

TANTALUM AND NIOBIUM ALKYLIDENE COMPLEXES VIA
LIGAND INDUCED alpha-HYDROGEN ABSTRACTION

by

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TO MY PARENTS.....

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ABBREVIATIONS USED IN THE TEXT

bipy	2,2'-bipyridyl
br	broad (NMR)
Bu	butyl
C_{α}	carbon bound to the metal
C_{β}	carbon bound to C_{α}
C_{γ}	carbon bound to C_{β}
Cp	cyclopentadienyl, cyclopentadienide
Cp''	pentamethylcyclopentadienyl, pentamethylcyclopentadienide
d	doublet (NMR)
δ	chemical shift in ppm downfield from the reference
diars	1,2-bis(dimethylarsino)benzene
diox	1,4-dioxane
diphos	1,2-bis(diphenylphosphino)ethane
dmpe	1,2-bis(dimethylphosphino)ethane
ϵ	extinction coefficient (UV-VIS)
Et	ethyl
GLC	gas-liquid chromatography
H_{α}	hydrogen bound to C_{α}
H_{β}	hydrogen bound to C_{β}
IR	infrared
J	NMR coupling constant
L	neutral, $2e^{-}$, σ -donor ligand
m	multiplet (NMR), moderate (IR)
M	transition metal (usually Nb or Ta)

ABBREVIATIONS (continued)

Me	methyl
Mes	mesityl (2,4,6-trimethylphenyl)
NMR	nuclear magnetic resonance
Ph	phenyl
Pr	propyl
py	pyridine
q	quartet (NMR)
R	alkyl,aryl
RT	room temperature
s	singlet (NMR)
t	triplet (NMR)
τ	chemical shift for ^1H NMR in 10 ⁻⁸
THF	tetrahydrofuran
THT	tetrahydrothiophene
tmeda	1,2-bis(dimethylamino)ethane
TMS	tetramethylsilane
μ	micron
UV-VIS	ultraviolet-visible
ν	IR absorption
vw	very weak (IR)
w	weak (IR)
X	halide (usually Cl or Br)

NUMBERING SCHEME FOR COMPOUNDS IN THE TEXT

- 1 $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$
- 2 $\text{Ta}(\eta^2\text{-CH}_2=\text{CHCH}_2\text{CMe}_3)(\text{CH}_2\text{CMe}_3)_3$
- 3 $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$
- 4 $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_2\text{Ph})_2$
- 5 $\text{Me}_3\text{CCH}=\text{Nb}(\text{CH}_2\text{CMe}_3)_3$
- 6 $\text{Nb}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$
- 7 $\text{Nb}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_2\text{Ph})_2$
- 8 $[\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{dmpe})]_x$
- 9 $[\text{Me}_3\text{CC}\equiv\text{Ta}(\text{CH}_2\text{CMe}_3)_3]\cdot\text{Li}(\text{tmeda})$
- 10 $\text{Ta}[\text{NC}(\text{Me})=\text{CHCMe}_3]_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2(\text{NCMe})$
- 11 $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3(\text{PMe}_3)$
- 12 $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Cl}_3]_2$
- 13 $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$
- 14 $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_2\text{Ph})\text{Cl}_3]_2$
- 15 $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PPh}_2\text{Me})\text{Cl}_3]_2$
- 16 $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Br}_3]_2$
- 17 $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_2\text{Ph})_2$
- 18 $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PPh}_2\text{Me})_2$
- 19 $\text{Me}_3\text{CCH}=\text{TaBr}_3(\text{PMe}_3)_2$
- 20 $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_3)_2$
- 21 $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_2\text{Ph})_2$
- 22 $[\text{Me}_3\text{CCH}=\text{Nb}(\text{PMe}_3)\text{Cl}_3]_2$
- 23 $[\text{Me}_3\text{CCH}=\text{Nb}(\text{PMe}_2\text{Ph})\text{Cl}_3]_2$

NUMBERING SCHEME FOR COMPOUNDS (continued)

- 24 $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{THF})_2$
 25 $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{THF})_2$
 26 $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{py})_2$
 27 $\text{Me}_3\text{CCH}=\text{TaBr}_3(\text{THF})_2$
 28 $\text{Me}_3\text{CCH}=\text{TaBr}_3(\text{THT})_2$
 29 $[\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})]_x$
 30 $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})$
 31 $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{tmeda})$
 32 $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{bipy})$
 33 $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{diars})$
 34 $\text{Me}_3\text{CCH}=\text{TaBr}_3(\text{dmpe})$
 35 $\text{Me}_3\text{CCH}=\text{TaBr}_3(\text{diphos})$
 36 $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{dmpe})$
 37 $\text{Me}_3\text{SiCH}=\text{TaCl}_3(\text{PMe}_3)_2$
 38 $(\text{Me}_3\text{CCH}_2)\text{TaCl}_4(\text{PMe}_3)_2$
 39 $\text{TaCl}_5(\text{PMe}_3)_2$
 40 $\text{Me}_3\text{CCH}=\text{C}(\text{Me})\text{N}=\text{TaCl}_3(\text{PMe}_3)_2$
 41 $\text{Me}_3\text{CCH}=\text{C}(\text{Me})\text{N}=\text{NbCl}_3(\text{PMe}_3)_2$
 42 $\text{Ta}(\eta^2\text{-O}=\text{C}=\text{CHCMe}_3)\text{Cl}_3(\text{PMe}_3)_2$
 43 $\text{Nb}(\eta^2\text{-O}=\text{C}=\text{CHCMe}_3)\text{Cl}_3(\text{PMe}_3)_2$
 44 $\text{Ta}(\eta^2\text{-O}=\text{C}=\text{CHCMe}_3)\text{Cl}_3(\text{dmpe})$
 45 $\text{CpTa}(\text{CHCMe}_3)\text{Cl}_2$
 46 $\text{CpNb}(\text{CHCMe}_3)\text{Cl}_2$
 47 $\text{Cp}^*\text{Ta}(\text{CHCMe}_3)\text{Cl}_2$

NUMBERING SCHEME FOR COMPOUNDS (continued)

- $\sim\sim$ Cp"Nb(CHCMe₃)Cl₂
 $\sim\sim$ Me₃CCH=Ta(OCMe₃)₂Cl(PMe₃)
 $\sim\sim$ Me₃CCH=Nb(OCMe₃)₂Cl(PMe₃)
 $\sim\sim$ Ta(C₂H₄)(PMe₃)₂Cl₃
 $\sim\sim$ Ta(C₂H₄)(PMe₂Ph)₂Cl₃
 $\sim\sim$ Ta(C₂H₄)(PPh₂Me)₂Cl₃
 $\sim\sim$ [Ta(C₂H₄)(PMe₃)Cl₃]₂
 $\sim\sim$ [Ta(C₂H₄)(PMe₂Ph)Cl₃]₂
 $\sim\sim$ [Ta(C₂H₄)(PPh₂Me)Cl₃]₂
 $\sim\sim$ [Nb(PMe₃)₂Cl₃]₂
 $\sim\sim$ [Nb(PMe₂Ph)₂Cl₃]₂
 $\sim\sim$ [Nb(PMe₃)Cl₃]_x
 $\sim\sim$ Ta(CH₂=CHMe)(PMe₃)₂Cl₃
 $\sim\sim$ Ta(CH₂=CHMe)(PMe₂Ph)₂Cl₃
 $\sim\sim$ Ta(CH₂=CHMe)(PPh₂Me)₂Cl₃
 $\sim\sim$ [Ta(CH₂=CHMe)(PMe₃)Cl₃]₂
 $\sim\sim$ [Ta(CH₂=CHMe)(PMe₂Ph)Cl₃]₂
 $\sim\sim$ [Ta(CH₂=CHMe)(PPh₂Me)Cl₃]₂
 $\sim\sim$ Ta(CH₂=CHPh)(PMe₃)₂Cl₃
 $\sim\sim$ Ta(C₂H₄)(PMe₃)₂(OCMe₃)₂Cl
 $\sim\sim$ Me₃CCH=Ta(CH₂PMe₂)Br₂(PMe₃)₂
 $\sim\sim$ [Ta(μ-CSiMe₃)(CH₂SiMe₃)₂]₂
 $\sim\sim$ Me₃SiCH=Ta(CH₂SiMe₃)₃
 $\sim\sim$ Me₃SiCH=Ta(CH₂SiMe₃)₃(PMe₃)

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TANTALUM AND NIOBIUM ALKYLIDENE COMPLEXES VIA
LIGAND INDUCED α -HYDROGEN ABSTRACTION

by

GREGORY ANDREW RUPPRECHT

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ABSTRACT

Chapter 1.

The reaction of $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$ with ethylene, which yields $\text{Ta}(\eta^2\text{-CH}_2=\text{CHCH}_2\text{CMe}_3)(\text{CH}_2\text{CMe}_3)_3$ initially, is discussed. In the presence of PMe_3 , however, $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$ is shown to catalytically dimerize ethylene to 1-butene selectively. The reactions of $\text{Me}_3\text{CCH}=\text{M}(\text{CH}_2\text{CMe}_3)_3$ ($\text{M}=\text{Nb}, \text{Ta}$) with PMe_3 or PMe_2Ph which yield bisneopentylidene complexes of the type $\text{M}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PR}_3)_2$ and neopentane via a ligand induced α -hydrogen abstraction process are described. The tantalum bisneopentylidene complexes are shown to be efficient catalysts for the selective production of 1-butene from ethylene at 25°C at a rate of $2.5 \text{ Ta}^{-1}\text{min}^{-1}$ by a mechanism involving metallocyclopentanes. Other reaction chemistry of the bisneopentylidene complexes which demonstrates the nucleophilicity of the neopentylidene ligands is described.

Chapter 2.

The reactions of dineopentyl trihalide complexes of Nb and Ta with neutral, $2e^-$, σ -donor ligands are described. The products of these reactions which are monomeric or dimeric mononeopentylidene complexes, $\text{Me}_3\text{CCH}=\text{MX}_3\text{L}_2$ or $[\text{Me}_3\text{CCH}=\text{MLX}_3]_2$, are formed via a ligand induced α -hydrogen abstraction

process. The characterization of a large class of these mononeopentylidene complexes in which monodentate or bidentate amines, phosphines, arsines, ethers, or sulfides are incorporated is reported. The neutron diffraction structure of one of these complexes, $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Cl}_3]_2$, which demonstrates the existence of a strong interaction between the $\text{C}_\alpha\text{-H}_\alpha$ bond and the metal center, is described.

Chapter 3.

The reaction chemistry of the mononeopentylidene complexes of Nb and Ta which demonstrates the nucleophilicity of the neopentylidene ligand is reported. These complexes react rapidly with the unsaturated functional groups of organic compounds. The preparation of imido and ketene complexes by this method is described. The application of halide replacement reactions to the mononeopentylidene complexes to yield new complexes such as $\text{Cp}^*\text{Nb}(\text{CHCMe}_3)\text{Cl}_2$ and $\text{Me}_3\text{CCH}=\text{Ta}(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ is discussed. The reactions of the mononeopentylidene complexes with olefins are described. The characterization of the resulting olefin complexes is reported. The catalytic dimerization of ethylene and the catalytic metathesis of cis-2-pentene by $\text{Me}_3\text{CCH}=\text{Ta}(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ is described. The thermolysis of the mononeopentylidene complexes is shown to yield products from the coupling of the neopentylidene ligands.

Thesis Supervisor: Richard R. Schrock

Title: Associate Professor

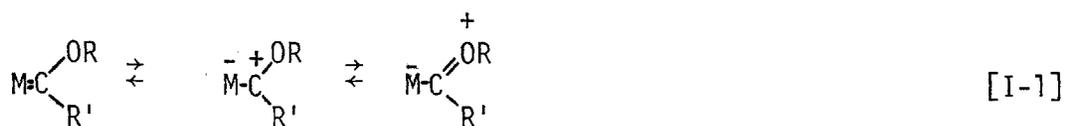
INTRODUCTION

Organotransition metal chemistry has been developing rapidly since the discovery of ferrocene almost 30 years ago.¹ Much of the emphasis in this work, however, has been devoted to the study of the later transition metals of Group VIII. The organometallic chemistry of the early transition elements, which has not been investigated as fully, is both theoretically interesting and industrially useful. For example many isolable carbene or alkylidene complexes^a are derived from the early transition metals. This includes the first carbene complex, $(OC)_5W=C(OMe)Ph$, which was prepared by Fischer in 1964.² Since then a large class of complexes of this general type has been prepared and characterized.³

Transition metal carbene complexes have been postulated as intermediates in a number of important reactions. These include olefin metathesis,⁴ Fischer-Tropsch reduction of CO by H₂,⁵ rearrangement of strained ring hydrocarbons,⁶ cyclopropanation of olefins with diazoalkanes,⁷ Ziegler-Natta oligomerization of olefins,⁸ and decomposition of transition metal alkyl complexes.⁹

In the fifteen years since the first carbene complex, few complexes possessing alkylidene ligands (i.e., carbene ligands consisting of only carbon and hydrogen) have been prepared. Alkylidene complexes may be more reactive and less stable than similar Fischer carbene complexes. The reason for this is that the Fischer carbene ligands are stabilized by resonance structures involving the nonbonded electron pairs of the heteroatom (Eq. I-1).

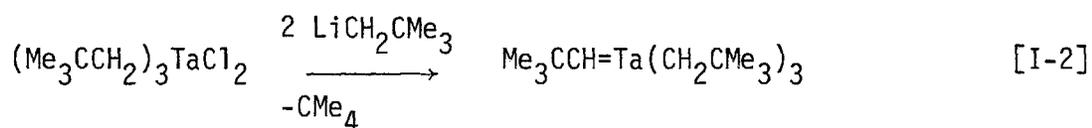
^aA carbene or alkylidene complex possesses a metal-to-carbon double bond.



Fischer carbene complexes are also 18 e⁻ complexes in which the transition metal is in a low oxidation state and in which the carbene ligand (as characterized by its reaction chemistry¹⁰) is electrophilic.^a

A few alkylidene complexes, which are similar to Fischer carbene complexes, have been prepared, however. These include primary alkylidene complexes - (OC)₅W=CHPh,¹¹ Cp(OC)₂Re=CHPh,¹² and Cp(OC)₂Fe=CHPh¹³ - as well as secondary alkylidene complexes - (OC)₅W=CPh₂,¹⁴ (OC)₅Cr(2,3-diphenylcyclopropenylidene),¹⁵ Cp(OC)₂Fe(benzocyclobutenylidene)⁺,¹⁶ and Cp(OC)₂Mn=CPh₂.¹⁷ Like Fischer carbene complexes, these alkylidene complexes are all 18 e⁻ complexes which possess a metal in a low oxidation state and which have various resonance structures.

In contrast, the first primary alkylidene complex, which was Me₃CCH=Ta(CH₂CMe₃)₃,¹⁸ is completely different from either the Fischer carbene complexes or the alkylidene complexes discussed above. This complex, which was prepared by Schrock through an α-hydrogen abstraction process (Eq. I-2), is only a 10 e⁻ complex with a metal in a relatively high



oxidation state. This complex possesses no resonance stabilizing structures and has a nucleophilic neopentylidene ligand.^b Therefore, the metal-carbon

^aIn an electrophilic carbene ligand, the polarization of the M-C bond is M(δ⁻)=C(δ⁺).

^bIn a nucleophilic alkylidene ligand, the polarization of the M-C bond is M(δ⁺)=C(δ⁻).

double bond is polarized in a manner opposite to that of the Fischer carbene complexes but similar to that of main group analogues such as phosphorous ylids. Since the discovery of this tantalum neopentylidene complex many other nucleophilic alkylidene complexes of Nb and Ta¹⁹ have been prepared, including the first methylene complex, $\text{Cp}_2\text{Ta}(\text{CH}_2)\text{Me}$.²⁰

Other interesting complexes which possess carbon multiply bonded to the metal include biscarbene complexes - $\text{cis}-(\text{OC})_4\text{Cr}[\overline{\text{CN}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})}]_2$ ²¹ and $(\text{MeNC})_4\text{Os}[\text{C}(\text{NHMe})_2]_2$ ^{+2 22} - and triscarbene complexes - $(\text{OC})\text{Ir}[\overline{\text{CN}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})}]_3$ ^{+ 21} and $(\text{MeNC})_3\text{Os}[\text{C}(\text{NHMe})_2]_3$ ^{+2 22}. Alkylidyne complexes^a - $\text{Cl}(\text{OC})_4\text{W}\equiv\text{CPh}$,²³ $\text{Me}_3\text{CC}\equiv\text{Ta}(\text{CH}_2\text{CMe}_3)_3^-$,²⁴ and $\text{Cp}[\text{P}(\text{OMe})_3]_2\text{Mo}\equiv\text{CCH}_2\text{CMe}_3$ ²⁵ - have also been prepared.

This work describes research dealing with attempts to devise new routes to yield metal-to-carbon multiply bonded species from Nb and Ta alkyl complexes. Previously, α -hydrogen abstraction,¹⁸ deprotonation,²⁰ dehydrohalogenation,²⁶ and alkylidene transfer reactions²⁷ had been successfully employed in this endeavor. The new method described in this text is a variation on the α -hydrogen abstraction reaction. A crowded coordination sphere as well as an electron deficient metal center are required for α -hydrogen abstraction to occur. Formerly, a crowded coordination sphere was generally achieved by attaching bulky, anionic groups ($-\text{CH}_2\text{Ph}$, $-\text{CH}_2\text{CMe}_3$, $-\text{CH}_2\text{SiMe}_3$, C_5H_5^- , or C_5R_5^-) to the metal through σ or π covalent bonds. In the new approach neutral, $2 e^-$, σ -donor ligands are introduced to the coordination sphere to provide the steric crowding necessary for α -hydrogen abstraction to occur.

This modification has been called ligand induced α -hydrogen abstraction.

^aAn alkylidyne complex possesses a metal-to-carbon triple bond.

In order for this approach to succeed other modes of transition metal alkyl decomposition must be suppressed or eliminated.

These alternate decomposition pathways include α -, β -, and γ -hydrogen elimination, reductive coupling, homolytic bond cleavage, and ligand hydrogen abstraction.²⁸ The application of ligand induced α -hydrogen abstraction to the synthesis of alkylidene, bisalkylidene, and alkylidyne complexes is described below. Many novel complexes with multiple metal-to-carbon bonds have been prepared and characterized. These new complexes of Nb and Ta possess interesting properties in themselves and in their reactions with a variety of organic compounds.

Portions of this research have been published previously.^{29,30,31}

Chapter 1

The Synthesis, Characterization, and Reactions of
Bisalkylidene Complexes of Niobium and Tantalum

INTRODUCTION

Carbene complexes or intermediates have been implicated in many catalytic systems.⁴⁻⁸ For this reason, the reactions of the first primary alkylidene complex, $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$,¹⁸ with olefins were investigated. It was discovered that ethylene can be catalytically dimerized to 1-butene in the presence of this neopentylidene complex and PMe_3 .³² The first part of this chapter deals with the study of this reaction. The reaction of $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$ with ethylene is complex. Only the initial unstable intermediate $\text{Ta}(\eta^2\text{-CH}_2=\text{CHCH}_2\text{CMe}_3)(\text{CH}_2\text{CMe}_3)_3$ can be observed. The reaction of $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$ with PMe_3 , however, is much more straightforward. The product is a stable bisalkylidene complex, $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$. This reaction is an example of a ligand induced α -hydrogen abstraction which is believed to occur through a five coordinate intermediate. The second part of this chapter is concerned with some of the reaction chemistry of bisalkylidene complexes including the role of these complexes in the catalytic dimerization of ethylene to 1-butene.

Biscarbene complexes are not numerous but have been observed in other systems. Indeed, some of the Chugaev salts³³ which were first prepared in 1915 have been shown to contain chelating biscarbene ligands (i.e. $\text{MeNH}-\ddot{\text{C}}-\text{NH}-\text{NH}-\ddot{\text{C}}-\text{NHMe}$).³⁴ The preparation of these biscarbene complexes involved the attack of hydrazine on isocyanide ligands in Pd or Pt complexes. Recently, the attack of amines³⁵ and alcohols³⁶ on isocyanide ligands of various transition metal complexes has led to the preparation of carbene complexes. The application of this method to complexes containing a number of isocyanide ligands can lead to the preparation of biscarbene complexes. An example of this is the synthesis²² of

$(\text{MeNC})_4\text{Os}[\text{C}(\text{NHMe})_2]_2^{+2}$ from the reaction of $\text{Os}(\text{CNMe})_6^{+2}$ and MeNH_2 . The reaction of electron rich olefins with transition metal complexes can also yield carbene complexes.³⁷ Many biscarbene complexes have synthesized with this procedure.^{21,38} These include trans- $\text{RhCl}(\text{CO})\text{L}_2$, AuL_2^+ , trans- $\text{NiCl}(\text{PPhEt}_2)\text{L}_2^+$, and cis- $\text{PtCl}(\text{PPh}_3)\text{L}_2^+$ (where $\text{L} = \overline{\text{CN}(\text{Me})\text{CH}_2\text{CH}_2\text{N}(\text{Me})}$ or $\overline{\text{CN}(\text{Me})\text{C}_6\text{H}_4\text{S}}$).

In addition to $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$, other bisalkylidene complexes are known. These include $\text{Ta}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$ and $\text{CpTa}(\text{CHCMe}_3)_2(\text{PMe}_3)$.²⁹ These examples and those discussed above indicate that this "novel" type of complex may be far more stable and more common than it was previously believed to be possible.

