extracted with Et<sub>2</sub>O (50 mL) and filtered. The filtrate was concentrated until crystallization occurred, then cooled to -30° for 12 h. The product, a red-orange powder, was isolated by filtration and dried in vacuo. The mother liquor was reduced in vacuo and cooled to -30°. An additional crop was collected by the above procedure to give a total yield of 1.21 g (60% yield).

$[\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}(\text{PMe}_3)_3]_x(\text{N}_2)$  can be crystallized as an orange powder which contains solvated THF ( $0.5 \text{ eq. dimer}^{-1}$ ) from concentrated THF solutions cooled to  $-30^\circ$ .

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 270 and 89.6 MHz; IX, 39-1B, 2B, 1C through 6C;  $80^\circ$  to  $-70^\circ$ ):

(89.6 MHz;  $60^\circ$ ): 1.351 (t, 18,  $^2J_{\text{PH}} = 3.03 \text{ Hz}$ ,  $\text{PMe}_3(\text{A})$ ); 0.701 (d, 12,  $^2J_{\text{PH}} = 3.91 \text{ Hz}$ ,  $\text{PMe}_3(\text{B})$ ); 0.43 (br, 2, olefinic H).

(89.6 MHz;  $0^\circ$ ): coalescence of  $\text{PMe}_3(\text{A})$  and  $\text{PMe}_3(\text{A}')$ .

(89.6 MHz;  $-60^\circ$ ): 1.503 (br, 9,  $\text{PMe}_3(\text{A})$ ); 1.229 (br, 9,  $\text{PMe}_3(\text{A}')$ ); 0.745 (br, 2, olefinic H); 0.518 (d, 11,  $^2J_{\text{PH}} = 4.69 \text{ Hz}$ ,  $\text{PMe}_3(\text{B})$ ).

At  $T_c = 0^\circ \pm 10^\circ\text{C}$ ,  $\Delta\nu = 25 \pm 5 \text{ Hz}$  and  $\Delta G^\ddagger = 14 \pm 1 \text{ kcal mol}^{-1}$ .

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 22.5 and 62.83 MHz; IX, 39-1E through 9E; 40-1A through 6A;  $\{^1\text{H}\}$  and gated  $\{^1\text{H}\}$ ;  $30^\circ$  to  $-60^\circ$ ):

(22.5 MHz;  $30^\circ$ ): 30.27 (tt,  $^2J_{\text{PC}} \approx 6 \text{ Hz}$ ,  $^1J_{\text{CH}} = 144 \text{ Hz}$ ,  $\underline{\text{CH}_2\text{CH}_2}$ );

16.53 (qt,  $^1J_{\text{PC}} = 9.76 \text{ Hz}$ ,  $^1J_{\text{CH}} = 126 \text{ Hz}$ ,  $\text{PMe}_3(\text{A})$ ); 14.56 (qd,  $^1J_{\text{PC}} = 10.74 \text{ Hz}$ ,  $^1J_{\text{CH}} = 127 \text{ Hz}$ ,  $\text{PMe}_3(\text{B})$ ).

(62.83 MHz;  $-30^\circ$ ): 29.48 (m,  $\underline{\text{CH}_2\text{CH}_2}$ ); 29.03 (m,  $\text{CH}_2\underline{\text{CH}_2}$ ); 16.21 (br t,  $\text{PMe}_3(\text{A})$ ); 13.89 (br s,  $\text{PMe}_3(\text{B})$ ).

$^{31}\text{P}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 109.3 and 36.2 MHz; IX, 39-1A through 4A; 39-1D through 6D;  $\{^1\text{H}\}$ ;  $80^\circ$  to  $-70^\circ$ ):

(36.2 MHz;  $60^\circ$ ): -14 (s, 2,  $\text{PMe}_3(\text{A})$ ); -46.4 (br s, 1,  $\text{PMe}_3(\text{B})$ ).

(109.3 MHz;  $-30^\circ$ ): coalescence of  $\text{PMe}_3(\text{B})$  and free  $\text{PMe}_3$ .

(109.3 MHz;  $-70^\circ$ ): -14.3 (d,  $^2J_{\text{PAPB}} = 10.2 \text{ Hz}$ ,  $\text{PMe}_3(\text{A})$ ); -45 (t,  $^2J_{\text{PAPB}} = 10.3 \text{ Hz}$ ,  $\text{PMe}_3(\text{B})$ ).

At  $T_c = 30 \pm 10^\circ\text{C}$ ,  $\Delta\nu = 1847 \pm 5 \text{ Hz}$  and  $\Delta G^\ddagger = 10 \pm 1 \text{ kcal mol}^{-1}$ .

IR ( $\text{cm}^{-1}$ ; Nujol/NaCl; IX, 40-1): 960, s ( $\nu_{\text{P-C}}$ ).

Preparation of  $[\text{Ta}(\text{C}_2\text{H}_4)\text{Br}(\text{PMe}_3)_3]_x(\text{N}_2)$  (VII, 53)

$\text{Ta}(\text{C}_2\text{H}_4)\text{Br}_3(\text{PMe}_3)_2$  (0.6 g, 1.0 mmol) was reacted with Na/Hg (0.41%, 11.2 g, 2.0 mmol) and  $\text{PMe}_3$  (0.6 mL, 6.0 mL, excess) in 20 mL of a 1:1  $\text{Et}_2\text{O}$ /THF solution. The solution turned red after stirring vigorously for 2.5 h at 25°.  $[\text{Ta}(\text{C}_2\text{H}_4)\text{Br}(\text{PMe}_3)_3]_x(\text{N}_2)$  (0.3 g) was isolated as red crystals containing solvated  $\text{Et}_2\text{O}$  by following a similar procedure used for the chloro-analog (see above) (60% yield).

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{H}_6$ ; 60 MHz; VII, 53-1; 25°): 1.50 (t,  $^2J_{\text{PH}} = 3.3$  Hz,  $\text{PMe}_3(\text{A})$ ); 0.72 (d,  $^2J_{\text{PH}} = 4.6$  Hz,  $\text{PMe}_3(\text{B})$ ).

Preparation of  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}(\text{PMe}_3)_4$  (IX, 28)

$\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2$  (2.33 g, 5.0 mmol) was dissolved in 75 mL of a 1:1  $\text{Et}_2\text{O}$ /THF solution, under Ar.  $\text{PMe}_3$  (1.1 mL, 10.5 mmol, excess) and Na/Hg (0.41%, 56.1 g, 10.0 mmol) were added via syringe and stirred for 2.5 h at 25° giving an emerald green solution. The solvent was removed in vacuo leaving a red-brown residue. De-nitrogenated  $\text{Et}_2\text{O}$  (120 mL) was added to the residue and the solution was filtered. The volume was concentrated in vacuo to ~30 mL and cooled to -78° for 2 h. The mother liquor was decanted. The remaining violet crystals were dissolved in 30 mL of  $\text{Et}_2\text{O}$  and cooled to -10° overnight. The mother liquor was again decanted and the product was dried in vacuo. Crude  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}(\text{PMe}_3)_4$  was dissolved in 20 mL of  $\text{Et}_2\text{O}$  containing ~0.2 mL of  $\text{PMe}_3$  to give a cloudy green solution. The solution was filtered and cooled to -78° for 2 h. The product, 0.62 g of violet crystals containing solvated  $\text{PMe}_3$  were isolated by decanting the mother liquor and dried in vacuo. Greenish  $\text{Et}_2\text{O}$  solutions of  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}(\text{PMe}_3)_4$  quickly turn brown upon exposure to dry dinitrogen. No attempt was

made to collect any additional product from the mother liquors above (23% yield).

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 250 MHz; IX, 41-1C, 2C; 25°): 2.210 (quintet, 4,  $^3\text{J}_{\text{PH}} = 3.68$  Hz,  $\text{C}_2\text{H}_4$ ); 1.374 (t, 36,  $^2\text{J}_{\text{PH}} = 2.39$  Hz,  $\text{PMe}_3$ ).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_5\text{CD}_3$ ; 22.5 MHz; IX, 41-1A through 9A;  $\{^1\text{H}\}$  and gated  $\{^1\text{H}\}$ ; 30° and -30°):

(30°): 35.39 (tm,  $^2\text{J}_{\text{PC}} = 3.5$  Hz,  $^1\text{J}_{\text{CH}} = 149$  Hz,  $\text{C}_2\text{H}_4$ ); 33.34 (qt,

$^1\text{J}_{\text{PC}} = 8.55$  Hz,  $^1\text{J}_{\text{CH}} = 126$  Hz,  $\text{PMe}_3$ ).

There were no resonances attributable to  $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}(\text{PMe}_3)_4$  at 30° or -30°, by  $^{31}\text{P}$  NMR (IX, 41, 1B, 2B). However, free  $\text{PMe}_3$  was seen by  $^{31}\text{P}$ ,  $^{13}\text{C}$ , and  $^1\text{H}$  NMR.