RESULTS AND DISCUSSION

A. Reactions of $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$ with Olefins

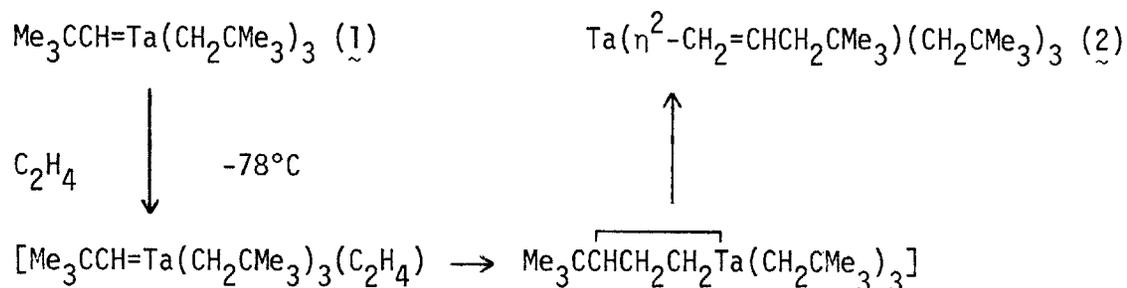
$\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$, $\underline{1}$,^{18a} was the first transition metal complex containing a primary alkylidene ligand. This complex is quite stable thermally either in the solid state or in solution. Due to the electrophilic metal center and the nucleophilic neopentylidene ligand, however, $\underline{1}$ reacts with a number of organic compounds possessing unsaturated functional groups. When the unsaturated group contains a heteroatom such as oxygen or nitrogen, the reaction is stoichiometric and generally yields a well-behaved organometallic complex as the product.^{18b} When the unsaturated group is olefinic, however, the reaction is more complex. The nature of the organometallic product is not always clear and there are usually many organic byproducts.^a

The reaction of $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$, $\underline{1}$, with ethylene is vigorous and exothermic. Even at -78°C the reaction is rapid. An orange toluene solution of $\underline{1}$, on treatment with C_2H_4 at -78°C , immediately becomes a very deep red. Initially, this red color was attributed to an ethylene adduct of $\underline{1}$ such as $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{C}_2\text{H}_4)$. This adduct must be unstable, however, since the only species that is observed at -78°C has been tentatively identified by ^{13}C NMR as $\text{Ta}(\eta^2\text{-CH}_2=\text{CHCH}_2\text{CMe}_3)(\text{CH}_2\text{CMe}_3)_3$, $\underline{2}$. Because it is very soluble and thermally unstable, $\underline{2}$ has not been isolated. Since $\text{Ta}(\eta^2\text{-CH}_2=\text{CHCH}_2\text{CMe}_3)(\text{CH}_2\text{CMe}_3)_3$, $\underline{2}$, is the first observable product, the proposed intermediate (the ethylene adduct) must be converted rapidly to $\underline{2}$.

^aThese reactions were first investigated by R. R. Schrock.³²

This reaction may occur through a metallocyclobutane complex,

$\text{Me}_3\text{CCHCH}_2\text{CH}_2\text{Ta}(\text{CH}_2\text{CMe}_3)_3$, which then yields 2 by a β -hydrogen elimination (Eq. 1-1).

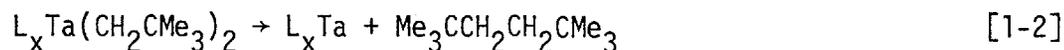


[1-1]

$\text{Ta}(\eta^2\text{-CH}_2=\text{CHCH}_2\text{CMe}_3)(\text{CH}_2\text{CMe}_3)_3$, 2, is stable up to -15°C in the presence or absence of ethylene. If 2 is allowed to warm to 0°C in the absence of ethylene, an intricate decomposition reaction occurs in which $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$, 1, is the major product. The yield of 1 appears to be quite high. Other organometallic and organic compounds are also produced. Although these products are unknown, they probably include CMe_4 and $\text{MeCH}_2\text{CH}_2\text{CMe}_3$ (*vide infra*). The reaction mechanism must be complex and similar in nature to the formation of $\text{Me}_3\text{CC}\equiv\text{W}(\text{CH}_2\text{CMe}_3)_3$ from its postulated precursor, $\text{W}(\text{CH}_2\text{CMe}_3)_3(\text{OEt}_2)_x$.^{39,40}

If a toluene solution of 2 is allowed to decompose at RT under ethylene, the dark red solution lightens very slowly to orange and finally to yellow after 3 hours. At this point there is no further reaction with ethylene. Although this yellow solution does not react with additional ethylene, it is unstable in the absence of excess ethylene. The ^{13}C NMR spectrum

of this yellow solution is very complex. There appear to be several organometallic species present as well as many organic products. This same yellow solution can be obtained much more rapidly in an aliphatic solvent such as pentane.^a If $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$, 1, is dissolved in pentane and allowed to react with C_2H_4 at RT, the orange solution of 1 immediately changes to the deep red color of 2. After 20 mins. the red color has faded to give the final yellow colored solution at which point the consumption of ethylene ceases. Several of the organic products in this solution have been identified by GLC. The major products are neopentane (CMe_4) and neoheptane ($\text{MeCH}_2\text{CH}_2\text{CMe}_3$). These may be produced when either a neopentyl or neoheptyl group perform an α -hydrogen abstraction. The other known products which include 2,2,5,5-tetramethylhexane (dineopentyl) and cis- and trans-2,2,5,5-tetramethyl-3-hexene are listed in Table 1.1. These three C_{10} products can be formed in the reductive elimination of two neopentyl groups (Eq. 1-2) or two neopentylidene groups (Eq. 1-3), respectively. Surprisingly, there is no 4,4-dimethyl-1-pentene ($\text{CH}_2=\text{CHCH}_2\text{CMe}_3$) produced. When measured quantitatively, these five products account for less than two of the four neopentyl or neopentylidene groups originally present in 1. The remaining groups must still be bound to the tantalum.



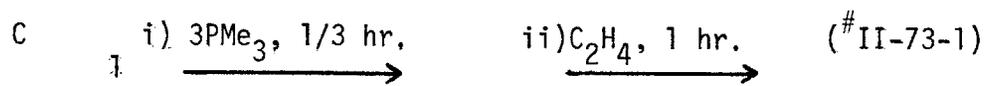
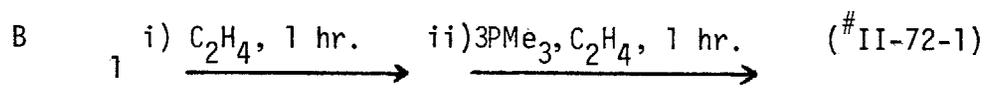
^aAromatic solvents such as benzene or toluene seem to slow the rate of the reaction of 2 with ethylene considerably.



Since the organometallic products of the decomposition of $Ta(\eta^2-CH_2=CHCH_2CMe_3)(CH_2CMe_3)_3$, **2**, under ethylene are unknown, it is not possible to explain how the reaction proceeds. It may be, however, that the initial steps in the decomposition of **2** are identical whether ethylene

Table 1.I. The Yield* of Organic Products from the Reaction of $Me_3CCH=Ta(CH_2CMe_3)_3$, **1**, with C_2H_4

Reaction**	CMe_4						Total	min^{-1}
A	0.624	0.507	0	0.102	0.039	0.141	1.70	0
B	0.517	0.474	0.437	0.114	0.122	0.113	2.13	0.69
C	0.227	0.372	2.82	0.028	0.056	0.009	3.61	2.21

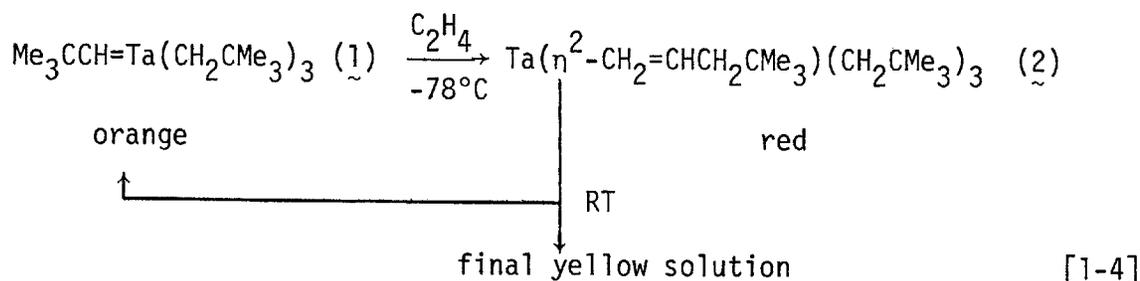


* All yields and rates are absolute and presented in units per Ta. It is possible, however, due to the low stability of these samples that small amounts of the products observed were actually formed during the work up of the sample for analysis rather than in the reaction itself. Despite this the trends discussed in the text are clear.

** All reactions were performed in pentane at 25°C under 50 PSIG of C_2H_4 .

is present or not. In either case then, **2** decomposes to yield primarily $Me_3CCH=Ta(CH_2CMe_3)_3$, **1**, along with small amounts of other organometallic

products. If ethylene is present during the decomposition the regenerated 1 would be converted into more 2 which decomposes until finally all of the tantalum is funneled into the unknown products (Eq. 1-4).



As shown above, the decomposition of 2 is extremely complex. There are several unknown organometallic products, five known organic products, and traces of three unknown organic products. Additionally, 1 is a decomposition intermediate of 2 and no $\text{CH}_2=\text{CHCH}_2\text{CMe}_3$ forms during the decomposition reaction. The three unknown organic products have the longest GLC retention times. These may be 2,2,7,7-tetramethyloctane and cis- and trans-2,2,7,7-tetramethyl-3-octene. These three C_{12} products could be formed in the reductive elimination of a neopentyl and a neoheptyl group or of a neopentylidene and a neoheptylidene group, respectively. This would be similar to the manner in which the C_{10} products are proposed to be formed.

Still unexplained is the fate of the $\text{CH}_2=\text{CHCH}_2\text{CMe}_3$ bound to the tantalum in 2 since this olefin is not one of the final products. Since neoheptane is one of the final products, one explanation involves the use of this olefin as a hydrogen sink. The source of the hydrogen used to reduce the 4,4-dimethyl-1-pentene could be α -hydrogen abstraction and/or elimination reactions which might occur in the decomposition of 2.

Once the reaction of $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$, 1, with C_2H_4 reaches the yellow stage, there is no further change in the solution and no further consumption of ethylene. However, on adding PMe_3 to this yellow solution, R. R. Schrock discovered that the mixture began to take up ethylene again and that the system produced 1-butene catalytically.^{31,32}

The yellow reaction solution changes to red immediately on the addition of several equivalents of PMe_3 . Ethylene is rapidly consumed and 1-butene is selectively produced. Although it was not possible to identify the active catalyst in solution, the organic products were identified by GLC and are listed in Table 1.I. Under these conditions a significant amount of $\text{CH}_2=\text{CHCH}_2\text{CMe}_3$ is present in solution but the total yield of neopentyl groups is only two per tantalum. The reaction is very specific for 1-butene, and for these conditions the rate of production of 1-butene is about one $\text{Ta}^{-1} \text{min}^{-1}$ at 25°C . If any 2-butene is present, the level for each isomer is below the limit of detection.

If a solution of $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$, 1, which contains several equivalents of PMe_3 is allowed to react with C_2H_4 , the orange solution immediately becomes dark red and remains this color. There is no yellow stage in this reaction. From the beginning of the reaction 1-butene is produced catalytically and selectively. The other organic products of this reaction, which are listed in Table 1.I., were identified by GLC and include almost three equivalents of 4,4-dimethyl-1-pentene per Ta. Under these conditions the total yield of neopentyl groups almost equals four per Ta. In addition, this alternate procedure yields a more active catalyst

for which the dimerization rate is approximately two $\text{Ta}^{-1} \text{min}^{-1}$ at 25°C . It can be seen that the stage at which the PMe_3 is introduced has a large influence on the reaction.

B. Reactions of $\text{Me}_3\text{CCH}=\text{M}(\text{CH}_2\text{CMe}_3)_3$ with PR_3

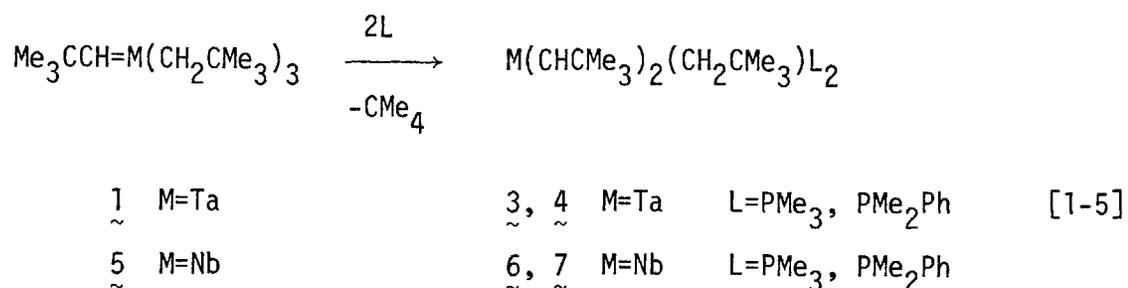
1. The Preparation of Niobium and Tantalum Bisalkylidene Complexes

The results presented in the previous section show that PMe_3 has a profound effect on the reaction of $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$, 1, with ethylene. Since J. Fellmann discovered that PMe_3 trapped the decomposition product of $(\text{Me}_3\text{CCH}_2)_4\text{TaCl}$ as a bisalkylidene complex, $\text{Ta}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$,²⁹ the reaction of $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$ with PMe_3 was investigated.

When several equivalents of PMe_3 were added to a benzene solution of 1, there was no visible change in the orange solution. However, monitoring the reaction by ^1H NMR showed that neopentane was produced steadily. The resonances due to $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$ diminished while a new set of resonances due to the bisalkylidene complex, $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$, 3, and one equivalent of CMe_4 per Ta grew in. This transformation was rapid^a and not complicated by side reactions. The yield of 3 was quantitative when the reaction stoichiometry provided at least two equivalents of PMe_3 per tantalum. The bisalkylidene, 3, crystallized from concentrated reaction mixtures, since it was less soluble than the precursor, 1. It was also possible to recrystallize 3 from pentane at -30°C if desired.

Eq. 1-5 illustrates the preparation of 3 as well as some its analogues which have been synthesized by the same method.

^aThe reaction is complete in 2 hrs at RT if a slight excess of PMe_3 is present. Attempts to increase the rate of reaction by warming samples to 40°C result in a less pure product.



When a ligand which is less basic or more bulky than PMe₃ is employed to prepare bisalkylidenes analogous to $\underset{\sim}{3}$, the reaction takes longer and the product is less pure. The addition of two equivalents of PMe₂Ph to a benzene solution of Me₃CCH=Ta(CH₂CMe₃)₃ did not cause any significant evolution of neopentane over a period of several hours. Only starting materials were observed by ¹H NMR. If the orange solution was allowed to stand at RT for an interval of ten to fourteen days, it became dark brown. After the solvent was removed in vacuo, the resulting brown oil was dissolved in pentane. The solution was treated with activated charcoal, filtered, and cooled to -30°C. The Ta(CHCMe₃)₂(CH₂CMe₃)(PMe₂Ph)₂, $\underset{\sim}{4}$, was isolated as yellow crystals in 77% yield.^a The reaction of Me₃CCH=Ta(CH₂CMe₃)₃, $\underset{\sim}{1}$, with bulky tertiary phosphines such as PEt₃ or PPh₂Me and with other ligands such as THF, NEt₃, or py did not produce any bisalkylidene complexes.

When Me₃CCH=Nb(CH₂CMe₃)₃, $\underset{\sim}{5}$,¹⁸ is the starting material, the niobium analogues of both $\underset{\sim}{3}$ and $\underset{\sim}{4}$ can be prepared. The reaction of $\underset{\sim}{5}$ with excess PMe₃ in pentane at 0°C gave Nb(CHCMe₃)₂(CH₂CMe₃)(PMe₃)₂, $\underset{\sim}{6}$. A similar reaction between $\underset{\sim}{5}$ and PMe₂Ph gave the expected product, Nb(CHCMe₃)₂(CH₂CMe₃)(PMe₂Ph)₂, $\underset{\sim}{7}$. The yields of $\underset{\sim}{6}$ and $\underset{\sim}{7}$ were approximately 70%.^b The reactions were

^a If the reaction is shielded from light, the yield and purity of the product are increased somewhat.

^b The yields were based on (Me₃CCH₂)₃NbCl₂ since $\underset{\sim}{5}$ was prepared and used in situ.

performed at 0°C to prevent the decomposition of 5 which resulted in lower yields of 6 and 7.^a

When $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$, 1, or $\text{Me}_3\text{CCH}=\text{Nb}(\text{CH}_2\text{CMe}_3)_3$, 5, are allowed to react with chelating ligands such as dmpe, diphos, or bipy, the results are not as simple as when the ligands are monodentate. When dmpe was added to an orange pentane solution of 1, an off-white microcrystalline powder slowly precipitated from solution. After several hours, the pentane solution was colorless and the product which was insoluble^b could be collected by filtration. One equivalent of CMe_4 per Ta was given off in this reaction which consumed one equivalent each of 1 and dmpe. The product is postulated to be a polymeric bisalkylidene complex, $[\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{dmpe})]_x$, 8.^c The yield was quantitative based on this formulation. When the reaction was performed in CHCl_3 ,^d the only observed products (in addition to the unreacted dmpe) were CMe_4 and $(\text{Me}_3\text{CCH}_2)_3\text{TaCl}_2$. The $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$ decomposed in the chlorinated solvent faster than it could react with dmpe. While $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$, 1 would not react with diphos because the ligand is too bulky, 1 did react with bipy. The reaction of 1 with bipy produced a blue-black crystalline solid which was slightly soluble in pentane and very soluble in aromatic solvents. Approximately one equivalent of CMe_4 was evolved while one equivalent of 1 and bipy was consumed in the reaction. However, this product (which is soluble unlike 8) does not possess a NMR spectrum, and therefore, it may not be at all similar to the other

^aThe niobium complex, 5, is unstable at 25°C.

^bThis compound is insoluble in pentane, benzene, toluene, ether, THF, CH_2Cl_2 , and CHCl_3 .

^cThis same compound, 8, can be prepared from the reaction of 3 with dmpe.

^dThis solvent has been shown to enhance the rate of α -hydrogen abstraction^{41,42} and to inhibit polymerization of organometallic intermediates (see Chap. 2).

bisalkylidenes.

When isolated $\text{Me}_3\text{CCH}=\text{Nb}(\text{CH}_2\text{CMe}_3)_3$, 5, was allowed to react with dmpe in pentane at 0°C , an off-white microcrystalline precipitate forms rapidly. This is thought to be $[\text{Nb}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{dmpe})]_x$ by comparison to the Ta analogue, 8. There was no reaction between 5 and diphos at 0°C . If 5 was allowed to decompose at RT in the presence of diphos, however, it appeared that a small amount (~20%) of the decomposition product could be trapped. This complex was isolated as pentane or toluene soluble orange crystals at low temperature. The ^1H NMR spectrum indicated that the product might be a bisalkylidene, $\text{Nb}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{diphos})$. This formulation is tentative, however, because the complex is unstable in solution. Further work is necessary to fully characterize this product. There was no reaction between 5 and THF at 0°C and nothing was trapped during the decomposition of 5 in the presence of THF at RT. It appears that THF is too weak a ligand.

2. The Characterization of the Bisalkylidene Complexes

It has been shown that several bisalkylidene complexes with the general formula $\text{M}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)\text{L}_2^a$ can be prepared in good yield. Spectral and other experimental data confirm the formulation of these compounds as bisalkylidene complexes.

The ^1H NMR spectral data of these four complexes (3, 4, 6, and 7) are listed in Table I.II. The resonances for the two tertiary phosphines per complex indicate that both ligands are equivalent. In complex 3, the PMe_3 resonance appears as a virtually coupled triplet. In the case of the PMe_2Ph ligands in 4, however, the methyl groups are diastereotopic

^aM=Ta, Nb; L= PMe_3 , PMe_2Ph .

Table 1.II. The ^1H NMR Data* for the $\text{M}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)\text{L}_2$ Series

	$=\text{CHCMe}_3(\text{J}_{\text{HP}})$	$-\text{CH}_2\text{CMe}_3(\text{J}_{\text{HP}})$	$-\text{CMe}_3$	$\text{PMe}(\text{J}_{\text{HP}})$	PPh
$\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ (3)	3.07(3.0) 7.92(<2)	9.39(18.9)	8.79 8.80 8.84	8.68(2.4)	
$\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_2\text{Ph})_2$ (4)	2.39(<2) 8.06(<2)	9.47(18.2)	8.62 8.64 9.28	8.32(<2) 8.35(<2)	2.44-3.07
$\text{Nb}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ (6)	0.62(3.1) 5.71(<2)	9.94(17.6)	8.77 8.78 8.80	8.79(2.6)	
$\text{Nb}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_2\text{Ph})_2$ (7)	0.07(<2) 5.82(<2)	10.00(17.0)	8.56 8.62 9.05	8.43(<2) 8.43(<2)	2.25-3.00

*Shifts are listed in τ while coupling constants are listed in Hz.

(i.e. PMeMe'Ph). Therefore, a plane of symmetry may pass between the two ^{31}P nuclei but no plane of symmetry can contain the two phosphorus nuclei.

All four complexes have two clearly distinct neopentylidene α -hydrogen resonances. These resonances are separated in chemical shift by almost 6 ppm. For example, the neopentylidene H_α resonances in $\text{Nb}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_2\text{Ph})_2$, 7, occur at 0.07 and 5.82 τ . This indicates that the two neopentylidene ligands per complex are very different in nature and/or environment. The phosphorus coupling to the neopentylidene H_α nuclei is 3Hz or less, so that some of these resonances are virtually coupled triplets while others are only broadened by the coupling. The α -hydrogens of the neopentyl group appear as a virtual triplet due to ^{31}P coupling in the region of 9-10 τ for each complex. The coupling of the neopentyl H_α nuclei to phosphorus is very large and is on the order of 18 Hz. There are three types of ^tBu group resonances as expected: two for the nonequivalent neopentylidene ligands and one for the neopentyl group. In broad band ^{31}P decoupling of the ^1H NMR spectrum of 3, the virtual triplets collapse to singlets while the broadened resonances become sharper.