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Appendix I

Organization of Notebooks and Spectra

## Appendix I

Nine notebooks (I-IX) were used to record experimental data for the research presented in this thesis. Each experiment is identified by a notebook number followed by the page number on which it is found (e.g. Preparation of  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{C}_2\text{H}_5)_2$  (IV, 24) is located in notebook IV on page 24). The NMR spectra are referenced to the field strength of the nucleus observed, followed by the page number and the notebook in which it is located [e.g. the 270 MHz  $^1\text{H}$  NMR spectrum of  $\text{Nb}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$ ; N(270)-58-1-1 through N(270)-58-3-1, is on page 58, spectra 1 through 3 located in notebook I). For convenience the spectra are organized in the following manner: NMR spectra for each experiment (except 60 and 90 MHz  $^1\text{H}$  NMR spectra) were collected and bound with any IR data. These data are in the order in which they appear in the experimental section of this thesis.

All kinetic data (with graphs and calculations) were collected and placed in a folder so marked. The GLC traces are collected per chapter and placed in separate folders in the order in which they appear in the experimental section.

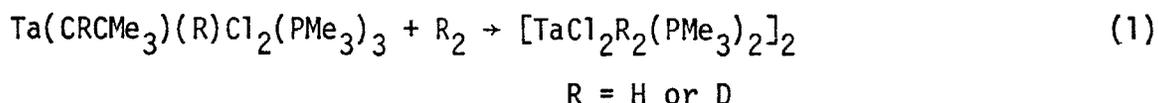
Appendix II

Synthesis, Characterization, and Reactions of  $[\text{TaCl}_2\text{H}_2(\text{PMe}_3)_2]_2$

Appendix II

The recent report of CO insertion into a bridging tantalum hydride bond to give a stabilized formyl complex is of theoretical as well as of practical interest.<sup>80</sup> The number of known hydride complexes of tantalum is relatively small. In an effort to extend the number of known species of this type hydrogen was reacted with  $\text{Ta}(\text{CHCMe}_3)(\text{H})\text{Cl}_2(\text{PMe}_3)_3$ .

$\text{Ta}(\text{CHCMe}_3)(\text{H})\text{Cl}_2(\text{PMe}_3)_3$  reacts with  $\text{H}_2$  to give emerald crystals which analyze as  $[\text{TaCl}_2\text{H}_2(\text{PMe}_3)_2]_2$ . The deuterio analogue can be prepared by reacting  $\text{D}_2$  with  $\text{Ta}(\text{CDCMe}_3)(\text{D})\text{Cl}_2(\text{PMe}_3)_3$  (equation 1).



The infrared spectrum of  $[\text{TaCl}_2\text{H}_2(\text{PMe}_3)_2]_2$  shows a medium strength absorbance at  $1224 \text{ cm}^{-1}$  which shifts to  $870 \text{ cm}^{-1}$  for  $[\text{TaCl}_2\text{D}_2(\text{PMe}_3)_2]_2$ . The hydride stretch is in the range commonly expected for a bridging hydride.<sup>61c</sup>

A cryoscopic molecular weight determination of  $[\text{TaCl}_2\text{H}_2(\text{PMe}_3)_2]_2$  was found to be low for a dimer (mol. wt., found 580). The insolubility of  $[\text{TaCl}_2\text{H}_2(\text{PMe}_3)_2]_2$  may be responsible for the low results obtained.

The  $^1\text{H}$  NMR spectrum of  $[\text{TaCl}_2\text{H}_2(\text{PMe}_3)_2]_2$  shows two phosphorous coupled multiplets at 8.80 and 1.48 ppm in a 1:9 ratio for the hydride and  $\text{PMe}_3$  ligands, respectively. Also, only one resonance is observed by  $^{31}\text{P}\{^1\text{H}\}$  NMR. Selective  $^1\text{H}$  decoupling at 1.48 ppm splits the single resonance into a broad quintet ( $J_{\text{PH}} \approx 3 \text{ Hz}$ ), indicating the presence of four hydride ligands.

The  $^{13}\text{C}$  NMR spectrum of  $[\text{TaCl}_2\text{H}_2(\text{PMe}_3)_2]_2$  shows a pattern which is best described as two overlapping triplets. This indicates that the  $\text{PMe}_3$  ligands are magnetically inequivalent.  $[\text{TaCl}_2\text{H}_2(\text{PMe}_3)_2]_2$  can also be prepared in good yield by reacting  $\text{H}_2$  with  $[\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_5)\text{Cl}_2(\text{PMe}_3)_2 \rightleftharpoons \text{Ta}(\text{CH}_2\text{CMe}_3)(\text{C}_2\text{H}_4)\text{Cl}_2(\text{PMe}_3)_2]$ .