The ^{13}C resonances for three of the bisalkylidenes (3, 4, and 6) are listed in Table 1.III. All three complexes have two clearly distinct resonances between 240 and 290 ppm which are in the region for carbon nuclei^{43,44} doubly bonded to a transition metal. The chemical shift difference between the two neopentylidene C_α per complex is 30-40 ppm. In the tantalum bisalkylidenes (3 and 4), each neopentylidene C_α resonance is a doublet due

Table 1.III. The ^{13}C NMR Data* for the $\text{M}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)\text{L}_2$ Series

	$=\underline{\text{C}}\text{H}\text{CMe}_3(\text{J}_{\text{CH}})$	$-\underline{\text{C}}\text{H}_2\text{CMe}_3(\text{J}_{\text{CH}})$	$-\underline{\text{C}}\text{Me}_3$	$-\underline{\text{C}}\text{Me}_3(\text{J}_{\text{CH}})$	$\text{P}\underline{\text{M}}\text{e}(\text{J}_{\text{CH}})$	$\text{P}\underline{\text{P}}\text{h}(\text{J}_{\text{CH}})$
$\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ (3)	274.1(95) 245.6(85)	72.0(108)	47.3 44.5 38.4	37.4(122) 35.6(122) 34.5(125)	20.2(128)	
$\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_2\text{Ph})_2$ (4)	277.0(95) 243.9(82)	74.3(105)	47.8 44.8 37.7	36.6(123) 35.2(124) 34.7(128)	22.5(131) 19.2(129)	138.6 132.2(159) 129.1(162) 128.3(159)
$\text{Nb}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ (6)	281.8(br) 245.3(br)	59.6(br)	44.6 42.7 37.7	36.9(123) 34.3(125) 33.3(123)	19.3(129)	

*Shifts are listed in ppm while coupling constants are listed in Hz.

to coupling to one hydrogen while the neopentyl C_{α} resonance is a triplet because of coupling from two hydrogens as expected. The magnitude of these coupling constants is much smaller than usual.^a The values of $J_{C_{\alpha}H_{\alpha}}$ for the neopentylidene ligands range from 80 to 95 Hz while the values of $J_{C_{\alpha}H_{\alpha}}$ for the neopentyl groups are less than 110 Hz. When the metal is niobium, however, all C_{α} resonances are broad due to coupling to ^{93}Nb (100% abundance, $I=9/2$) so that $J_{C_{\alpha}H_{\alpha}}$ could not be determined. There are three sets of ^tBu group resonances for each complex as expected. The two phosphine ligands per complex are equivalent as in the ^1H NMR spectra. The PMe_3 ligands in 3 appear as a quartet. The PMe_2Ph ligands in 4 give rise to two quartets for the two diastereotopic pairs of methyl groups as well as one set of resonances for the two equivalent phenyl groups.

The IR spectrum of 3 contains a C-H stretch at a much lower frequency than normal.^b This stretch appears at 2650 cm^{-1} and has been assigned as

$\nu_{C_{\alpha}H_{\alpha}}$.^c

The molecular weight of $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$, 3, has been measured cyroscopically in cyclohexane. The complex was shown to be monomeric (calcd 544.5, found 540) at several different concentrations.

Because of similarities in the ^1H NMR spectra and in the ^{13}C NMR spectra, these four bisalkylidene complexes (3, 4, 6, and 7) are believed to possess the same coordination geometry around the metal center. There are several structures which meet the requirements of possessing equivalent phosphine

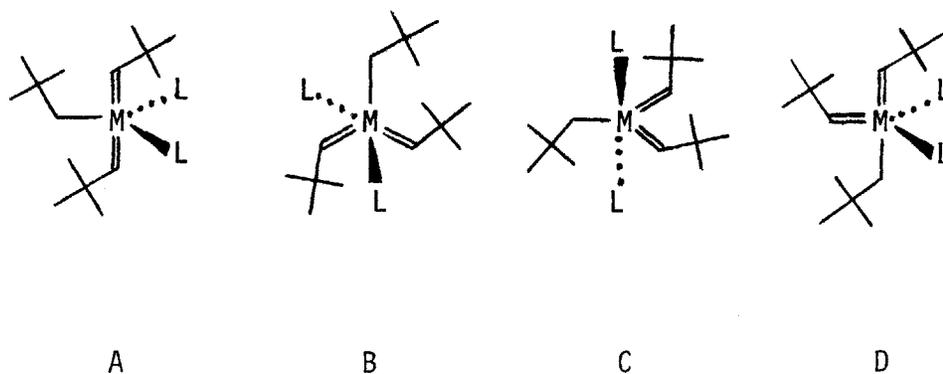
^aThe normal value of J_{CH} for a sp^2 carbon is 160Hz while the value of J_{CH} for a sp^3 carbon is usually 125Hz.⁴⁵

^bThe usual C-H stretching frequency range is $2850\text{--}3100\text{ cm}^{-1}$.⁴⁶

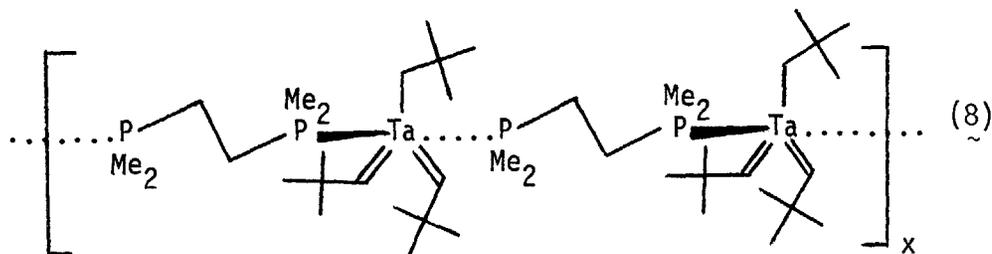
^cMany other electron deficient neopentylidene complexes of tantalum and niobium exhibit a $C_{\alpha}\text{--}H_{\alpha}$ stretch at low frequencies.¹⁹

ligands and inequivalent neopentylidene ligands. Four of these possible structures are shown in Figure 1.1. Three of the structures (A, C, D) are trigonal bipyramidal (tbp) while one structure (B) is square pyramidal (spy). Structure A seems to be the most likely geometry based on comparison of the large value of J_{HP} for the neopentyl α -hydrogens and the small value of J_{HP} for the α -hydrogens of the neopentylidenes. The actual structure, at least in the crystalline state, is structure C. An analogue of **3**, in which a mesityl group replaces the neopentyl group, was prepared by J. Fellmann and the five ligands are oriented around the Ta exactly as depicted in structure C.^{47,48}

Figure 1.1. Some Possible Bisalkylidene Coordination Geometries



The observed preference of these bisalkylidene complexes for trans axial phosphine ligands may explain the anomalous results obtained from the reactions of chelating ligands such as dmpe with $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$, **1**. Since the dmpe ligand cannot span 180° as required, a polymer results (Figure 1.2).

Figure 1.2. The Structure of $[\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{dmpe})]_x$ 

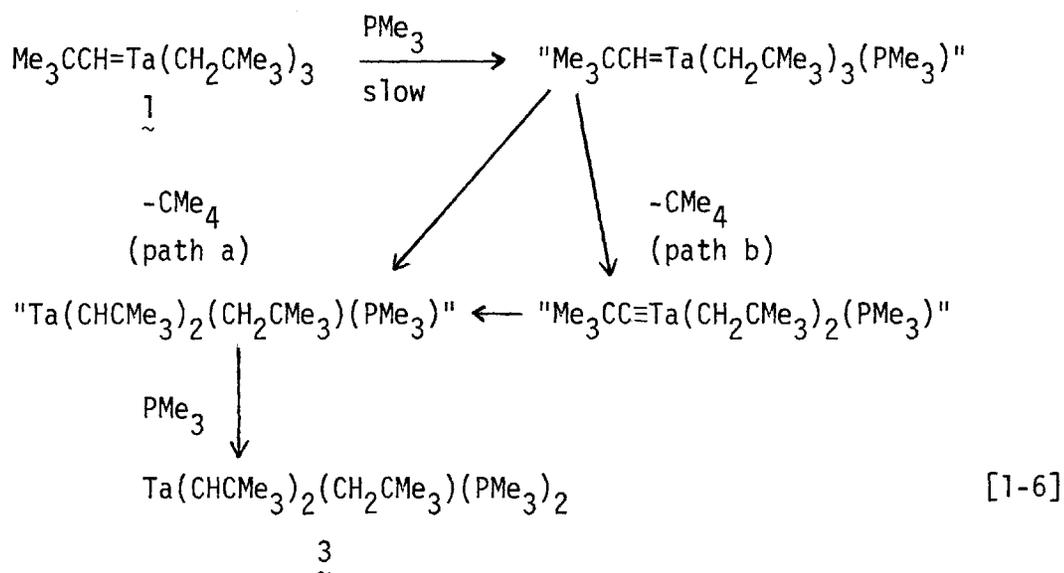
3. The Formation and Stability of Bisalkylidene Complexes

Although it is not possible to isolate or even detect intermediates during the formation of $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$, **3**, several facts are known about the reaction mechanism by which $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$, **1**, is converted into **3**. This mechanism involves more than the trapping of decomposition products of **1** by PMe_3 since **1** is stable for weeks under N_2 at 25°C and can be sublimed in vacuo at 75°C without decomposition.^a Therefore, the PMe_3 in some way must be responsible for the α -hydrogen abstraction which transforms **1** into **3**. It is known that α -hydrogen abstraction in electron deficient complexes of the early transition metals is favored when the coordination sphere is sterically crowded.¹⁸⁻⁴² In most cases a crowded coordination sphere is provided by the use of

^aThe sterically crowded coordination sphere of **1** inhibits intermolecular decomposition while degenerate α -hydrogen scrambling is the lowest energy intramolecular process.¹⁸

bulky σ -bonded groups such as $-\text{CH}_2\text{CMe}_3$, $-\text{CH}_2\text{SiMe}_3$, and $-\text{CH}_2\text{Ph}$ or π -bonded groups such as C_5H_5 and C_5Me_5 . In the preparation of 3 from 1, it appears that coordination of neutral $2e^-$ σ -donor ligands such as PMe_3 can also provide the proper steric conditions for α -hydrogen abstraction to occur. For these reasons this process has been designated as ligand induced α -hydrogen abstraction.

The reaction of $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$, 1, with PMe_3 must involve intermediates although these have never been observed. Because of this it is believed that the first step of the reaction must be the slowest or rate determining step while all subsequent steps are fast. The first step is postulated as the formation of a five coordinate PMe_3 adduct of 1. The coordination of PMe_3 to 1 would be slow, since the coordination sphere of 1 is crowded, and would require a reorganization of the coordination



geometry. The steric crowding in this intermediate's coordination sphere would be significantly greater than that in 1. This would cause the intermediate to be very unstable and would favor the rapid loss of neopentane by α -hydrogen abstraction (Eq. 1-6).

In the α -hydrogen abstraction step a neopentyl group could theoretically remove an α -hydrogen either from another neopentyl group (path a) or from the neopentylidene ligand (path b). In the first case (path a), a four coordinate alkyl bisalkylidene complex would be produced. In the second case, a four coordinate dialkyl alkylidyne complex would be formed. This intermediate could then rearrange to the alkyl bisalkylidene complex by an α -hydrogen transfer from a neopentyl to the neopentylidyne. This four coordinate intermediate would then add another PMe_3 ligand to give 3.

Although "path a" is the simplest mechanism, it has not been determined which pathway is the correct one. There is evidence from other systems that can support either pathway. The preparation of $\text{CpTa}(\text{CHCMe}_3)\text{Cl}_2$ from $\text{CpTa}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_2$ ⁴² is an example of "path a" while the synthesis of $\text{CpTa}(\text{CCMe}_3)\text{Cl}(\text{PMe}_3)_2$ from $\text{CpTa}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)\text{Cl}$ ²⁶ illustrates "path b". The conversion of an alkyl alkylidyne complex to a bisalkylidene complex (which is necessary in "path b") has also been observed before. The complex $\text{CpTa}(\text{CHCMe}_3)_2(\text{PMe}_3)$ ²⁹ has been prepared from $\text{CpTa}(\text{CCMe}_3)\text{Cl}(\text{PMe}_3)_2$ presumably through a $\text{CpTa}(\text{CCMe}_3)(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ intermediate. The driving force which favors the alkyl alkylidyne to bisalkylidene rearrangement is unknown at this time.

There are a number of stable complexes which possess alkyl and alkylidyne ligands. These include $[\text{Ta}(\text{CH}_2\text{SiMe}_3)_2(\text{CSiMe}_3)]_2$ ⁴⁹ and

$[\text{W}(\text{CH}_2\text{CMe}_3)_3(\text{CCMe}_3)]_2$.³⁹ These complexes are dimeric, however, and contain bridging alkylidyne ligands. It appears that alkyl complexes with bridging alkylidyne groups are not inclined to rearrange to bis-alkylidene complexes. If the alkyl alkylidyne complex is monomeric, this rearrangement appears to be much more favorable but still may not be a general reaction. The complex, $[\text{Me}_3\text{CC}\equiv\text{Ta}(\text{CH}_2\text{CMe}_3)_3]\cdot\text{Li}(\text{tmeda})^a$ is actually a mixture of two isomers.⁴⁰ The mixture contains up to 15% of $[\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)_2]\cdot\text{Li}(\text{tmeda})$. So in this case at least, the rearrangement is not complete and the bisalkylidene is actually the minor isomer.^b It can be seen that this rearrangement depends to a large extent on the kinds of ligands and the type of structure in the initial complex.

The bisalkylidene complex is remarkably stable once it has formed. $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$, **3**, is stable for weeks under N_2 at 25°C either in solution or in the solid state. It decomposes, however, on attempted sublimation unlike $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$, **1**, from which **3** is derived. Loss of CMe_4 by further α -hydrogen abstraction in **3** to give an alkylidene alkylidyne complex^c does not occur even on heating in the presence of additional PMe_3 . On heating, however, the neopentylidene ligands which are distinct at RT become equivalent.^{29,47} Despite this equilibration process, the neopentylidene ligands do not reductively couple to form a Ta(I) olefin complex such as $\text{Ta}(\eta^2\text{-Me}_3\text{CCH}=\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ (Eq. 1-7).

^aThis complex is prepared by base abstraction of H_α from $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$.²⁴
^bWhen the Li cation is coordinated by phosphorous or oxygen donor ligands none of the bisalkylidene isomer appears to be present.⁴⁰
^cComplexes of this type, however, are known for W and include $\text{W}(\text{CH}_2\text{CMe}_3)(\text{CHCMe}_3)(\text{CCMe}_3)(\text{dmpe})$ and $\text{W}(\text{CHCMe}_3)(\text{CCMe}_3)\text{Cl}(\text{PMe}_3)_2$.^{39,40}

Even though the neopentylidene ligands are adjacent, this reductive elimination of di-tert-butylethylene is not favorable since the electron count on the already electron deficient Ta would be reduced from 14 to 12.



Not only is the Ta atom in 3 adverse to losing electron density, but it also appears to be attracting additional electron density from the C_α-H_α bonds in the neopentylidene ligands.^a As the tantalum interacts more strongly with these C_α-H_α bonds, the bonds would have reduced electron density and would be weaker. Evidence of this diminished C_α-H_α bond strength can be seen in the ¹³C NMR and IR spectra. The values for J_{C_αH_α} (85 and 95 Hz) and ν_{C_αH_α} (2650 cm⁻¹) are significantly lower than normal (vide supra). If this interaction were increased the ultimate result could be loss of H_α as a proton and formation of an anionic complex with a Ta-to-C triple bond. Alternatively, H_α could transfer to the metal, but only as a hydride since Ta(V) is d⁰, and this would leave C_α electron deficient. Neither of these extremes occurs and the best description may involve H_α bridging C_α and Ta in a three center, two electron bond.

It has been shown that several members of another class of alkylidene

^aThis type of interaction is seen in the crystal structure of [Me₃CCH=Ta(PMe₃)Cl₃]₂.³⁰

complexes, namely the bisneopentylidenes discussed above, can be prepared. These complexes were synthesized by a route involving ligand induced α -hydrogen abstraction. The reactions of these complexes with small molecules should be interesting as well.

C. Reactions of $M(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PR}_3)_2$ with Olefins

The selective production of 1-butene from the catalytic dimerization of ethylene by $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$, 1, in the presence of two equivalents of PMe_3 is rapid (vide supra). This homogeneous system is potentially useful but unfortunately is not well understood. Therefore, the reaction of $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$, 3, with ethylene was investigated since 3 is derived from components required for the dimerization system.

The reaction of $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$, 3, with C_2H_4 was also rapid. A pentane solution of 3 immediately changed from orange to red^a when the solution was stirred under 50 PSIG of ethylene at RT. The liquid volume of the reaction mixture increased visibly with time, and the ethylene pressure in a closed system quickly decreased. These observations indicated that ethylene was being consumed continuously. Analysis of a sample of the reaction mixture by GLC showed that 1-butene was being produced catalytically at the rate^b of $2.5 \text{ Ta}^{-1} \text{ min}^{-1}$. The sample also contained three equivalents of 4,4-dimethyl-1-pentene (neopentylethylene) per Ta (see Table 1.IV.).

The reaction of the other bisalkylidene complexes with ethylene was not as straightforward as that of 3. As in the case of 3, a yellow solution

^aThis was the same color that was produced when pentane solutions of 1 and PMe_3 were exposed to ethylene.

^bThe rates of dimerization are slower in toluene and benzene.

of $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_2\text{Ph})_2$, $\underline{4}$, turned red instantly under 50 PSIG of ethylene. The ethylene was consumed and 1-butene was produced catalytically. The dimerization reaction which proceeded at a rate of approximately $2 \text{ Ta}^{-1} \text{ min}^{-1}$ was not as rapid as when $\underline{3}$ was employed. A sample of the reaction solution was analyzed by GLC and was found to contain (in addition to 1-butene) 2.77 equivalents of 4,4-dimethyl-1-pentene per Ta as well as small amounts of neopentane, 2,2-dimethylpentane (neohexane) and cis- and trans- 2,2,5,5-tetramethyl-3-hexene (di-tert-butylethylene) (see Table 1.IV.).

The niobium bisalkylidenes, however, did not function as effective ethylene dimerization catalysts. A yellow solution of $\text{Nb}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$, $\underline{6}$, became red immediately after exposure to 50 PSIG of ethylene. Analysis of a sample of the reaction mixture by GLC, however, showed only traces of 1-butene. In addition, 2.11 equivalents of 4,4-dimethyl-1-pentene per Ta were produced as well as significant amounts of neopentane, 2,2-dimethylpentane, and trans-2,2,5,5-tetramethyl-3-hexene (see Table 1.IV.)

While $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$, $\underline{3}$, offered a very selective means of producing 1-butene from ethylene, $\underline{3}$ did not seem to promote the dimerization of other α -olefins such as propylene. The initial reaction of $\underline{3}$ with propylene at 50 PSIG and RT appeared to be fast. The orange solution of $\underline{3}$ rapidly became red; however, the consumption of propylene ceased after several minutes. There was no increase in the volume of the reaction solution. A sample of the reaction mixture was analyzed by GLC and was found to contain a large number of organic compounds which were formed in

Table 1.IV. The Yield* of Organic Products from the Reactions** of Bisalkylidenes with Ethylene.

Bisalkylidene		CMe ₄				Total	 min ⁻¹
3	2.99	0	0	0	0	2.99	2.51
4	2.77	0.02	0.08	0.03	0.03	2.99	2.14
6	2.11	0.54	0.07	0	0.15	3.02	0.01
3-d ₂	3.00	0	0	0	0	3.00	

* All yields and rates are absolute and are presented in units per Ta.

** All reactions were performed in pentane at 25°C under 50 PSIG of C₂H₄.

small amounts. These included 0.82 equivalents of 2,4,4-trimethyl-1-pentene, 0.44 equivalents of neopentane, and 0.25 equivalents of 2,2,4-trimethylpentane per Ta. Only 1.5 equivalents per Ta of products containing neopentyl groups could be accounted for. Although there were traces of many unknown organic compounds in the sample, no linear or branched dimers of propylene were produced catalytically.

The ethylene dimerization system derived from $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$, **3**, has been shown to be very efficient and selective for the production of 1-butene. There are few catalysts which demonstrate such high selectivity as this system.⁵⁰ Many ethylene dimerization catalysts, especially those of the later transition metals, produce a thermodynamic mixture of butenes because the initial product, 1-butene, is isomerized by the catalyst.⁵¹ Other ethylene dimerization catalysts prepared from the early transition metals do not isomerize the 1-butene which is produced; however, they usually catalyze the formation of significant amounts of higher oligomers and/or polyethylene.⁵²

This dimerization system which is derived from **3** was active for several days at RT although the rate of 1-butene production decreased slowly with time. The analysis of samples collected after long reaction times, however, showed that a number of C_6 and C_8 olefins were present. These side products were formed only when 1-butene became the major component of the total solution. Under these conditions, in which 1-butene was acting as the solvent for the catalyst, 1-butene competed with ethylene in the catalytic cycle and small amounts of various hexenes and octenes were produced. When the concentration of 1-butene was low,

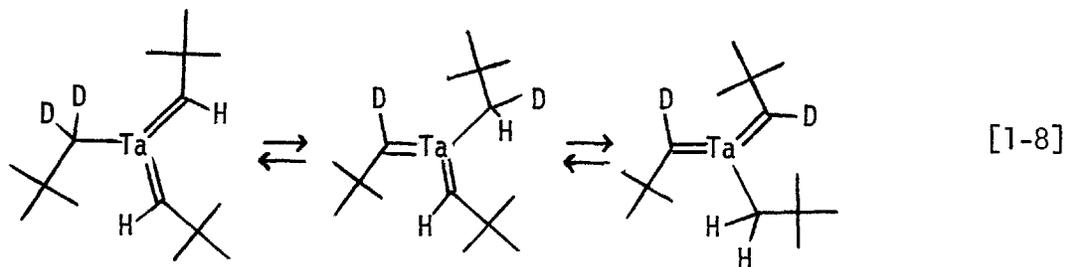
these side reactions did not occur. In addition, the production of 1-butene was fastest at high ethylene pressures and moderate temperatures (25°C) in aliphatic solvents while low ethylene pressures, low temperatures, and aromatic solvents decreased the rate of formation of 1-butene.

Since three equivalents of 4,4-dimethyl-1-pentene are produced in the beginning of the reaction between $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$, $\tilde{3}$, and C_2H_4 (*vide supra*), the loss of this olefin from $\tilde{3}$ appears to involve the transformation of the neopentyl group into a neopentylidene ligand. The first two equivalents of 4,4-dimethyl-1-pentene are evolved from $\tilde{3}$ in a manner similar to that shown in Eq. 1-1. In this mechanism coordinated C_2H_4 attacks the neopentylidene ligand to form a metallocyclobutane complex which decomposes by β -hydride elimination to yield 4,4-dimethyl-1-pentene. The third equivalent of 4,4-dimethyl-1-pentene can be produced in this manner only after the neopentyl group is converted to a neopentylidene ligand. Another alternative to this mechanism would involve insertion of C_2H_4 into the $\text{Ta}-\text{C}_\alpha$ bond of the neopentyl group to form a neoheptyl group which would yield 4,4-dimethyl-1-pentene after β -hydrogen elimination.

The reaction of a deuterium labeled analogue of $\tilde{3}$ with ethylene was investigated to distinguish between the two possible mechanisms. The reaction of C_2H_4 with $\text{Ta}(\text{CHCMe}_3)_2(\text{CD}_2\text{CMe}_3)(\text{PMe}_3)_2$, $\tilde{3}\text{-d}_2$, which was prepared by Fellmann from $\text{Ta}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$ and $\text{LiCD}_2\text{CMe}_3$, gave three equivalents of 4,4-dimethyl-1-pentene. Analysis of the sample by GS-MS showed that it contained a 1:1 mixture of 4,4-dimethyl-1-pentene -d_0 and -d_1 while little (if any) 4,4-dimethyl-1-pentene -d_2 was present. This

result indicated that in the presence of C_2H_4 there was rapid scrambling of H_α and D_α in $\overset{\sim}{3}\text{-d}_2$, although this process did not occur during the preparation and handling of the complex (vide infra). Therefore, this scrambling must take place after C_2H_4 interacts with $\overset{\sim}{3}\text{-d}_2$ but before any of the neopentylidene ligands are cleaved.

Since this scrambling is the first process in the reaction, any definite mechanistic conclusion is impossible. This scrambling of H_α and D_α , however, does not involve the loss of neopentane, and the neopentyl group must be converting into a neopentylidene ligand and vice versa (Eq. 1-8). This data is consistent with (but does not prove) the mechanism



involving a neopentylidene intermediate. Furthermore, the mechanism which proceeds through a neoheptyl intermediate is unfavorable for several reasons. First, no products from double ethylene insertion such as 6,6-dimethyl-1-heptene are seen. And second, ethylene does not insert into the Ta- C_α bonds of neopentyl groups in compounds such as $(Me_3CCH_2)_2TaCl_3$ (see Chap. 2).

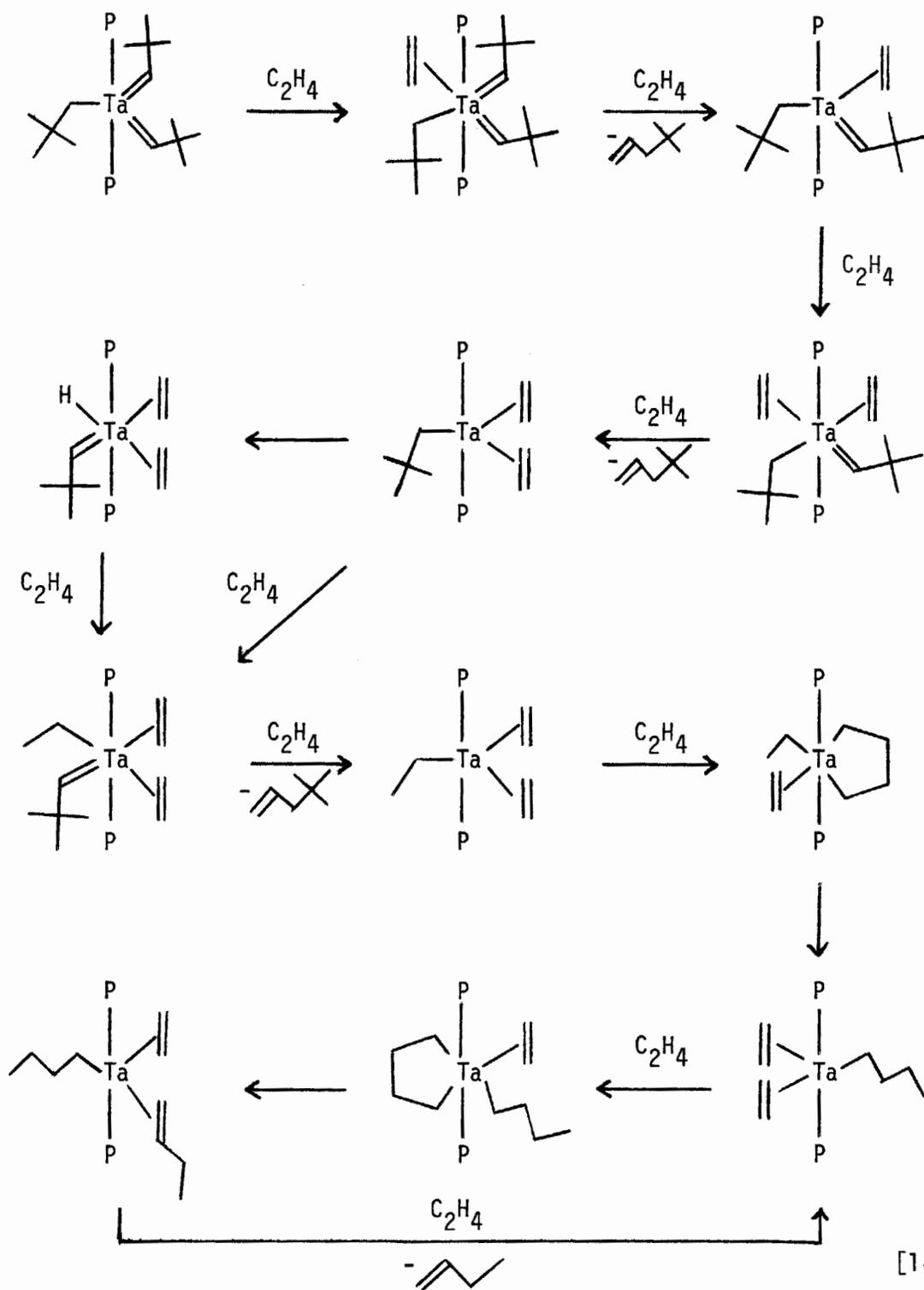
The conversion of the neopentyl group into a neopentylidene ligand

can occur either by α -hydrogen abstraction or α -hydrogen elimination. In the abstraction process a ligand such as ethylene can abstract H_{α} from the neopentyl group to yield an ethyl neopentylidene complex. In the elimination process the neopentyl group loses H_{α} to the metal to form an intermediate hydride which can insert ethylene into the TaH bond to give an ethyl neopentylidene complex. In either case the reaction of the newly formed neopentylidene ligand with ethylene yields the third equivalent of 4,4-dimethyl-1-pentene (Eq. 1-9).

The organometallic species remaining in solution would be an ethyl-Ta(I) complex such as $Ta(C_2H_4)_2(PMe_3)_2Et$. This complex has been synthesized by Fellmann and has been shown to yield the same catalytic dimerization system as $\underline{3}$.³¹ Further work by Fellmann has shown that the ethylene dimerization occurs via a metallocyclopentane mechanism^a rather than an ethylene insertion mechanism (Eq. 1-9). The key intermediate in this system was shown to be $Ta(C_2H_4)_2(PMe_3)_2(nBu)$ from which a metallocyclopentane complex is formed on further reaction with ethylene and from which 1-butene is produced by β -hydride elimination (Eq. 1-9).

It has been shown that $Ta(CHCMe_3)_2(CH_2CMe_3)(PMe_3)_2$, $\underline{3}$, is converted in the presence of ethylene into a very active and selective catalyst for the production of 1-butene. Unfortunately, the niobium analogue, $Nb(CHCMe_3)_2(CH_2CMe_3)(PMe_3)_2$, $\underline{6}$, does not give an active ethylene dimerization system. In the reaction of $\underline{6}$ with ethylene three equivalents of cleavage products are produced. Even $Nb(C_2H_4)_2(PMe_3)_2Et$ has been shown to

^aOlefin dimerization via a metallocyclopentane mechanism is known to occur in other catalytic systems.^{53,54}



be present in solution by Fellmann.³¹ Despite these similarities with 3 there is no production of 1-butene. There is evidence in other olefin dimerization systems, where tantalacyclopentanes are formed, that the analogous niobacyclopentane complexes are not produced.^{54,55}

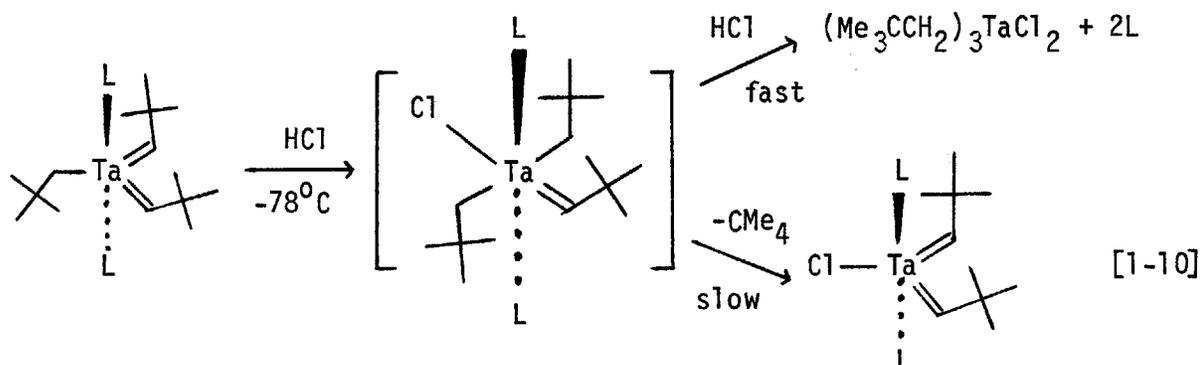
Other α -olefins such as propylene are not dimerized by $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$, 3. The reason for this limitation is not clear since metallocycles have been prepared in other systems with propylene.^{53,54} However, $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ will dimerize ethylene selectively which is rare. Additionally, 3 functions by a metallocyclopentane mechanism for ethylene oligomerization which differs significantly from the ethylene insertion mechanism of Ziegler-Natta type catalysts.

D. Miscellaneous Reactions of $\text{M}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PR}_3)_2$

The bisalkylidene complex, $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$, 3, undergoes a number of reactions which indicate that the α -carbon of the neopentylidene ligands is nucleophilic and that the tertiary phosphine ligands are exchangeable.

The reaction of $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$, 3, with HCl was investigated to determine if $\text{Ta}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$ could be prepared cleanly and conveniently. One equivalent of anhydrous HCl was injected into a stirred toluene solution of 3 at -78°C . The orange solution became yellow-orange and was allowed to warm slowly to RT. The product was isolated after solvent removal in vacuo and was shown by ^1H NMR to be a 50/50 mixture of $(\text{Me}_3\text{CCH}_2)_3\text{TaCl}_2$ and starting material, 3. Little (if any) $\text{Ta}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$ was produced. Apparently the intermediate from the reaction of 3 with one HCl was attacked by a second equivalent of HCl much more rapidly than neopentane was eliminated to give the desired product

(Eq. 1-10). The use of a weaker or buffered acid might slow the undesirable



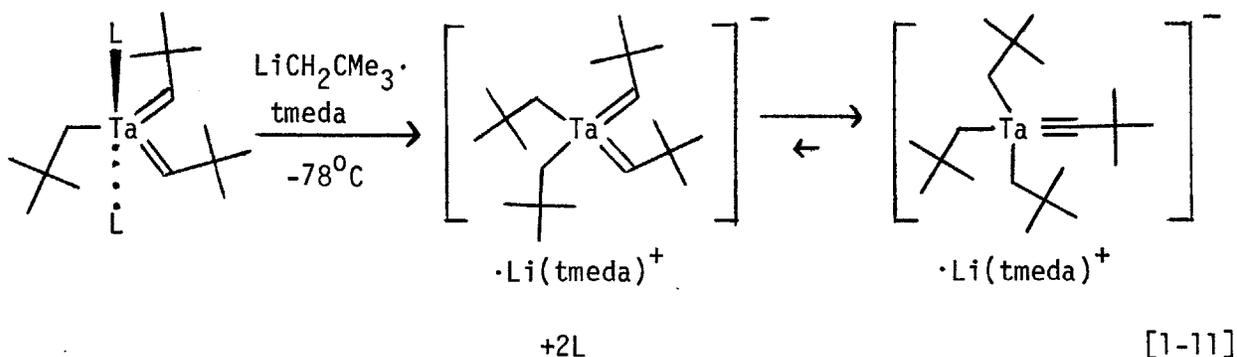
attack of the second equivalent of acid enough to allow the elimination of neopentane and the formation of $\text{Ta}(\text{CHCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$. A good substitute for HCl might be $\text{HPMe}_3^+\text{Cl}^-$, but its reaction with $\mathbf{3}$ was never investigated.

Although it was not possible to prepare interesting complexes from the protonation of $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$, $\mathbf{3}$, the reaction of $\mathbf{3}$ with bases might lead to novel complexes through the deprotonation of $\mathbf{3}$. Specifically, proton abstraction from $\mathbf{3}$ could lead, theoretically, to an anionic trisneopentylidene complex or an anionic neopentyl neopentylidene neopentylidyne complex.^a When a phosphorus ylid such as $\text{Ph}_3\text{P}=\text{CH}_2$ was employed as the base, no tractable product could be isolated possibly due to side reactions in which the ylid attacks the metal center.^{56,57} The use of $\text{LiCH}_2\text{CMe}_3 \cdot \text{tmeda}$ as the base, however, gave an unexpected but interesting result.

A solution of $\text{LiCH}_2\text{CMe}_3 \cdot \text{tmeda}$ (prepared *in situ*) was added dropwise with stirring to a pentane solution of $\mathbf{3}$ at -78°C . After warming slowly

^aA tungsten neopentyl neopentylidene neopentylidyne which is isoelectronic has been synthesized.³⁹

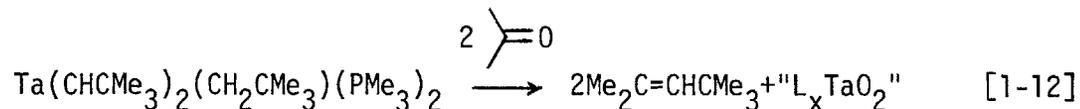
to RT, the solvent was removed in vacuo to yield yellow crystals of $[\text{Me}_3\text{CC}\equiv\text{Ta}(\text{CH}_2\text{CMe}_3)_3]\cdot\text{Li}(\text{tmeda})$, 9. Alkylation of the metal center of 3 occurred in preference to deprotonation of the hydrocarbon ligands (Eq. 1-11).



The intermediate bisneopentylidene complex then rearranged (or isomerized) to a large extent to the neopentyl neopentylidyne isomer, 9. This rearrangement is not complete, but 9 is favored by an 85:15 ratio over the bisneopentylidene form. This mixture of isomers was also observed in the synthesis of 9 directly from $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$, 1.^{24,40} The rearrangement which occurred in the formation of 9 from 3 is the reverse of a similar rearrangement which may be involved in the preparation of 3 from 1. It is interesting (and may be more than coincidence) that PMe_3 coordinates to the Ta when the bisneopentylidene isomer is favored as in 3 while PMe_3 is lost completely from the Ta coordination sphere when the neopentyl neopentylidyne isomer is favored as in 9.

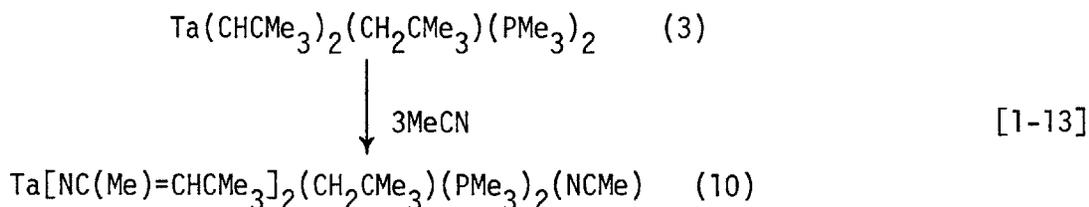
The neopentylidene ligands in 3 not only react with olefins (vide supra) but also with other unsaturated functional groups in which carbon is multiply bound to oxygen or nitrogen. For instance, $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$, 3, reacted with acetone in a Wittig sense.

The products included an uncharacterized tantalum oxide and two equivalents of 2,4,4-trimethyl-2-pentene (diisobutylene) per Ta (Eq. 1-12).



Other nucleophilic tantalum neopentylidene complexes such as $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$ ⁵⁸ and $\text{CpTa}(\text{CHCMe}_3)\text{Cl}_2$ ⁴¹ react with ketones and aldehydes in the same fashion.

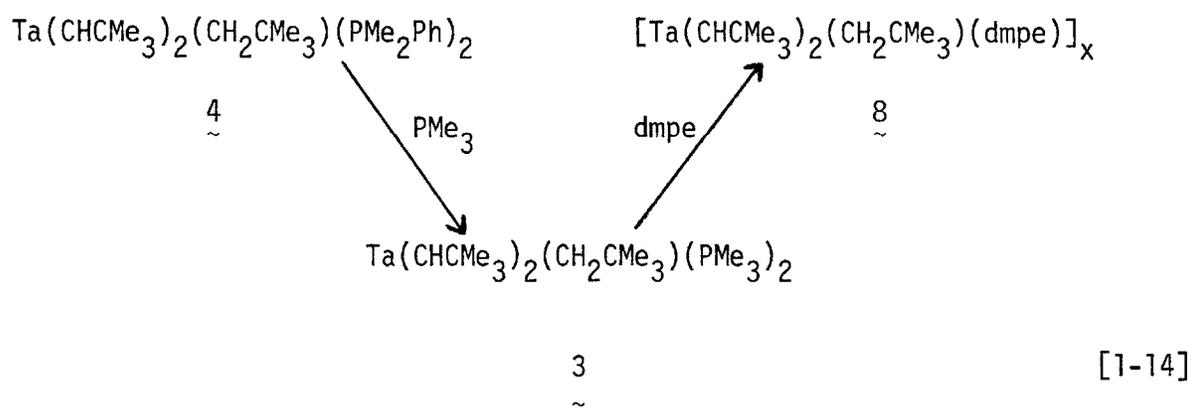
The reaction of $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$, 3, with nitriles such as acetonitrile did not result in the cleavage of the neopentylidene group from the metal but rather in the insertion of the nitrile into the Ta-C_α bond. This product is believed to possess two imido ligands (Ta=NR) and to have the formula $\text{Ta}[\text{NC}(\text{Me})=\text{CHCMe}_3]_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2(\text{NCMe})$, 10, (Eq. 1-13). Since the carbon-carbon double bond in the imido ligands of 10 can possess either the E or Z configuration, it is possible for a number of isomers of 10 to exist. The ¹H NMR of 10 indicates that this is true and that the E:Z ratio is 1:2. As in the case of ketones and aldehydes,



other nucleophilic tantalum neopentylidene complexes react with nitriles in the same way as 3.^{18,42}

The tertiary phosphine ligands in the tantalum bisneopentylidene

complexes, $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)\text{L}_2$, can be exchanged simply and cleanly with different tertiary phosphines. The reaction of $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_2\text{Ph})_2$, 4, with excess PMe_3 leads to the replacement of PMe_2Ph by PMe_3 in the Ta coordination sphere to yield 3 by ^1H NMR (Eq. 1-14). The reaction requires approximately two days at RT but will proceed faster at higher temperatures. Another example of this type of



exchange involves the reaction of $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$, 3, with dmpe . Over a period of one day at RT, the polymeric bisalkylidene, 8, is produced quantitatively from 3 in the presence of one equivalent of dmpe (Eq. 1-14). These reactions are consistent with the replacement of weaker or nonchelating phosphines by more basic or chelating phosphines. The replacement of the tertiary phosphine ligands in the bisalkylidene complexes by ligands other than phosphines was not investigated.

The reactions of the bisalkylidene complexes with small molecules indicate that the Ta-to- C_α double bond is polarized such that the tantalum is electrophilic and the C_α is nucleophilic [i.e. $\text{Ta}(\delta^+) = \text{C}_\alpha(\delta^-)$]. Additionally, it appears that stronger ligands will replace weaker ligands in the bisalkylidene complexes.

GENERAL EXPERIMENTAL PROCEDURES

All experiments were performed either in standard Schlenk apparatus⁵⁹ or in a Vacuum Atmospheres' Dri-Lab (HE-43)/Dri-Train (HE-493) drybox system under an atmosphere of prepurified nitrogen. Reagent grade tetrahydrofuran,^a toluene, and anhydrous ether were distilled under N₂ from sodium/potassium benzophenone ketyl. Pentane and hexane were washed with 5/95 (V/V) HNO₃/H₂SO₄ and then with distilled water. After storage over CaCl₂, the pentane and hexane were distilled under N₂ from ⁿBuLi or NaH. Reagent grade acetonitrile, chloroform, benzene,^b acetone, and dimethylformamide were dried under N₂ over Linde 3Å molecular sieves. Methylene chloride and chlorobenzene were distilled under N₂ from P₂O₅. Chloroform-d₁, acetonitrile-d₃,^c benzene-d₆,^c toluene-d₈,^c and all internal standards were dried under N₂ over Linde 3Å molecular sieves.