Although only neutron diffraction studies would be able to determine the exact location of the hydrogen atoms, the fact that only one Ta-H stretch is observed indicates that only one type of hydride is present. The only other dinuclear hydride complex of this type is  $\text{Re}_2\text{H}_8(\text{PR}_3)_4$ .<sup>81</sup> It is reasonable to assume  $[\text{Ta}_2\text{Cl}_2\text{H}_2(\text{PMe}_3)_2]_2$  to be of similar structure.<sup>82</sup>

$[\text{TaCl}_2\text{H}_2(\text{PMe}_3)_2]_2$  does not react with CO (30 psi) after 16 h at  $60^\circ\text{C}$ . It does react with ethylene to give an unidentified brown crystalline compound.

ExperimentalPreparation of  $[\text{TaCl}_2\text{H}_2(\text{PMe}_3)_2]_2$ 1. From  $[\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_5)\text{Cl}_2(\text{PMe}_3)_2]$   $\rightleftharpoons$   $[\text{Ta}(\text{CH}_2\text{CMe}_3)(\text{C}_2\text{H}_4)\text{Cl}_2(\text{PMe}_3)_2]$  (VIII, 7)

$[\text{Ta}(\text{CHCMe}_3)(\text{C}_2\text{H}_5)\text{Cl}_2(\text{PMe}_3)_2] \rightleftharpoons [\text{Ta}(\text{CH}_2\text{CMe}_3)(\text{C}_2\text{H}_4)\text{Cl}_2(\text{PMe}_3)_2]$  (4.62 g, 9.18 mmol) was dissolved in 30 mL of  $\text{Et}_2\text{O}$  containing  $\text{PMe}_3$  (0.9 mL, ~9 mmol) and reacted with  $\text{H}_2$  (40 psi) at  $25^\circ$ . After 24 h a green powder precipitated from solution.  $\text{Et}_2\text{O}$  (100 mL) was added and the solution was filtered. The volume was reduced (in vacuo) to 50 mL and 2.37 g of green crystals were collected by filtration, washed with cold  $\text{Et}_2\text{O}$  and dried in vacuo. Repeating the above procedure gave an additional 0.36 g.  $[\text{TaCl}_2\text{H}_2(\text{PMe}_3)_2]_2$  can be isolated as large green crystals from concentrated toluene solutions at  $-30^\circ$ . Exposure to a vacuum causes these crystals to become a powder (73% yield).

2. From  $\text{Ta}(\text{CMe}_3)(\text{R})\text{Cl}_2(\text{PMe}_3)_3$ ; R=D (VIII, 46)

$\text{Ta}(\text{CMe}_3)(\text{D})\text{Cl}_2(\text{PMe}_3)_3$  was reacted with  $\text{D}_2$  (40 psi) for 24 h. Following the above procedure gave 0.2 g of green needles (84% yield).  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$  does not react with  $\text{H}_2$  (40 psi) in the presence of  $\text{PMe}_3$  after 16 h at  $25^\circ$  (VII-46).

Molecular Weight (benzene, VIII, 8): Calculated: 810. Found: 580.

Anal. (VIII, 12; VIII, 12-5): Calcd. for  $\text{Ta}_2\text{C}_{12}\text{H}_{38}\text{Cl}_4\text{P}_4$ : C, 17.79; H, 4.73. Found: C, 17.71; H, 5.12.

$^1\text{H}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 270 MHz; VII, 37-2A;  $25^\circ$ ): 8.80 (m, 1,  $J_{\text{HP}} \approx 8.5$  Hz, Ta-H); 1.48 (m, 9,  $J_{\text{HP}} \approx 4$  Hz,  $\text{PMe}_3$ ).

$^{13}\text{C}$  NMR ( $\delta$ ;  $\text{C}_6\text{D}_6$ ; 22.5 MHz; VIII, 54-1c, 2c;  $\{^1\text{H}\}$ ;  $30^\circ$ ): 14.53 (t,  $J_{\text{CP}} = 11.72$  Hz,  $\text{PMe}_3$ ); 14.32 (t,  $J_{\text{CP}} = 11.72$  Hz,  $\text{PMe}_3'$ ).

<sup>31</sup>P NMR ( $\delta$ ; C<sub>6</sub>D<sub>6</sub>; 109 and 36 MHz; VIII, 54, 1D, 2D, 5D; 55-1A, 3A; {<sup>1</sup>H} and selective {<sup>1</sup>H} at 1.48 ppm; -30° and 30°): -3.4 (quintet, <sup>2</sup>J<sub>PH</sub>  $\approx$  3 Hz).

IR (cm<sup>-1</sup>; Nujol/NaCl; VIII, 7, 1; 46, 1): 1224, m

( $\nu_{\text{TaH}}$ ); 870, m ( $\nu_{\text{TaD}}$ ).

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