The metal halides TaCl₅ and TaBr₅ (ROC/RIC and Cerac) were used as received while NbCl₅ (ROC/RIC) was sublimed before use. TICp (Strem) was also sublimed before use. ZnEt₂ (Alfa/Ventron) and diphos, PPh₂Me, and PPh₃ (all Strem) were used as received. The following compounds were prepared and purified by published methods: PMe₃,^{60,61} PMe₂Ph,⁶² dmpe,^{40,63} C₅Me₅H,⁶⁴ Me₃CCH₂OH,⁴¹ Me₃CCH₂Cl,^{41,65} [Me₂N=CHCl]Cl,^{41,65} ZnCl₂(dioxane).^{61,66} Literature procedures¹⁸ were used to synthesize Me₃CCH₂Li, Me₃CCH₂MgCl, (Me₃CCH₂)₂Zn, (Me₃CCH₂)₂TaCl₃, (Me₃CCH₂)₃TaCl₂,

^aTHF was predried over KOH.

^bBenzene was predried by azeotropic distillation under N₂.

^cThese solvents were predried on a column of grade I alumina.

$(\text{Me}_3\text{CCH}_2)_3\text{NbCl}_2$, $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$, and $\text{Me}_3\text{CCH}=\text{Nb}(\text{CH}_2\text{CMe}_3)_3$.
 $(\text{Me}_3\text{CCH}_2)\text{TaCl}_4$ and $(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_3$ as well as LiC_5Me_5 were prepared by reported methods.⁴¹ $\text{Me}_3\text{SiCH}_2\text{Li}$ ⁶⁷ and $\text{Me}_3\text{SiCH}_2\text{MgCl}$ ⁶⁸ were made by published procedures.

Ethylene, propylene, hydrogen, carbon monoxide, and hydrogen chloride (all Matheson, all C.P. grade) were used as received. Styrene (Eastman, stabilized) was vacuum distilled from CaH_2 . TlC_5Me_5 (X-40,43) was prepared from Tl_2SO_4 and LiC_5Me_5 in THF, followed by sublimation of the mixture and recrystallization of the crude sublimate from pentane at -30°C . tert-Butylcyclopropane (IX-59) was prepared from 3,3-dimethyl-1-butene, methylene iodide, and a Zn/Cu couple in ${}^n\text{Bu}_2\text{O}$, followed by distillation of the volatiles.

NMR data was collected on the following instruments:

${}^1\text{H}$ NMR (referenced to $\text{TMS} \equiv 10\tau$)

60 MHz Varian T-60; Hitachi-Perkin-Elmer R-20B; Jeol FX-60Q

90 MHz Hitachi-Perkin-Elmer R-22B

270 MHz Brüker HFX-270

${}^{13}\text{C}$ NMR (referenced to literature deuterated solvent shifts, $\text{TMS} \equiv 0\delta$)

15.00 MHz Jeol FX-60Q

22.63 MHz Brüker HFX-90

67.89 MHz Brüker HFX-270

${}^{31}\text{P}$ NMR (referenced to external 95% $\text{H}_3\text{PO}_4 \equiv 0\delta$)

36.43 MHz Brücker HFX-90

109.3 MHz Brücker HFX-270

Infrared spectra were recorded on a Perkin-Elmer 567 grating infrared spectrophotometer while visible and ultraviolet spectra were collected on a Cary 17 spectrophotometer. Analytical GLC yields were measured on a

Hewlett-Packard 5730A gas chromatograph which was equipped with a programmable temperature controller, a flame ionization detector, and a Hewlett-Packard 3380A electronic integrator-recorder. Organic products were identified by coinjection with authentic samples. Yields were based on internal standard procedures in which response factors for acyclic hydrocarbons were determined by the ratio of the molecular weight of the standard compared to the molecular weight of the product. The analytical GLC columns included:

0.125" x 8'	10% SP-2100 on 100/120 Supelcoport
0.125" x 8'	10% SE-30 on 100/120 Gas Chrom Q
0.125" x 8'	20% saturated $\text{AgNO}_3/\text{HO}(\text{C}_2\text{H}_4\text{O})_4\text{H}$ on 80/100 Chromosorb P
0.125" x 8'	20% propylene carbonate on 80/100 Chromosorb P
0.125" x 25'	20% propylene carbonate on 80/100 Chromosorb P

GC-MS studies were performed on a Hewlett-Packard 5990A gas chromatograph-mass spectrometer.

Photolyses were carried out with a 450 W Hanovia medium-pressure mercury lamp which was equipped with a water cooled quartz jacket and a power supply. Molecular weights were determined cyroscopically under N_2 in either benzene or cyclohexane. Elemental analyses were performed by Alfred P. Bernhardt (West Germany) and Schwarzkopf Microanalytical Labs (New York). Complexes containing more than one monodenate tertiary phosphine generally did not analyze properly due to the lability of the phosphines and the high sensitivity of the complexes to air and water.

EXPERIMENTAL

1. The Reaction of $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$ with One Equivalent of C_2H_4 [VII-20, X-23].

$\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$ (0.116 g, 0.25 mmol) was dissolved in 0.75 mL of toluene- d_8 , placed in a NMR tube, and cooled to -78°C . Then, gaseous C_2H_4 (16.8 mL, 0.75 mmol, 2 fold excess) was injected by syringe into the cold sample. The orange solution immediately became dark red. The ^{13}C NMR at -75°C is consistent with the complete conversion of starting material to a new product, $\text{Ta}(\eta^2\text{-CH}_2=\text{CHCH}_2\text{CMe}_3)(\text{CH}_2\text{CMe}_3)_3$, 2, which is stable to -15°C .

^{13}C NMR (#180-D, ppm, $\text{C}_6\text{D}_5\text{CD}_3$, -45°C , 15 MHz, ^1H gated decoupled):

121.6 (t, $J_{\text{CH}}=106$ Hz, $-\text{CH}_2\text{CMe}_3$), 84.8 (d, $J_{\text{CH}}=148$ Hz, $\text{Me}_3\text{CCH}_2\text{CH}=\text{CH}_2$),
 76.7 (t, $J_{\text{CH}}=148$ Hz, $\text{Me}_3\text{CCH}_2\text{CH}=\text{CH}_2$), 51.4 (t, $J_{\text{CH}}=128$ Hz, $\text{Me}_3\text{CCH}_2\text{CH}=\text{CH}_2$),
 37.5 (s, $\text{Me}_3\text{CCH}_2\text{CH}=\text{CH}_2$), 35.2 (s, $-\text{CH}_2\text{CMe}_3$), 35.0 (q, $J_{\text{CH}}=126$ Hz, $-\text{CH}_2\text{CMe}_3$),
 30.5 (q, $J_{\text{CH}}=128$ Hz, $\text{Me}_3\text{CCH}_2\text{CH}=\text{CH}_2$).

2. The Reaction of $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$ with Excess C_2H_4 [III-4, X-25].

a. $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$ (0.25 g, 0.54 mmol) was dissolved in 0.75 mL of toluene- d_8 , placed in a pressure bottle, and stirred at RT for 3 hrs. under 50 PSIG of C_2H_4 . The orange solution immediately became red but then slowly changed to yellow at which point there was no further reaction. This solution was transferred to an NMR tube. The ^{13}C NMR spectrum (#181) at 0°C is quite complex and shows the presence of several organic and organo-metallic products.

b. $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$ (0.29 g, 0.63 mmol) and n-heptane (0.067 g, 0.67 mmol, for use as an internal standard) were dissolved in 3 mL of pentane, placed in a pressure bottle, and stirred at RT for 1/2 hr. under 50 PSIG of C_2H_4 . The orange solution immediately became red and changed to yellow after 20 mins. An aliquot of the reaction solution was passed down a 6" alumina column (activity grade #1) and eluted with additional pentane. The eluant was analyzed by GLC. The sample contained 0.624 equivalents of neopentane and 0.507 equivalents of 2,2-dimethylpentane. Significant amounts of 2,2,5,5-tetramethylhexane and cis- and trans-2,2,5,5-tetramethyl-3-hexene were present (see Table 1.I.). The sample also included traces of three unknown products.

3. The Reaction of $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$ with C_2H_4 in the Presence of PMe_3 [II-72, II-73].

a. $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$ (0.28 g, 0.60 mmol) and n-heptane (0.060 g, 0.60 mmol, for use as an internal standard) were dissolved in 3 mL of pentane, placed in a pressure bottle, and stirred at RT for 1 hr. under 50 PSIG of C_2H_4 . Then PMe_3 (0.14 g, 1.84 mmol) was injected by syringe into the yellow reaction solution which turned red instantly. At this point, the reaction solution began to consume more C_2H_4 and to produce 1-butene catalytically. After 1 hr. an aliquot of the reaction solution was passed down a 6" alumina column (activity grade #1) and eluted with additional pentane. The eluant was analyzed by GLC. The sample contained 0.517 equivalents of neopentane, 0.474 equivalents of 2,2-dimethylpentane, and 0.437 equivalents of 4,4-dimethyl-1-pentene. Significant amounts of 2,2,5,5-tetramethylhexane and cis- and trans-2,2,5,5-tetramethyl-3-hexene were present (see Table 1.I.). In this reaction 1-butene was produced

at the rate of $0.69 \text{ Ta}^{-1} \text{ min}^{-1}$. The sample also included traces of several unknown products.

b. $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$ (0.28 g, 0.60 mmol), PMe_3 (0.14 g, 1.84 mmol), and *n*-heptane (0.060 g, 0.60 mmol, for use as an internal standard) were dissolved in 3 mL of pentane, placed in a pressure bottle, and stirred at RT under 50 PSIG of C_2H_4 . The initial orange solution turned red immediately after the C_2H_4 was introduced. At this point the reaction mixture also began to produce 1-butene catalytically. Throughout the course of the reaction, the solution stayed red. After 1 hr. an aliquot of the reaction solution was passed down a 6" alumina column (activity grade #1) and eluted with additional pentane. The eluant was analyzed by GLC. The sample contained 0.227 equivalents of neopentane, 0.372 equivalents of 2,2-dimethylpentane, and 2.82 equivalents of 4,4-dimethyl-1-pentene. Traces of 2,2,5,5-tetramethylhexane, and *cis*- and *trans*-2,2,5,5-tetramethyl-3-hexene were present (see Table 1.I.). In this reaction 1-butene was produced at the rate of $2.21 \text{ Ta}^{-1} \text{ min}^{-1}$. The sample also included traces of several unknown products.

4. The Preparation of $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ (3) [III-20].

$\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$ (5.00 g, 10.8 mmol) and PMe_3 (1.80 g, 23.8 mmol, 10% excess) were dissolved in 4 mL of benzene and allowed to stand at RT for 4 hrs. The mother liquor was decanted from the orange crystals of 3 and the volume was reduced *in vacuo* to obtain a second crop. Both crops of 3 were combined and recrystallized from pentane at -30°C to yield 5.63 g of 3 (96.1%).

^1H NMR ($\#_{\text{H}}-001$, τ , C_6D_6 , 35°C , 270 MHz): 3.07 (t, 1, $^3J_{\text{HP}}=3.0$ Hz, $=\text{CHCMe}_3$), 7.92 (br s, 1, $=\text{CHCMe}_3$), 8.68 (t, 18, $^2J_{\text{HP}}=2.4$ Hz, PMe_3), 8.79 (s, 9, $-\text{CMe}_3$), 8.80 (s, 9, $-\text{CMe}_3$), 8.84 (s, 9, $-\text{CMe}_3$), 9.39 (t, 2, $^3J_{\text{HP}}=18.9$ Hz, $-\text{CH}_2\text{CMe}_3$).

^1H (^{31}P) NMR ($\#_{135}-\text{B}$, τ , $\text{C}_6\text{D}_5\text{CD}_3$, 35°C , 90 MHz): 3.06 (s, 1, $=\text{CHCMe}_3$), 7.92 (s, 1, $=\text{CHCMe}_3$), 8.66 (s, 18, PMe_3), 8.79 (s, 9, $-\text{CMe}_3$), 8.80 (s, 9, $-\text{CMe}_3$), 8.83 (s, 9, $-\text{CMe}_3$), 9.38 (s, 2, $-\text{CH}_2\text{CMe}_3$).

^{13}C NMR ($\#_{\text{C}}-001$, ppm, $\text{C}_6\text{D}_5\text{CD}_3$, 35°C , 67.89 MHz, ^1H gated decoupled): 274.1 (d, $J_{\text{CH}}=95$ Hz, $=\text{CHCMe}_3$), 245.6 (d, $J_{\text{CH}}=85$ Hz, $=\text{CHCMe}_3$), 72.0 (t, $J_{\text{CH}}=108$ Hz, $-\text{CH}_2\text{CMe}_3$), 47.3 (s, $=\text{CHCMe}_3$), 44.5 (s, $=\text{CHCMe}_3$), 38.4 (s, $-\text{CH}_2\text{CMe}_3$), 37.4 (q, $J_{\text{CH}}=122$ Hz, $-\text{CMe}_3$), 35.6 (q, $J_{\text{CH}}=122$ Hz, $-\text{CMe}_3$), 34.5 (q, $J_{\text{CH}}=125$ Hz, $-\text{CMe}_3$), 20.2 (q, $J_{\text{CH}}=128$ Hz, PMe_3).

IR ($\#_{132}$, cm^{-1} , nujol mull, NaCl plates): 2650 (w, $\nu_{\text{C}_\alpha\text{H}_\alpha}$).

MW (IV-52, 53, 54; cyclohexane): calcd 544.5, found 540.

5. The Preparation of $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_2\text{Ph})_2$ (4) [III-46].

$\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$ (6.50 g, 14.0 mmol) and PMe_2Ph (3.87 g, 28.0 mmol) were dissolved in 5 mL of benzene and allowed to stand in the dark at RT for ten days. The benzene was removed from the dark red-brown solution in vacuo to yield an oil. This is dissolved in pentane, treated with activated charcoal, filtered, reduced in volume in vacuo, and stored at -30°C . Two crops of light brown crystals were collected. Further purification including treatment with activated charcoal and recrystallization from pentane at -30°C gave 7.24 g of bright yellow crystals of 4 (77.3%).

^1H NMR ($\#H-002$, τ , $\text{C}_6\text{D}_5\text{CD}_3$, -30°C , 270 MHz): 2.39 (br s, 1, $=\text{CHCMe}_3$), 2.44-3.07 (m, 10, Ph), 8.06 (br s, 1, $=\text{CHCMe}_3$), 8.32 (br s, 6, $\text{PMeMe}'\text{Ph}$), 8.35 (br s, 6, $\text{PMeMe}'\text{Ph}$), 8.62 (s, 9, $-\text{CMe}_3$), 8.64 (s, 9, $-\text{CMe}_3$), 9.28 (s, 9, $-\text{CMe}_3$), 9.47 (t, 2, $^3J_{\text{HP}}=18.2$ Hz, $-\text{CH}_2\text{CMe}_3$).

^{13}C NMR ($\#C-002$, ppm, C_6D_6 , 35°C , 67.89 MHz, ^1H gated decoupled): 277.0 (d, $J_{\text{CH}}=95$ Hz, $=\text{CHCMe}_3$), 243.9 (d, $J_{\text{CH}}=82$ Hz, $=\text{CHCMe}_3$), 138.6 (s, i-C Ph), 132.2 (d, $J_{\text{CH}}=159$ Hz, m-C Ph), 129.1 (d, $J_{\text{CH}}=162$ Hz, p-C Ph), 128.3 (d, $J_{\text{CH}}=159$ Hz, o-C Ph), 74.3 (t, $J_{\text{CH}}=105$ Hz, $-\text{CH}_2\text{CMe}_3$), 47.8 (s, $=\text{CHCMe}_3$), 44.8 (s, $=\text{CHCMe}_3$), 37.7 (s, $-\text{CH}_2\text{CMe}_3$), 36.6 (q, $J_{\text{CH}}=123$ Hz, $-\text{CMe}_3$), 35.2 (q, $J_{\text{CH}}=124$ Hz, $-\text{CMe}_3$), 34.7 (q, $J_{\text{CH}}=128$ Hz, $-\text{CMe}_3$), 22.5 (q, $J_{\text{CH}}=131$ Hz, $\text{PMeMe}'\text{Ph}$), 19.2 (q, $J_{\text{CH}}=129$ Hz, $\text{PMeMe}'\text{Ph}$).

6. The Preparation of $\text{Nb}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ ($\underline{6}$) [IV-36].

A pentane solution containing $\text{Me}_3\text{CCH}=\text{Nb}(\text{CH}_2\text{CMe}_3)_3$ (6.3 mmol, prepared in situ) was cooled to 0°C and PMe_3 (1.44 g, 18.9 mmol, 50% excess) was added with stirring. After 1 hr. at 0°C the reaction was allowed to warm slowly to RT. The reaction solution was filtered, treated with activated charcoal, refiltered, reduced in volume in vacuo, and stored at -30°C . The crude product was collected by filtration and recrystallized from pentane at -30°C after treatment with additional activated charcoal. The yield was 1.98 g of yellow crystalline $\underline{6}$ (68.9%)

^1H NMR ($\#H-003$, τ , C_6D_6 , 35°C , 270 MHz): 0.62 (t, 1, $^3J_{\text{HP}}=3.1$ Hz, $=\text{CHCMe}_3$), 5.71 (br s, 1, $=\text{CHCMe}_3$), 8.77 (s, 9, $-\text{CMe}_3$), 8.78 (s, 9, $-\text{CMe}_3$), 8.79 (t, 18, $^2J_{\text{HP}}=2.6$ Hz, PMe_3), 8.80 (s, 9, $-\text{CMe}_3$), 9.94 (t, 2, $^3J_{\text{HP}}=17.6$ Hz, $-\text{CH}_2\text{CMe}_3$).

^{13}C NMR ($\#^{\text{C}}\text{-003}$, ppm, C_6D_6 , 35°C , 67.89 MHz, ^1H gated decoupled): 281.8 (br, $=\text{CHCMe}_3$), 245.3 (br, $=\text{CHCMe}_3$), 59.6 (br, $-\text{CH}_2\text{CMe}_3$), 44.6 (s, $=\text{CHCMe}_3$), 42.7 (s, $=\text{CHCMe}_3$), 37.7 (s, $-\text{CH}_2\text{CMe}_3$), 36.9 (q, $J_{\text{CH}}=123$ Hz, $-\text{CMe}_3$), 34.3 (q, $J_{\text{CH}}=125$ Hz, $-\text{CMe}_3$), 33.3 (q, $J_{\text{CH}}=123$ Hz, $-\text{CMe}_3$), 19.3 (q, $J_{\text{CH}}=129$ Hz, PMe_3).

7. The Preparation of $\text{Nb}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_2\text{Ph})_2$ (7) [III-67].

A pentane solution containing $\text{Me}_3\text{CCH}=\text{Nb}(\text{CH}_2\text{CMe}_3)_3$ (4.6 mmol, prepared in situ) was cooled to 0°C and PMe_2Ph (1.40 g, 10.1 mmol, 10% excess) was added with stirring. After 3 hrs. at 0°C the reaction was allowed to warm slowly to RT. The reaction solution was worked up as in case of 6. The yield was 1.77 g of yellow crystalline 7 (66.3%).

^1H NMR ($\#162$, τ , C_6D_6 , 35°C , 60 MHz): 0.07 (br s, 1, $=\text{CHCMe}_3$), 2.20-3.00 (m, 10, Ph), 5.82 (br s, 1, $=\text{CHCMe}_3$), 8.43 (m, 12, PMe_2Ph), 8.56 (s, 9, $-\text{CMe}_3$), 8.62 (s, 9, $-\text{CMe}_3$), 9.05 (s, 9, $-\text{CMe}_3$), 10.00 (t, 2, $^3J_{\text{HP}}=17.0$ Hz, $-\text{CH}_2\text{CMe}_3$).

8. The Preparation of $[\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{dmpe})]_x$ (8).

a. from $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$ [IV-40].

$\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$ (1.39 g, 3.00 mmol) and dmpe (0.45 g, 3.00 mmol) were dissolved in 10 mL of pentane. A white powder began to precipitate from the orange solution. After 10 hrs. the product was collected by filtration, rinsed with pentane, and dried in vacuo. The yield was 1.56 g of white, microcrystalline 8 (95.5%).

b. from $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ [III-49].

$\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ (0.14 g, 0.25 mmol) and dmpe (0.04 g, 0.25 mmol) were dissolved in 3 mL of pentane. A white powder began to form. After 1 day 0.133 g of 8 was isolated as above (97.7%).

IR (#133, cm^{-1} , nujol mull, NaCl plates): 2640 (vw, $\nu_{\text{C}_\alpha\text{H}_\alpha}$).

9. The Reaction of $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ with C_2H_4 [IV-27].

$\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ (0.185 g, 0.340 mmol) and n-pentane (0.1005 g, 1.003 mmol, for use as an internal standard) were dissolved in 5 mL of pentane in a pressure bottle and stirred at 25°C under 50 PSIG of C_2H_4 . The orange solution immediately became red as the C_2H_4 was introduced. After 1/4 hr. an aliquot of the reaction solution was quenched with O_2 and analyzed by GLC. The sample contained 2.99 equivalents of 4,4-dimethyl-1-pentene as well as a large quantity of 1-butene which was produced at the rate of $2.51 \text{ Ta}^{-1}\text{min}^{-1}$ (see Table I.IV.).

10. The Reaction of $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_2\text{Ph})_2$ with C_2H_4 [III-30].

$\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_2\text{Ph})_2$ (0.231 g, 0.345 mmol) and n-heptane (0.1005 g, 1.003 mmol, for use as an internal standard) were dissolved in 5 mL of pentane in a pressure bottle and stirred at 25°C under 50 PSIG of C_2H_4 . The yellow solution immediately became red as the C_2H_4 was introduced. After 1/2 hr. an aliquot of the reaction solution was quenched with O_2 and analyzed by GLC. The sample contained 2.77 equivalents of 4,4-dimethyl-1-pentene. Small amounts of neopentane, 2,2-dimethylpentane, cis-2,2,5,5-tetramethyl-3-hexene, and trans-2,2,5,5-tetramethyl-3-hexene were also present (see Table I.IV.). The production of 1-butene occurred at a rate of $2.14 \text{ Ta}^{-1}\text{min}^{-1}$.

11. The Reaction of $\text{Nb}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ with C_2H_4 [IV-16].

$\text{Nb}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ (0.150 g, 0.329 mmol) and *n*-heptane (0.1005 g, 1.003 mmol, for use as an internal standard) were dissolved in 5 mL of pentane in a pressure bottle and stirred at 25°C under 50 PSIG of C_2H_4 . The yellow solution immediately became red as the C_2H_4 was introduced. After 2 hrs. an aliquot of the reaction solution was quenched with O_2 and analyzed by GLC. The sample contained 2.11 equivalents of 4,4-dimethyl-1-pentene. Neopentane, 2,2-dimethylpentane, and *trans*-2,2,5,5-tetramethyl-3-hexene were also present in significant amounts (see Table I.IV.). A slight amount of 1-butene was produced at a rate of $0.01 \text{ Nb}^{-1} \text{ min}^{-1}$.

12. The Reaction of $\text{Ta}(\text{CHCMe}_3)_2(\text{CD}_2\text{CMe}_3)(\text{PMe}_3)_2$ with C_2H_4 [V-4].

$\text{Ta}(\text{CHCMe}_3)_2(\text{CD}_2\text{CMe}_3)(\text{PMe}_3)_2$ (0.182 g, 0.333 mmol) and *n*-heptane (0.1005 g, 1.003 mmol, for use as an internal standard) were dissolved in 2 mL of pentane in a pressure bottle and stirred at 25°C under 50 PSIG of C_2H_4 . The orange solution immediately became red as the C_2H_4 was introduced. After 1/2 hr. an aliquot of the reaction solution was quenched with O_2 and analyzed by GLC and GC-MS. The sample contained 3.00 equivalents of 4,4-dimethyl-1-pentene and a large quantity of 1-butene. The 4,4-dimethyl-1-pentene was a 50/50 mixture of the d_0 olefin and d_1 labeled olefin.

13. The Reaction of $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ with Propylene [III-27].

$\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ (0.175 g, 0.321 mmol) and *n*-octane (0.0326 g, 0.285 mmol, for use as an internal standard) were dissolved in 5 mL of pentane in a pressure bottle and stirred at 25°C under 50 PSIG of C_3H_6 . The orange solution immediately became red as the C_3H_6 was

introduced. After 1 1/2 hrs. an aliquot of the reaction solution was quenched with O_2 and analyzed by GLC. The sample contained 0.82 equivalents of 2,4,4-trimethyl-1-pentene. Neopentane and 2,4,4-trimethyl-pentane were also present. Although there were traces of many other products in the sample, no propylene dimers (linear or branched) were produced catalytically.

14. The Reaction of $Ta(CHCMe_3)_2(CH_2CMe_3)(PMe_3)_2$ with HCl [III-30].

$Ta(CHCMe_3)_2(CH_2CMe_3)(PMe_3)_2$ (0.27 g, 0.5 mmol) was dissolved in 10 mL of toluene and cooled to $-78^\circ C$. Then anhydrous gaseous HCl (12.3 mL, 0.55 mmol, 10% excess) was added to the stirred reaction solution by syringe. The orange solution became yellow-orange as the reaction was allowed to warm to RT. The solvent was removed in vacuo and the crude product was dissolved in C_6D_6 . The 1H NMR spectrum (#149) of the sample showed the presence of a 50/50 mixture of starting material and $(Me_3CCH_2)_3TaCl_2$. Little (if any) $Ta(CHCMe_3)_2Cl(PMe_3)_2$ was present.

15. The Reaction of $Ta(CHCMe_3)_2(CH_2CMe_3)(PMe_3)_2$ with $LiCH_2CMe_3 \cdot tmeda$ [III-57].

{An Alternate Synthesis of $[Me_3CC \equiv Ta(CH_2CMe_3)_3] \cdot Li(tmeda)$ (9)}

$Ta(CHCMe_3)_2(CH_2CMe_3)(PMe_3)_2$ (0.55 g, 1.0 mmol) was dissolved in 30 mL of pentane and cooled to $-78^\circ C$. Then $LiCH_2CMe_3 \cdot tmeda$ (1 mmol, prepared in situ from $LiCH_2CMe_3$ (0.08 g) and $tmeda$ (0.12 g) in 15 mL of pentane) was added with stirring. The reaction was allowed to warm to RT slowly and then filtered. As the volume of the filtrate was reduced in vacuo, a first crop of yellow crystals of 9 was collected. Further removal of pentane

in vacuo from the filtrate produced a second crop of yellow crystalline 9. The final yield was 0.45 g of 9 (76.7%). As previously reported, 9 is actually a mixture of two isomers in a 85:15 ratio.

^1H NMR (#165, τ , C_6H_6 , 35°C , 60 MHz): 8.05 (s, 12, $-\text{NMe}_2$), 8.21 (s, 4, $-\text{CH}_2\text{NMe}_2$), 8.40 (s, 9 $\equiv\text{CCMe}_3$), 8.62 (s, 27, $-\text{CH}_2\text{CMe}_3$), 9.45 (s, 6, $-\text{CH}_2\text{CMe}_3$). Resonances for the minor isomer occur at 6.52, 7.45, 7.80, 8.48, 9.20, and 9.56.

16. The Reaction of $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ with Acetone [III-15].

$\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ (0.182 g, 0.33 mmol) and *n*-heptane (0.0335 g, 0.334 mmol, for use as an internal standard) were dissolved in 5 mL of ether and cooled to -30°C . Then dry acetone (0.116 g, 2.00 mmol, 2 fold excess) was added dropwise with stirring. The reaction is immediate and vigorous. The solution was decolorized as a white solid precipitated. The supernatant was analyzed by GLC and it contained 1.942 equivalents of $\text{Me}_2\text{C}=\text{CHCMe}_3$ (97.1%).

17. The Reaction of $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ with MeCN [III-28].

$\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ (0.109 g, 0.20 mmol) was dissolved in 0.5 mL of benzene. Acetonitrile (0.025 g, 0.60 mmol) was added. The reaction was exothermic as the orange solution became red. The ^1H NMR spectrum (#147-D) of the sample showed that the bisalkylidene complex had been converted quantitatively to $\text{Ta}[\text{NC}(\text{Me})=\text{CHCMe}_3]_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2(\text{NCMe})$, 10, which is a mixture of isomers for which a 1:2 E:Z ratio was observed for the imido ligands.

^1H NMR (#147-D, τ , C_6H_6 , 35°C , 60 MHz): 5.08 (m, $=\text{NC}(\text{Me})=\text{CHCMe}_3$),
6.01 (m, $=\text{NC}(\text{Me})=\text{CHCMe}_3$), 7.97 (m, $=\text{NC}(\text{Me})=\text{CHCMe}_3$), 8.05 (m, $=\text{NC}(\text{Me})$
 $=\text{CHCMe}_3$), 8.68 (s, $-\text{CH}_2\text{CMe}_3$), 8.79 (s, MeCN), 8.81-9.08 (m, PMe_3),
8.81-9.08 (m, $=\text{NC}(\text{Me})=\text{CHCMe}_3$), 9.33 (m, $-\text{CH}_2\text{CMe}_3$).

Chapter 2

The Synthesis and Characterization of Monoalkylidene Complexes of Niobium and Tantalum

INTRODUCTION

The preparation of $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$, which was described in Chapter 1, is an example of ligand induced α -hydrogen abstraction. This is not a very general reaction for the preparation of bisalkylidene complexes, however. Only very basic, monodentate phosphines can be used in this reaction. Because of this limitation, the reaction of tertiary phosphines (as well as other types of ligands) with various tantalum and niobium alkyl complexes was examined. This chapter details the results of those investigations.

This approach was very successful. A large number of new monoalkylidene complexes of the type $\text{Me}_3\text{CCH}=\text{MX}_3\text{L}_n$ were prepared. This result indicated that under the proper conditions ligand induced α -hydrogen abstraction was a very general reaction. At the same time, it also provided a more thorough understanding of the ligand induced α -hydrogen abstraction process which, in this case, is believed to occur through a seven coordinate intermediate. This type of reaction provides an additional route to nucleophilic alkylidene ligands that complements the previous methods of preparation which include "normal" α -hydrogen abstraction,¹⁸ deprotonation,²⁰ dehydrohalogenation,²⁶ and alkylidene transfer.²⁷

In addition to a better understanding of the formation process, this study has resulted in a more detailed knowledge of the nature of the alkylidene ligands themselves. The neutron diffraction structure³⁰ of one of these new monoalkylidene complexes, $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Cl}_3]_2$, demonstrates the existence of a strong interaction between the $\text{C}_\alpha\text{-H}_\alpha$ bond and the metal center. This type of interaction had been postulated as the cause of some anomalous spectral data for nucleophilic alkylidenes.

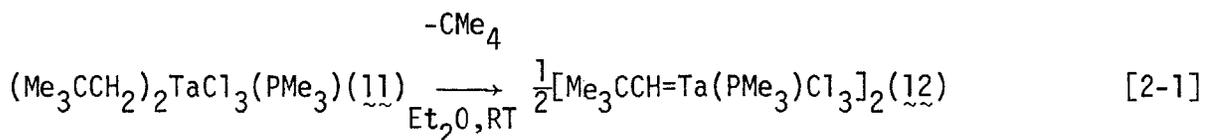
In addition to neopentylidene complexes, this scheme has been

expanded to include trimethylsilylmethylene, neophilylidene,⁴⁷ and benzylidene⁵⁶ complexes. The result of this investigation is that a new and highly diverse class of monoalkylidene complexes is available for the study of their properties and reaction chemistry.

RESULTS AND DISCUSSION

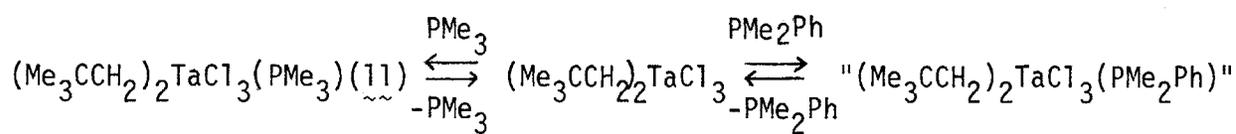
A. Reactions of $(\text{Me}_3\text{CCH}_2)_2\text{TaX}_3$ with One Equivalent PR_3 1. The Preparation and Properties of the $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PR}_3)\text{X}_3]_2$ Series

The reaction of yellow $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ ¹⁸ with one equivalent of PMe_3 in cold pentane yields red-orange needles of $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3(\text{PMe}_3)$, 11. The solubility of 11 is low in pentane or toluene but high in ether or chloroform. This six coordinate, 12e-complex is thermally unstable but can be isolated at low temperature. The thermal instability of 11 is a result of the crowded coordination sphere and the electron deficient metal center. These two factors work synergistically to promote the decomposition of 11 by means of an α -hydrogen abstraction. This occurs on allowing 11 to stand at RT in ether solution. The products consist of one equivalent of neopentane and a half equivalent of a dimeric neopentylidene complex, 12 (Eq. 2-1). The reaction is quantitative and 12 can be isolated as large, red crystals from ether. This dimer, 12, is insoluble in pentane, slightly soluble in benzene or toluene, and very soluble in ether or chloroform.



The conversion of 11 to 12 is another example of a ligand induced α -hydrogen abstraction similar to that seen in the formation of $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$, 3, in Chapter 1 (vide supra). Complex 11 meets all the requirements for this type of process. These requirements include an electron deficient metal center, two or more alkyl groups

In the case of PMe_2Ph or PPh_2Me the reaction with $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ in pentane yields dimeric neopentylidene complexes analogous to 12. These reactions are slower. With these bulkier, less basic phosphines the six coordinate phosphine adducts are not isolated either because they are more soluble or more likely because the equilibrium favors starting materials (Eq. 2-3). This may account for the



[2-3]

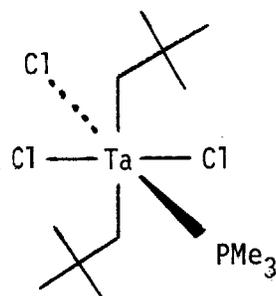
decrease in the rates of reaction. The reaction of $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ with one equivalent of either PMe_2Ph or PPh_2Me in pentane gives a red solution which deposits a red oil after several hours at RT. These oils crystallize overnight to yield red crystals of $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_2\text{Ph})\text{Cl}_3]_2$, 14, or $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PPh}_2\text{Me})\text{Cl}_3]$, 15. The solubilities of 14 and 15 are similar to those of $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Cl}_3]_2$, 12, except that 14 and 15 are more soluble in aromatic solvents due to the phenyl rings present on the phosphine ligands.

The reaction of yellow $(\text{Me}_3\text{CCH}_2)_2\text{TaBr}_3$ with one equivalent of PMe_3 in cold ether yields red crystals of $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Br}_3]_2$, 16, on standing overnight at RT. The bromide analogue of 11, which is $(\text{Me}_3\text{CCH}_2)_2\text{TaBr}_3(\text{PMe}_3)$, is too unstable and reactive to be isolated. Presumably, it is prepared in situ in the formation of 16. The solubility properties of 16 parallel those of the chloride analogue, 12.

2. The Characterization of the $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PR}_3)\text{Cl}_3]_2$ Series

The ^1H NMR spectrum of $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3(\text{PMe}_3)$, 11, which is a precursor to 12 and 13, confirms the presence of one PMe_3 per tantalum. This PMe_3 ligand is labile especially above 0°C . At RT as well as at -50°C (where the phosphine exchange is stopped), the neopentyl groups are equivalent by ^1H and ^{13}C NMR. One possible structure contains the three chloride ligands in the same meridional configuration seen in the products which then requires the neopentyl groups to be trans. The other possible structure possesses cis neopentyl groups with three facial chlorides. The former structure is favored^a for steric reasons since the best arrangement for the bulky alkyl groups is trans. The proposed structure of 11 is shown in Figure 2.1.

Figure 2.1. The Proposed Structure of $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3(\text{PMe}_3)$



^aUnder conditions where the PMe_3 ligand is labile 11 may actually be a mixture of rapidly interconverting isomers.

A molecular weight measurement in benzene (freezing point depression) gave a value of 853 (calcd 867.0) for $\underline{12}$. This confirms that $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Cl}_3]_2$, $\underline{12}$, is dimeric. The IR and NMR spectra of complexes $\underline{12}$, $\underline{14}$, $\underline{15}$, and $\underline{16}$ are consistent with their formulation as neopentylidene complexes. The ^1H NMR data for these four complexes are listed in Table 2.I. The α -hydrogen resonances are broadened slightly by coupling to the

Table 2.I. The ^1H NMR Data* for $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PR}_3)\text{X}_3]_2$

		$\underline{\text{Me}_3\text{CCH}=\text{Ta}}$	$\underline{\text{Me}_3\text{CCH}=\text{Ta}}$	$\underline{\text{PMe}}(\text{J}_{\text{HP}})$	CONDITIONS
$[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Cl}_3]_2$	($\underline{12}$)	8.90	4.70	8.86(9.6)	$\text{C}_6\text{H}_6, 35^\circ\text{C}$
$[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_2\text{Ph})\text{Cl}_3]_2$	($\underline{14}$)	8.92	4.67	8.54(8.3)	$\text{C}_6\text{H}_6, 35^\circ\text{C}$
$[\text{Me}_3\text{CCH}=\text{Ta}(\text{PPh}_2\text{Me})\text{Cl}_3]_2$	($\underline{15}$)	8.90	4.49	8.12(8.0)	$\text{C}_6\text{H}_6, 35^\circ\text{C}$
$[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Br}_3]_2$	($\underline{16}$)	8.73	6.16	8.22(9.0)	$\text{CDCl}_3, 35^\circ\text{C}$

* Shifts are listed in τ while coupling constants are listed in Hz.

phosphorus nucleus. The value of $\text{J}_{\text{H}_\alpha\text{P}}$ is on the order of 1-2 Hz. The IR spectra of these complexes contain characteristic absorptions for the $\text{C}_\alpha\text{-H}_\alpha$ stretch.¹⁹ This stretch is shifted out of the normal C-H stretching range^a toward lower wavenumbers. The interaction of the electrons in the $\text{C}_\alpha\text{-H}_\alpha$ bond^b with the metal weakens the bond and causes this shift. Distinctive IR absorptions for these complexes are listed in Table 2.II. The ^{13}C NMR spectra of these complexes also contain features which are characteristic

^aThe usual range for C-H stretching is 2850 to 3100 cm^{-1} .⁴⁶

^bThis interaction is confirmed in the neutron diffraction study of $\underline{12}$ (vide infra).

Table 2.II. The IR Data* for $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PR}_3)_3]_2$

		$\nu_{\text{C}-\text{H}_\alpha}$	Ph combination modes
$[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Cl}_3]_2$	(12)	2605	
$[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_2\text{Ph})\text{Cl}_3]_2$	(14)	2595	1978, 1869, 1795, 1730
$[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Br}_3]_2$	(16)	2519	

* Absorptions are listed in cm^{-1} and were measured in nujol mulls.

of neopentylidene complexes. The α -carbons have shifts of 270-290 ppm downfield from TMS. These shifts are within the range expected for a carbon doubly bound to a transition metal.⁴³ These resonances appear as doublets in the ^1H gated decoupled spectra. This indicates that only one hydrogen is bound to the α -carbon as expected for a primary alkylidene ligand. The value of $J_{\text{C}_\alpha\text{H}_\alpha}$ is very low and is on the order of 80-100 Hz.^a The same interaction of the metal with the electrons in the $\text{C}_\alpha\text{-H}_\alpha$ bond which lowers the value of $\nu_{\text{C}_\alpha\text{H}_\alpha}$ also decreases the value of $J_{\text{C}_\alpha\text{H}_\alpha}$. The ^{13}C NMR data for these complexes is listed in Table 2.III.

The spectra of mixtures of 12 and 16 show evidence of an interesting reaction. The resonance for the α -hydrogens in the ^1H NMR of this mixture at RT is broad and weak. On cooling to -30°C this broad resonance sharpens and resolves into several resonances. There is one small resonance each for 12 and 16. There are two large resonances for what is proposed to be a mixed dimer, $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Cl}_3][\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Br}_3]$. This reaction presumably proceeds through a short lived, five coordinate intermediate, " $\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)_3$ ", which can recouple in a random manner. This

^aThe usual value of J_{CH} for a sp^2 carbon is ~ 160 Hz.⁴⁵

Table 2.III. The ^{13}C NMR Data* for $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PR}_3)_3]_2$

		$=\text{CHCMe}_3(J_{\text{C}_\alpha\text{H}_\alpha})(J_{\text{C}_\alpha\text{P}})$	$=\text{CHCMe}_3$	$=\text{CHCMe}_3(J_{\text{CH}})$	$\text{PMe}_3(J_{\text{CH}})(J_{\text{CP}})$	Conditions
$[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Cl}_3]_2$	(12)	276.0(101.0)(7.3)	46.6	33.5(126.0)	15.8(132.0)(29.0)	$\text{C}_6\text{D}_6, 28^\circ\text{C}$
$[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Br}_3]_2$	(16)	283.0(86.5)(10.3)	48.0	33.4(126.0)	17.7(130.9)(29.3)	$\text{CDCl}_3, 28^\circ\text{C}$

* Shifts are listed in ppm while coupling constants are listed in Hz.

intermediate has not yet been observed spectroscopically. The possibility that further scrambling of the halides around the metal to give dimers which contain ratios of Cl^- to Br^- differing from 1.0 has not yet been ruled out since there are several other small unexplained resonances in the α -hydrogen region.

3. The Neutron Diffraction Structure of $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Cl}_3]_2$ (12)

A neutron diffraction study of 12 was performed by J. M. Williams in order to determine the precise nature of the $\text{Ta}\cdots\text{H}_\alpha$ interaction^a in neopentylidene complexes.¹⁹ The structure of 12 is shown in Figure 2.2. The metal centers in 12 are joined by two bridging chlorides. The Ta-Ta distance of 4.061\AA seems to indicate that there is no direct metal-metal interaction. There are also two mutually trans chlorides per metal as well as the neopentylidene group which is cis to the PMe_3 ligand. The $\text{Ta}=\text{C}_\alpha$ bond length is 1.898\AA which is very close to the length of a Ta-to-C triple bond.²⁶ The $\text{C}_\alpha-\text{H}_\alpha$ bond length is 1.131\AA which is the longest high precision C-H distance ever determined in a crystal structure. The $\text{Ta}-\text{C}_\alpha-\text{C}_\beta$ angle is large (161.2°) while the $\text{Ta}-\text{C}_\alpha-\text{H}_\alpha$ angle is less than 90° . The steric crowding in the coordination sphere forces the ^tBu group away from the metal thus enlarging the $\text{Ta}-\text{C}_\alpha-\text{C}_\beta$ angle. As the ^tBu group moves away from the metal, the α -hydrogen is pushed closer to the tantalum. The electron deficient Ta(V) begins attracting the e^- density in the

^aInteractions between transition metals and C-H groups in coordinated ligands have been observed before.⁷¹ Both aliphatic⁷² and aromatic⁷³ C-H bonds are known to participate in these interactions which may be weak⁷⁴ or may involve complete oxidative-addition of the C-H bond across the metal.⁷⁵

Figure 2.2A.
The Neutron Diffraction Structure of
 $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Cl}_3]_2$

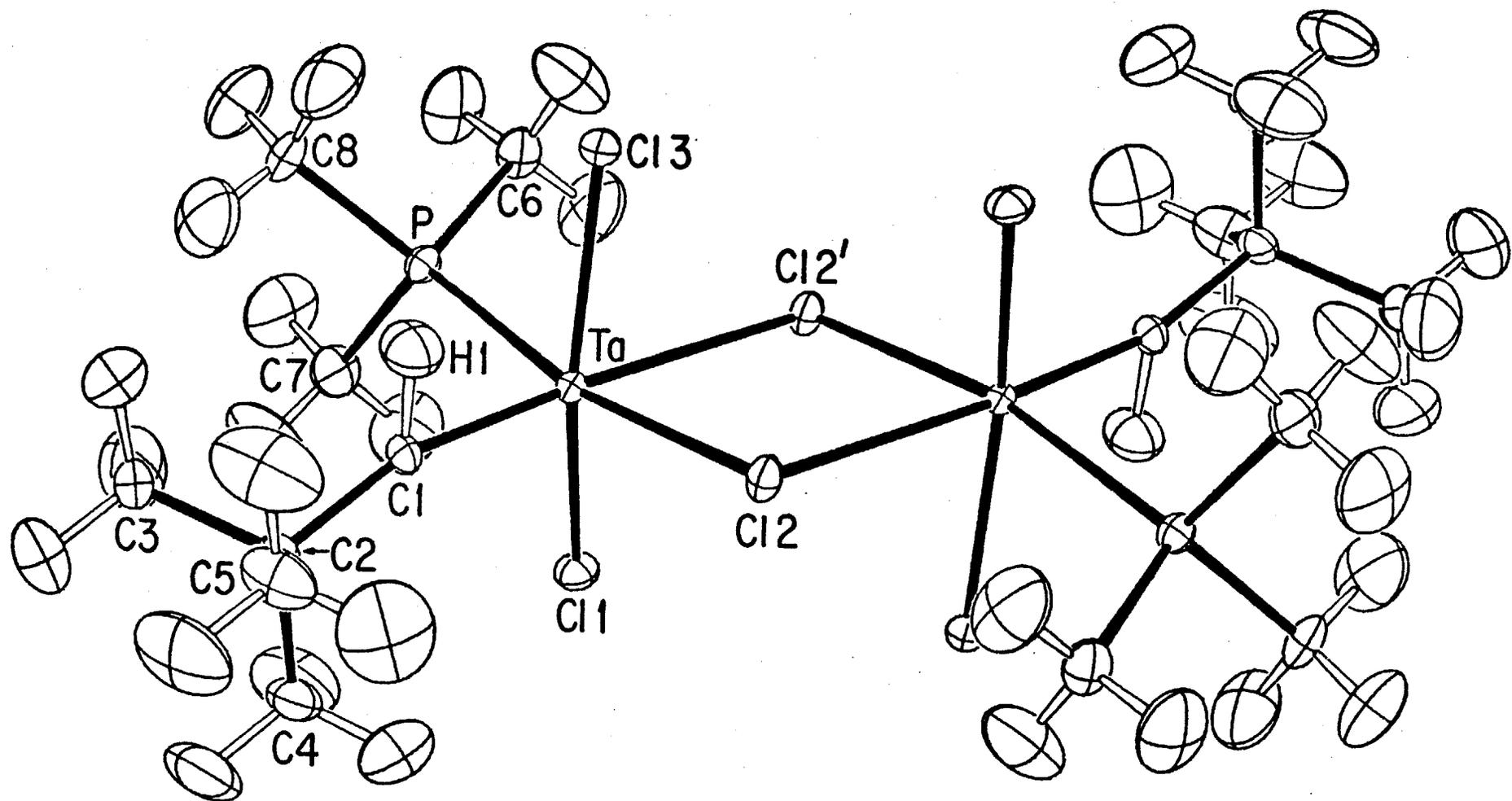


Figure 2.2B.
The Neutron Diffraction Structure of
 $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Cl}_3]_2$

$C_{\alpha}-H_{\alpha}$ bond which moves the α -hydrogen closer to the metal. This increases the Ta- C_{α} interaction which makes this bond shorter than normal.

Conversely, this interaction decreases the $C_{\alpha}-H_{\alpha}$ interaction which makes this bond much longer and weaker than normal. These observations are directly related to the small values obtained for $J_{C_{\alpha}H_{\alpha}}$ in the ^{13}C NMR and for the reduced frequency of the $C_{\alpha}-H_{\alpha}$ stretch measured in the IR of 12.

There are several other interesting features in this structure. The neopentylidene ligand is in a plane which contains the Cl(3)-Ta-Cl(1) axis and which is perpendicular to the $C_{\alpha}TaP$ plane. The α -hydrogen of the neopentylidene ligand is located very close to the tantalum and appears to be occupying a coordination position.^a The Ta $\cdots H_{\alpha}$ distance is 2.119Å which is less than the sum of the van der Waal's radii. Because of close contacts with the neopentylidene ligand, Cl(3) and Cl(1) are deflected from their ideal octahedral positions. The $C_{\alpha}-Ta-Cl(1)$ angle is expanded to 95.1° because of the close approach of two hydrogens of the ^tBu group [H(4B) $\cdots Cl(1)$ =3.061Å; H(4C) $\cdots Cl(1)$ =3.291Å]. The $C_{\alpha}-Ta-Cl(3)$ angle is expanded to 104.0° because of the close approach of H_{α} [$H_{\alpha}\cdots Cl(3)$ =2.657Å]. Despite this distortion the trans axial chlorides have similar bond lengths to tantalum [Ta-Cl(3)=2.370Å; Ta-Cl(1)=2.334Å] which are in the normal range. The bridging chlorides do not form a symmetric bridge. The chloride trans to the PMe_3 , Cl(2'), is 2.448Å from the metal while the chloride trans to the alkylidene, Cl(2), is 2.815Å from the metal. It can be seen that the neopentylidene is exerting

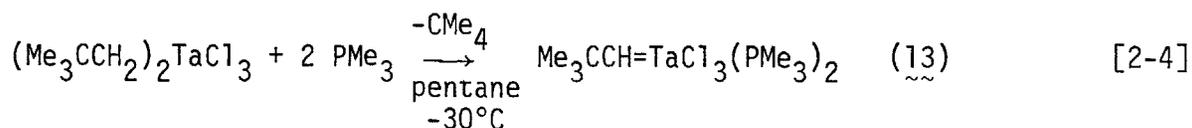
^aSince Ta(V) is a d^0 configuration it is not possible for H_{α} to transfer to the metal completely without making C_{α} electron deficient. The same is true in the formation of 12; hence, the formation process is called an abstraction rather than an elimination (via the metal).

a very large trans influence in this complex.⁷⁶

B. Reactions of $(\text{Me}_3\text{CCH}_2)_2\text{TaX}_3$ with Two Equivalents of PR_3

1. The Preparation and Properties of the $\text{Me}_3\text{CCH}=\text{TaX}_3(\text{PR}_3)_2$ Series

The reaction of $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ with two equivalents of PMe_3 in cold pentane yields purple, microcrystalline $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$, 13, (Eq. 2-4). This reaction proceeds through several stages. Initially, 11



crystallizes from the yellow $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ solution. These crystals of 11 dissolve slowly to give a red solution which becomes purple on warming to RT. One equivalent of neopentane per equivalent of 13 is produced in this exothermic ligand induced α -hydrogen abstraction. This six coordinate, $14 e^-$ complex, 13, is thermally stable. It is soluble in ether, benzene, toluene, CH_2Cl_2 and CHCl_3 . Recrystallization from cold ether-pentane yields 13 as purple fibers. An alternate route to 13 involves the reaction of the dimer $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Cl}_3]_2$ (12) with two moles of PMe_3 in which the chloride bridges are cleaved by the added ligand.

Although some steps in the formation of 12 and 13 are clearly understood, others are not. The first step in each case involves the formation of the PMe_3 adduct, $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3(\text{PMe}_3)$ (11). It is known that 11 possesses a labile PMe_3 at RT. This is most clearly seen in the ^{31}P NMR spectrum of 11. Above 0°C the resonance is very broad. On cooling the

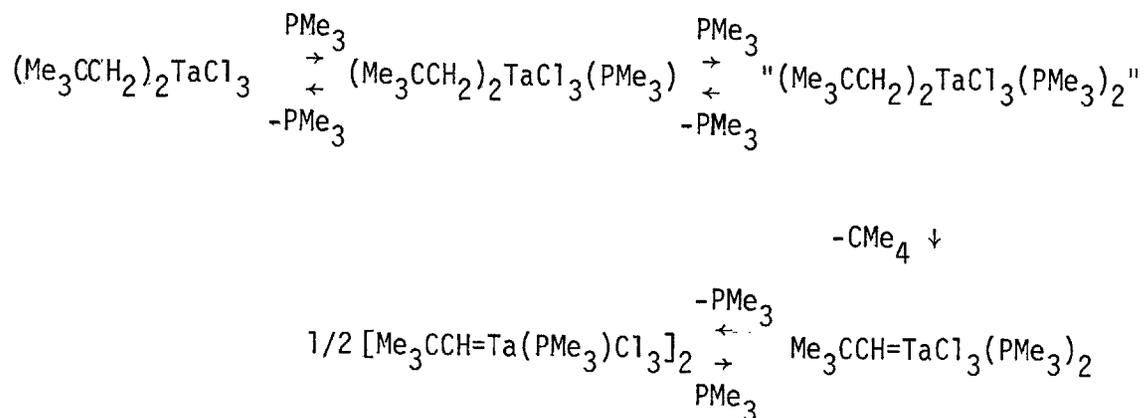
resonance sharpens significantly and moves to lower field strengths (away from the shift of free PMe_3) which indicates that the metal is binding the phosphine more tightly. A solution of $\underline{11}$ at RT most likely contains some $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ and some free PMe_3 .^a This free PMe_3 is available then to interact with $\underline{11}$.^b This kind of interaction is seen in the ^1H or $^{13}\text{C}(^1\text{H})$ NMR spectra of $\underline{11}$ plus PMe_3 at -50°C . At -50°C the PMe_3 ligand of $\underline{11}$ appears as a sharp doublet (due to phosphorous coupling) in either spectrum. There is no dissociative exchange at this temperature on the NMR time scale. The addition of PMe_3 to a sample of $\underline{11}$ causes the PMe_3 resonance to broaden due to an associative exchange of phosphine ligands. It is possible, therefore, that $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3(\text{PMe}_3)_2$ exists for some time in solution. Other seven coordinate complexes similar to $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3(\text{PMe}_3)_2$ have been isolated or observed including $(\text{Me}_3\text{CCH}_2)\text{TaCl}_4(\text{PMe}_3)_2$, $\text{Me}_2\text{TaCl}_3(\text{PMe}_3)_2$,⁶¹ and $(\text{PhCH}_2)_2\text{TaCl}_3(\text{PMe}_3)_2$.⁵⁶ It is proposed that α -hydrogen abstraction occurs in the seven coordinate, $14 e^-$ intermediate to yield $\underline{13}$ initially. Although a seven coordinate intermediate is less electron deficient than $\underline{11}$, it possesses a significantly more crowded coordination sphere which may be more important to α -hydrogen abstraction.^c When only one phosphine ligand per tantalum is present, $\underline{13}$ can lose PMe_3 to $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ to form the dimer, $\underline{12}$, and $\underline{11}$ which

^a The amount of free phosphine should be much larger in the case of other less basic phosphines, e.g. PMe_2Ph .

^b In the preparation of the monomer $\underline{13}$ at least one equivalent of PMe_3 per $\underline{11}$ is in solution from the stoichiometry.

^c Both an electron deficient metal center and a sterically crowded coordination sphere are necessary for α -hydrogen abstraction (vide supra).

undergoes further reaction. The complete proposed mechanism is shown in Eq. 2-5.



[2-5]

The other complexes in this series have been prepared similarly. The reaction of $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ with two equivalents of PMe_2Ph gives a red pentane solution which deposits a purple precipitate on warming to RT. This crude product can be recrystallized from toluene-pentane at -30°C to give red-purple flakes of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_2\text{Ph})_2$, 17. The reaction of $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ with two equivalents of PPh_2Me gives a red solution which deposits a red oil on warming to RT. This oil crystallizes on standing to yield red-purple prisms of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PPh}_2\text{Me})_2$, 18. The solubilities of 17 and 18 are similar to those of 13, $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$.

The reaction of $(\text{Me}_3\text{CCH}_2)_2\text{TaBr}_3$ with two equivalents of PMe_3 in cold pentane causes a purple crystalline product to precipitate. This presumably is $(\text{Me}_3\text{CCH}_2)_2\text{TaBr}_3(\text{PMe}_3)$. This six coordinate adduct is much less stable

than 11. It cannot be isolated since it redissolves rapidly even in cold pentane to give blue-purple solutions from which blue-purple crystals of $\text{Me}_3\text{CCH}=\text{TaBr}_3(\text{PMe}_3)_2$, 19, form. Addition of PMe_3 to $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Br}_3]_2$ (16) will also give 19 as in the case of the chlorides, 12 and 13. The solubility properties of 19 parallel those of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ (13); however, 19 is much easier to recrystallize.

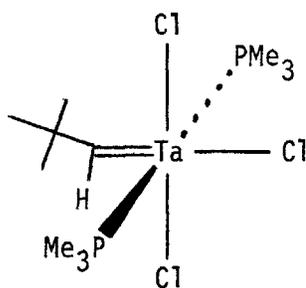
It is possible to prepare 13 which is partially deuterated at the α -carbon by the reaction of $(\text{Me}_3\text{CCHD})_2\text{TaCl}_3$ with two equivalents of PMe_3 . The measurement of the D/H ratio on the α -carbon gives a value of 4-5 for the deuterium isotope effect (vide infra) for α -hydrogen abstraction. (Presumably, 13 which is fully deuterated at the α -carbon can be made by treating $(\text{Me}_3\text{CCD}_2)_2\text{TaCl}_3$ with two equivalents of PMe_3 , but this has not been attempted.)

$(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ appears to be unreactive toward α -hydrogen abstraction in the presence of PPh_3 .^a $(\text{Me}_3\text{CCH}_2)_2\text{TaBr}_3$, however, which is more reactive than the chloride, will react with excess PPh_3 in CHCl_3 to give $\text{Me}_3\text{CCH}=\text{TaBr}_3(\text{PPh}_3)_x$ where $x=1$ or 2 . The reaction is slow, the yield is low, and the product, unfortunately, cannot be separated from the excess PPh_3 .

2. The Characterization of the $\text{Me}_3\text{CCH}=\text{TaX}_3(\text{PR}_3)_2$ Series

The monomeric neopentylidene complexes 13, 17, 18, and 19 were originally believed to possess a structure similar to those of the dimers in which the chloride trans to the PMe_3 ligand, Cl(2'), has been replaced with another phosphine ligand. This structure is shown in Figure 2.3.

^a $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ will react with bulky tertiary phosphines which are more basic than PPh_3 such as PEt_3 and P^iPr_3 .⁸⁰

Figure 2.3. The Proposed Structure of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ 

The trans, mer configuration^a shown is not a good representation of 13, however. The complex is a number of species in solution which are rapidly interconverting on the NMR time scale at RT due to exchange of the PMe_3 ligands. On cooling, however, the dynamic behavior of the sample ceases, and a mixture of two isomers is observed. The ^1H NMR data listed in Table 2.IV. for these complexes show that there is a trans, mer and a cis, mer isomer. The structures of the possible isomers are shown in Figure 2.4. Even under conditions where the isomers of 13 and 17 are distinguishable, the α -hydrogen resonances appear broad because of the small phosphorus coupling. The value of $J_{\text{H}_\alpha\text{P}}$ is on the order of 1-2 Hz. The low temperature ^1H gated decoupled ^{13}C NMR spectrum of 13 also shows the presence of two isomers in toluene- d_8 . This data is shown in Table 2.V. Additionally, the ^{31}P NMR spectra of the monomeric complexes, 13 and 17,

^aThe cis, mer isomer of 13 would have cis PMe_3 ligands and meridional chlorides.

Table. 2.IV. The ^1H NMR Data* for $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PR}_3)_2$

		$\underline{\text{Me}}_3\text{CCH}=\underline{\text{Me}}_3\text{CCH}=\underline{\text{P}}\underline{\text{Me}}(\text{J}_{\text{HP}})$	$\underline{\text{Me}}_3\text{CCH}=\underline{\text{Me}}_3\text{CCH}=\underline{\text{P}}\underline{\text{Me}}'(\text{J}_{\text{HP}})$	$\underline{\text{P}}\underline{\text{P}}\underline{\text{h}}$	Conditions
<u>trans,mer</u> - $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$	(13a)	8.82	3.91	8.70(4.1)	-60°C, $\text{C}_6\text{D}_5\text{CD}_3$
<u>cis,mer</u> - $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$	(13b)	8.87	6.03	8.78(8.7) 8.96(6.9)	" "
<u>trans,mer</u> - $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_2\text{Ph})_2$	(17a)	9.29	3.94	8.31(4.9) 8.84(3.9)	2.50-3.05 -50°C, "
<u>cis,mer</u> - $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_2\text{Ph})_2$	(17b)	8.88	5.95	8.65(8.4) 8.80(5.8)	2.50-3.05 " "

* Shifts are listed in τ while coupling constants are listed in Hz.

Table 2.V. The ^{13}C NMR Data* for $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$

	<u>trans,mer</u> - $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$			<u>cis,mer</u> - $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$			
	δ	J_{CH}	J_{CP}	δ	J_{CH}	J_{CP}	$J_{\text{CP}'}$
= <u>CH</u> CMe_3	256.5	75.3	11.6	255.9	96.1	11.6	33.0
= <u>CH</u> <u>C</u> Me_3	45.8			46.8			12.7
= <u>CH</u> $\text{C}Me_3$	34.4	125.3		33.2	127.0		
<u>P</u> Me_3	15.5	134.3	14.5	18.0	129.1	27.5	
<u>P</u> <u>Me</u> $_3$				12.3	132.0		15.6

*Shifts are listed in ppm while coupling constants are in Hz.

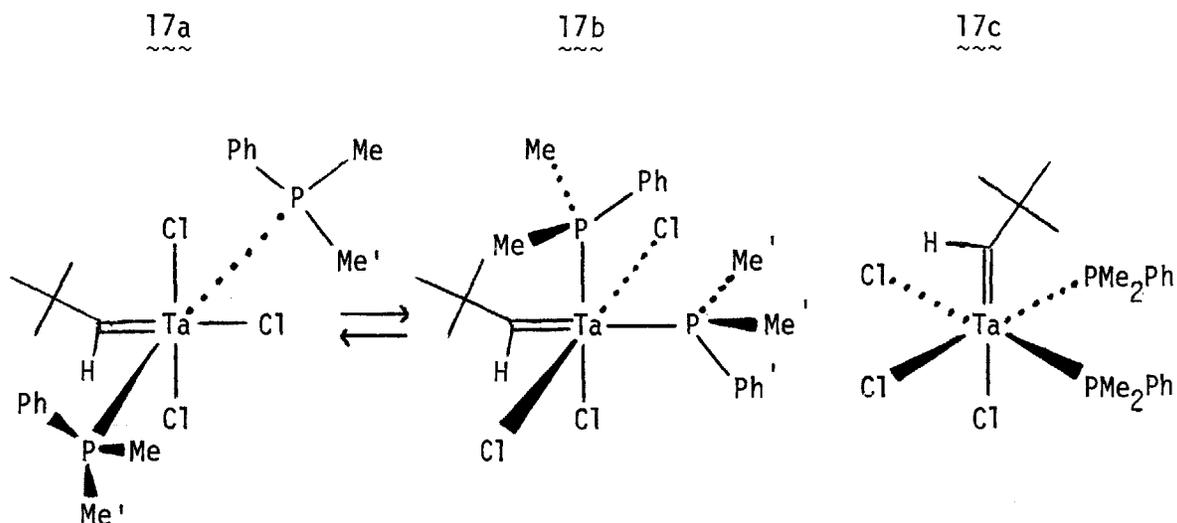
Table 2.VI. The $^{31}\text{P}(^1\text{H})$ NMR Data* and IR Data** for $\text{Me}_3\text{CCH}=\text{TaX}_3(\text{PR}_3)_2$

	IR(nujol) $\nu_{\text{C}=\text{H}}$	$^{31}\text{P}(^1\text{H})$ NMR		$J_{\text{PP}'}$
		trans,mer isomer PR_3	(-50°C, toluene) cis,mer isomer PR_3 PR'_3	
$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ (13)	2510	-4.3	-5.4 -30.5	7
$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_2\text{Ph})_2$ (17)	2518	1.8	-0.8(br) -25.7(br)	
$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PPh}_2\text{Me})_2$ (18)	2535			
$\text{Me}_3\text{CCH}=\text{TaBr}_3(\text{PMe}_3)_2$ (19)	2505	-4.0	-9.2(br) -31.1(br)	

* Shifts are listed in ppm while coupling constants are listed in Hz.

** Absorptions are listed in cm^{-1} .

Figure 2.4. The Structures of the trans, mer and cis mer Isomers of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_2\text{Ph})_2$



demonstrate that these two isomers are present. The IR spectra of these complexes shows the characteristic $\nu_{\text{C-H}}$ of the neopentylidene ligand. This data is combined in Table 2.VI.

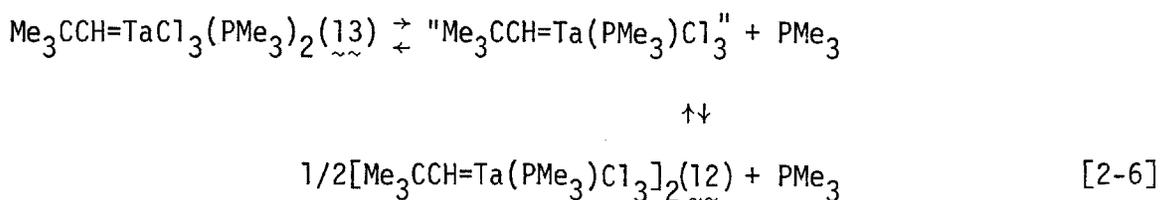
The ratios of these isomers depend on many factors. These include the solvent, the temperature, the halide, and the phosphine ligand. In CHCl_3 the trans, mer isomer is the predominant species by a ratio of 9:1 for $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$, 13. In toluene the cis, mer isomer is the major species by a ratio of 2:1 for 13. The amount of the trans, mer isomer increases with increasing temperature. Changing the halide to bromide increases the amount of the trans, mer isomer. Changing the ligand to a less basic phosphine such as PMe_2Ph , however, decreases the amount of the trans, mer isomer. These last two factors both indicate that the ligands that are bound most strongly to the metal prefer to be trans. This may occur for steric reasons since two tightly bound ligands

in a cis configuration would be in close proximity to each other. It is also possible that the neopentylidene ligand may exert a trans effect. The solvent effect on this cis-trans isomerization cannot be explained as satisfactorily. The trans, mer isomer would be expected to have a smaller dipole moment than the cis, mer isomer. However, polar solvents such as CHCl_3 favor the trans form while nonpolar solvents such as benzene or toluene favor the cis form. This is opposite what would be predicted on the basis of polarity. Chloroform must provide some extra stabilization to the trans isomer through solvation which is not possible in toluene.

The NMR data contained in Tables 2.IV., 2.V., and 2.VI. agree with the structure for the trans, mer isomer, 17a, shown in Figure 2.4. This data also provides information on the structure of the cis, mer isomer, 17b. The structures for complexes 17a and 17b are believed to be the ones shown in Figure 2.4. The $^{31}\text{P}(^1\text{H})$ NMR for 17a shows only one type of phosphorus nucleus while the ^1H NMR shows only two types of methyl groups bound to phosphorus. Each type of methyl group is virtually coupled to both phosphorus nuclei. This indicates that in 17a there is a plane of symmetry in the plane of the meridional chloride ligands while there is no plane of symmetry in the C_αPP plane. This is consistent with trans phosphine ligands in 17a where the neopentylidene lies in the plane of the meridional chlorides. (Although a cis, fac isomer cannot be ruled out by this data, structure 17c possesses two features which make it an unlikely possibility. First, the chlorides are in a facial arrangement which is not seen in either the dimers or any of the octahedral mononeopentylidenes complexes or any of the subsequent reaction products. Second, the

neopentylidene ligand must be in a plane bisecting two coordination axes rather than in a plane containing two coordination axes as is seen in all other cases.) The ^{31}P NMR of $\underline{17b}$ shows two types of phosphorus nuclei, while the ^1H NMR also shows two types of methyl groups bound to phosphorus. Each type of methyl group is coupled to only one phosphorus nucleus. This signifies that there must be a plane of symmetry in $\underline{17b}$ in the $\text{C}_\alpha\text{PP}'$ plane in order to make the methyls on each phosphorus equivalent. Because the neopentylidene ligand must lie in the plane it is aligned along a Cl-Ta-P axis rather than along a Cl-Ta-Cl axis as in $\underline{17a}$ or the dimer $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Cl}_3]_2$, $\underline{12}$.

The ^{13}C resonance of the α -carbon in $\underline{13b}$ is a double doublet due to coupling to ^{31}P . One coupling constant is large ($J_{\text{CP}}=33.0$ Hz) while the other is small ($J_{\text{CP}}=11.6$ Hz). This indicates that one phosphine is trans to the alkylidene and one is cis. The ^{13}C resonance for the α -carbon in $\underline{13a}$ is a triplet due to coupling to two equivalent ^{31}P nuclei cis to the alkylidene ($J_{\text{CP}}=11.6$ Hz). Hence, $\underline{13a}$ and $\underline{13b}$ are believed to have the same type of structures as $\underline{17a}$ and $\underline{17b}$. A molecular weight measurement in benzene (freezing point depression) gave a value of 377 (calcd 509.6) for $\underline{13}$. Some process must be occurring in $\underline{13}$ which increases the number of molecules in solution. One such process is depicted in Eq. 2-6.



Although " $\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Cl}_3$ " has never been observed spectroscopically (vide supra), this process is reasonable for a number of reasons. It is known that concentrated solutions of 13 in hydrocarbon solvents such as toluene will deposit crystals of dimeric 12. In polar solvents $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ will react with 13 to yield 12. The ^1H NMR of 13 at RT shows only a broad lump for the PMe_3 ligands which also exchange with free PMe_3 . All these observations indicate that the PMe_3 ligands in 13 are exchanging rapidly and that at least one is very labile.

C. Reactions of $(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_3$ with PR_3

1. The Preparation and Properties of the $[\text{Me}_3\text{CCH}=\text{Nb}(\text{PR}_3)\text{Cl}_3]_2$ and $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PR}_3)_2$ Series

The reactions of $(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_3$ ⁴¹ with tertiary phosphine ligands are not as clean or simple as those of $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$, although it is possible to prepare and isolate alkylidene complexes of niobium. The lower stability of $(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_3$, itself, and the tendency of Nb(V) ^{77,78} toward reduction on treatment with σ -donor ligands may account for this. An example of the reduction of Nb(V) by σ -donor ligands is shown in Eq. 2-7.



The reaction of red $(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_3$ in cold pentane with two equivalents of PMe_3 initially produces a red-brown precipitate which immediately redissolves. The red-brown material is thought to be

$(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_3(\text{PMe}_3)$ by analogy to the tantalum chemistry. This would be expected to be quite reactive and unstable.^a The resulting dark colored solution rapidly becomes blue-purple as a green-brown precipitate forms. This precipitate is a paramagnetic Nb(IV) byproduct from reduction. Since reduction is initiated by loss of halide, the byproduct most likely has the formula $(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_2(\text{PMe}_3)_2$, although this has not been proven. At this point the reaction must be filtered as the $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_3)_2$, 20, will soon begin to come out of solution as blue-purple crystals which are difficult to separate from the Nb(IV) product. The yield of 20 is only 60-65%^b as a result of this Nb(IV) byproduct which accounts for the remainder of the yield. That a fair yield of 20 is obtained indicates that α -hydrogen abstraction can compete successfully with reduction. The blue-purple crystalline $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_3)_2$, 20, is a 14 e⁻ complex whose solubility is the same as that of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$, 13.

The reaction of $(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_3$ with two equivalents of PMe_2Ph in cold pentane also has complications. After mixing at -30°C the reaction is allowed to warm to RT and a purple suspension forms while a brown tar oils out of solution. The suspension is decanted and filtered. The purple powder is recrystallized from toluene-pentane at -30°C to yield 50-60% of $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_2\text{Ph})_2$, 21. This 14 e⁻ complex has solubilities similar to $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_2\text{Ph})_2$, 17. Extraction of the brown tar with ether yields a brown paramagnetic Nb(IV) complex. As yet it is not clear that the next compound expected in this series, $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PPh}_2\text{Me})_2$, has been prepared.

^aIn general it has been observed that niobium complexes are more reactive and less stable than the corresponding tantalum analogues.¹⁹

^bThe same reactions involving tantalum are quantitative (vide supra).

The materials obtained from this reaction, which are soluble in aromatic solvents due to the PPh_2Me ligand, are all paramagnetic. One explanation for this may involve the rate of ligand induced α -hydrogen abstraction versus the rate of reduction of Nb(V). It has been observed for tantalum that the rate of α -hydrogen abstraction is proportional to the ligand strength: $\text{PMe}_3 > \text{PMe}_2\text{Ph} > \text{PPh}_2\text{Me} \gg \text{PPh}_3$. The rate of α -hydrogen abstraction in $(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_3$ induced by PPh_2Me may be considerably less than the rate of reduction.

It is possible, however, to prepare the niobium analogues of the dimeric tantalum alkylidenes 12 and 14. The dimers $[\text{Me}_3\text{CCH}=\text{Nb}(\text{PMe}_3)\text{Cl}_3]_2$, 22, and $[\text{Me}_3\text{CCH}=\text{Nb}(\text{PMe}_2\text{Ph})\text{Cl}_3]_2$, 23, have been synthesized. The reaction of $(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_3$ in cold pentane with one equivalent of the appropriate phosphine leads to the formation of a large quantity of brown precipitate. This is rinsed with pentane to remove any starting material, dissolved in toluene, and filtered to remove the Nb(IV) byproducts. The dimers, 22 and 23, are then isolated as red crystals by the addition of pentane at -30°C . The solubilities of 22 and 23 are similar to those of $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Cl}_3]_2$, 12, and $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_2\text{Ph})\text{Cl}_3]_2$, 14; however, 22 and 23 do not appear to be thermally stable. Unlike all the other niobium and tantalum alkylidene complexes described, the dimeric niobium alkylidene complexes decompose in solution in a few hours.

2. The Characterization of the $[\text{Me}_3\text{CCH}=\text{Nb}(\text{PR}_3)\text{Cl}_3]_2$ and $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PR}_3)_2$ Series

The presence of two isomers is observed in solutions of $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_3)_2$, 20, as in the case of the monomeric tantalum alkylidenes such as $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$, 13. The isomers of 20,

$\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_3)_2$, are believed to possess the trans, mer and the cis, mer coordination geometries. The amount of the cis, mer isomer, 20b, however, is larger even in CHCl_3 . It appears, therefore, that the nature of the metal center has an influence on the isomeric ratio. Changing the metal to niobium decreases the amount of the trans, mer isomer, 20a. The other factors, which influenced the ratio of the two isomers for the tantalum analogues, have been observed to apply to the niobium alkylidenes as well. In cold toluene 20b appears to be the exclusive species.^a The presence of isomers is observed in the ^1H , ^{13}C , and ^{31}P NMR spectra of 20.^b The ^1H NMR data for the monomeric niobium complexes as well as for the dimeric niobium complexes appears in Table 2.VII. This table lists spectral data for the monomeric complexes both under conditions where PMe_3 exchange is fast and where exchange is slow. Table 2.VIII. lists the $^{13}\text{C}(^1\text{H})$ data for the isomers of 20.

In these niobium alkylidene complexes there is a strong interaction between the metal center and the $\text{C}_\alpha\text{-H}_\alpha$ bond as observed in the tantalum analogues. The presence in the IR spectra of the characteristic low frequency $\text{C}_\alpha\text{-H}_\alpha$ stretch is evidence of this interaction. These stretches occur at 2510 cm^{-1} for 20 and at 2595 cm^{-1} for 22.

Since $(\text{Me}_3\text{CCH}_2)_2\text{NbBr}_3$ has not yet been synthesized, no complexes of the formula $\text{Me}_3\text{CCH}=\text{NbBr}_3(\text{PR}_3)_x$ have been prepared. Because the bromides

^aLow temperature and nonpolar solvents also favor the cis, mer isomer for tantalum (vide supra).

^bIt is observed in the NMR spectra of niobium complexes that resonances of nuclei bound to niobium are broadened significantly because of coupling to ^{93}Nb (100% abundance, $I=9/2$). By cooling the sample, this coupling is reduced and the resonances are sharper.

Table 2.VII. The ^1H NMR Data* for the Niobium Neopentylidene Complexes

		$=\text{CHCMe}_3$ (J_{HP})	$=\text{CHCMe}_3$	PMe (J_{HP})	PMe' (J_{HP})	PPh	Conditions
$\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_3)_2$	(20)	5.46(br)	8.82	8.80(br)			C_6D_6 , 35°C
$\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_3)_2$	(20a)	4.37(br)	8.71	8.31-8.54(complex)			CDCl_3 , -30°C
$\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_3)_2$	(20b)	5.84(6.5)	8.71	8.31-8.54(complex)			CDCl_3 , -30°C
$\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_3)_2$	(20b)	5.75(5.3)	8.88	8.82(8.4)	8.93(7.3)		tol-d_8 , -50°C
$\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_2\text{Ph})_2$	(21)	5.45(br)	8.95	8.61(br)		2.40-3.00	C_6D_6 , 35°C
$[\text{Me}_3\text{CCH}=\text{Nb}(\text{PMe}_3)\text{Cl}_3]_2$	(22)	3.64(br)	8.96	8.92(10.3)			C_6D_6 , 35°C
$[\text{Me}_3\text{CCH}=\text{Nb}(\text{PMe}_2\text{Ph})\text{Cl}_3]_2$	(23)	3.62(br)	8.84	8.43(8.8)		2.65-3.00	C_6D_6 , 35°C

* Shifts are listed in τ while coupling constants are listed in Hz.

Table 2.VIII. The $^{13}\text{C}(^1\text{H})$ NMR Data* for $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_3)_2$

	$=\text{CHC}\underline{\text{Me}}_3$	$=\text{CHC}\underline{\text{Me}}_3$	$=\text{CHC}\underline{\text{Me}}_3$	$\text{P}\underline{\text{Me}}_3(\text{J}_{\text{HP}})$	$\text{P}\underline{\text{Me}}_3'(\text{J}_{\text{HP}'})$
$\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_3)_2$ (20a)	29.8	46.5	252.8(br)	14.2(13.2)	
$\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_3)_2$ (20b)	29.2	45.9	252.8(br)	16.6(24.9)	11.6(16.1)

* Shifts are listed in ppm while coupling constants are listed in Hz.

of the Nb(V) are generally easier to reduce⁷⁸ than the chlorides, a very low yield might be expected if this reaction were attempted.

D. Reactions of $(\text{Me}_3\text{CCH}_2)_2\text{MX}_3$ with Ethers, Amines, Sulfides, and Other Ligands

1. The Preparation and Properties of the $\text{Me}_3\text{CCH}=\text{MX}_3\text{L}_2$ Series

A large class of neopentylidene complexes which are derived from $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$, $(\text{Me}_3\text{CCH}_2)_2\text{TaBr}_3$, or $(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_3$ can now be prepared. These syntheses involve the same phosphine induced α -hydrogen abstraction process as discussed in Chapter 1 for the preparation of bisalkylidene complexes of tantalum and niobium (*vide supra*). Unfortunately, only very basic phosphines can be used to prepare the bisalkylidenes.^a In contrast to this almost any tertiary phosphine (PR_3) seems capable of inducing α -hydrogen abstraction in compounds such as $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$. Presumably this occurs because $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ is less sterically crowded than $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$ and therefore the initial attack of the phosphine is easier. The isolation of $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3(\text{PMe}_3)$, 11,

^aOnly PMe_3 and PMe_2Ph work well (see Chapter 1).

while " $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{PMe}_3)$ " has never been observed, is good evidence of this. The scope of this reaction in the case of $(\text{Me}_3\text{CCH}_2)_2\text{MX}_3$ ($\text{M}=\text{Nb}, \text{Ta}$; $\text{X}=\text{Cl}, \text{Br}$) is broader still. Not only will a wide variety of tertiary phosphines induce α -hydrogen abstraction, but many other $2 e^-$, σ -donor ligands can function in this capacity as well. These ligands include amines, arsines, ethers, and sulfides.

The reactions of these ligands with $(\text{Me}_3\text{CCH}_2)_2\text{MX}_3$ are generally slower than those involving phosphines. The rates are lower because the ligands in this class which have been studied are less basic than PMe_3 . The use of polar solvents such as ether, CH_2Cl_2 , or CHCl_3 can compensate for this.^a This increase in the rate of α -hydrogen abstraction in polar solvents has been observed before.^{41,42} It is possible that an increase in solvent polarity facilitates the attack of ligands on $(\text{Me}_3\text{CCH}_2)_2\text{MX}_3$ or stabilizes some transition state in the α -hydrogen abstraction process. This is only a theory, however, since the exact mechanism of this reaction is not known.

Some of the complexes in this class that have been prepared are listed in Table 2.IX. These are prepared by allowing the appropriate dineopentyl metal trihalide to react with an excess (3 to 4 equivalents of ligand in ether, CH_2Cl_2 , or CHCl_3 ^b at RT for several hours in the case of Nb or overnight in the case of Ta. These complexes vary in color from red to blue-purple. They are all soluble in ether, CH_2Cl_2 , CHCl_3 , benzene or toluene and can be recrystallized at low temperature from ether.⁷⁹

The preparation of $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{THF})_2$, 24, is a clean, high yield

^aThe solvents in which ligand induced α -hydrogen abstractions proceed at the fastest rate are CH_2Cl_2 and CHCl_3 .

^b $(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_3$ is very sensitive to CH_2Cl_2 and this should not be used as a solvent in this case.

Table 2.IX. Several Complexes of the Type $\text{Me}_3\text{CCH}=\text{MX}_3\text{L}_2$

		<u>Color</u>
$\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{THF})_2$	(24)	blue-purple
$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{THF})_2$	(25)	red-purple
$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{py})_2$	(26)	red
$\text{Me}_3\text{CCH}=\text{TaBr}_3(\text{THF})_2$	(27)	blue-purple
$\text{Me}_3\text{CCH}=\text{TaBr}_3(\text{THT})_2$	(28)	red

reaction as opposed to the syntheses of the tertiary phosphine analogues, $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PR}_3)_2$, 20, in which a byproduct from the reduction of the metal accounts for approximately a 40% decrease in the yield of 20 or 21. A ligand exchange reaction between 24 and PMe_3 should provide an improved synthesis of 20. There are two reasons for expecting this to be true. First, in starting with 24 the α -hydrogen abstraction step has already been completed without interference from reduction. Second, 20 is stable in the presence of free PMe_3 which readily exchanges with coordinated PMe_3 . This approach proved to be very successful as a quantitative yield of 20 (based on $(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_3$) was obtained from the reaction of 24 with two equivalents of PMe_3 . This type of reaction appears to be fairly general since $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$, 13, can be prepared from the reaction of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{THF})_2$, 25, with two equivalents of PMe_3 .

One limitation in the use of these less basic ligands seems to be the inability of a ligand such as THF to form stable, dimeric neopentylidene complexes of the same type as $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Cl}_3]_2$, 12. The reaction of

$(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ with only one equivalent of THF leads to intractable products. Another limitation occurs when the ligand strength falls below that which is required to induce α -hydrogen abstraction. Although this aspect has not been studied extensively, it is known that diethyl ether will not induce alkylidene formation in any of the dineopentyl metal trihalides. Ether, however, does coordinate weakly to these compounds^a and is known to coordinate to other early transition metal alkyl compounds.⁸⁰

Phosphites, specifically $\text{P}(\text{OMe})_3$, have proven to be an exception to the ease of formation of alkylidenes from the reaction of ligands with $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$. Although $\text{P}(\text{OMe})_3$ is expected to be suitable on the basis of ligand strength, it is known to be susceptible to rearrangements. The attempted preparation of " $\text{Me}_3\text{CCH}=\text{TaCl}_3[\text{P}(\text{OMe})_3]_2$ " gave an amorphous, yellow, pentane soluble product which contained neopentyl groups but no neopentylidene.^b The product is believed to be $(\text{Me}_3\text{CCH}_2)_2\text{Ta}(\text{O})\text{Cl}$. This is formed, first, through the rearrangement of $\text{P}(\text{OMe})_3$ to $\text{O}=\text{PMe}(\text{OMe})_2$ (the Arbusov reaction).^{81,82} The $\text{O}=\text{PMe}(\text{OMe})_2$ then transfers the oxo group to the tantalum which loses two chlorides to yield the final product.

$(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ is also unreactive toward π -acceptor ligands such as ethylene. Ethylene does not induce α -hydrogen abstraction but neither does it insert into the Ta-to-C single bonds.

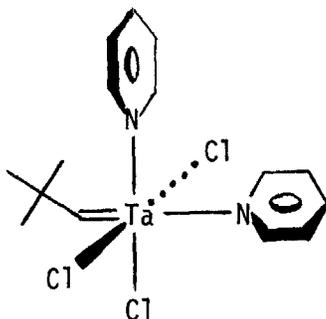
^aIt may not be possible for two molecules of diethyl ether to coordinate to $(\text{Me}_3\text{CCH}_2)_2\text{MX}_3$ as postulated in the ligand induced α -hydrogen abstraction mechanism (vide supra).

^bThere is no low field resonance in the ^{13}C NMR spectrum of this product and no diisobutylene is formed in its reaction with acetone (vide infra).

2. The Characterization of the $\text{Me}_3\text{CCH}=\text{MX}_3\text{L}_2$ Series

The spectroscopic data collected on this set of compounds agree with the proposed formulas. The IR spectrum of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{THF})_2$, 25, shows the $\text{C}_\alpha\text{-H}_\alpha$ stretch at 2540 cm^{-1} which is characteristic of the interaction between that bond and the metal. The ^1H NMR data for these complexes appear in Table 2.X. The ^{13}C NMR spectra for these complexes show the low field resonance which is characteristic of the α -carbon atom of the alkylidene ligand. The ^{13}C NMR data for several of these complexes are listed in Table 2.XI. These data point out one interesting and significant fact: these complexes appear to be entirely in the cis, mer isomer.^a The pyridine ligands in 26 are not exchanging at RT unlike the THF ligands of 24 or 25. On cooling to -20°C this process can be stopped in 24 and 25. The ^{13}C NMR data for 26 indicate that there are two nonequivalent pyridine ligands which either are rotating rapidly or are bisected by a plane of symmetry perpendicular to the heterocyclic ring (see Fig. 2.5.). This plane must also contain the neopentylidene ligand.

Figure 2.5. The Structure of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{py})_2$



^aThe low temperature ^1H NMR of 24 also shows the presence of two different types of THF ligand.

Table 2.X. The ^1H NMR Data* for the $\text{Me}_3\text{CCH}=\text{MX}_3\text{L}_2$ Series

	$\text{=CHC}\underline{\text{Me}}_3$	$\text{=CH}\underline{\text{C}}\text{Me}_3$	$\overline{\text{ACH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$	$\overline{\text{ACH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$	py	A	Conditions
$\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{THF})_2$ (24)	8.74	5.83	5.93(br)	8.45(br)		0	$\text{C}_6\text{D}_6, 35^\circ\text{C}$
$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{THF})_2$ (25)	8.76	6.50	5.67(br)	7.89(br)		0	$\text{CDCl}_3, 35^\circ\text{C}$
$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{py})_2$ (26)	8.77	6.37			0.78-2.75 (complex)		$\text{CDCl}_3, 35^\circ\text{C}$
$\text{Me}_3\text{CCH}=\text{TaBr}_3(\text{THF})_2$ (27)	8.63	7.20	5.53(br)	7.90(br)		0	$\text{CDCl}_3, 35^\circ\text{C}$
$\text{Me}_3\text{CCH}=\text{TaBr}_3(\text{THT})_2$ (28)	8.70		7.16(br)	8.08(br)		S	$\text{CH}_2\text{CH}_2, 35^\circ\text{C}$

* Shifts are listed in τ .

Table 2.XI. The $^{13}\text{C}(^1\text{H})$ NMR Data* for the $\text{Me}_3\text{CCH}=\text{MX}_3\text{L}_2$ Series

	$\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{THF})_2$ (24)	$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{THF})_2$ (25)	$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{py})_2$ (26)
$=\text{CHCMe}_3$	257.4	253.9	255.1
$=\text{CHCMe}_3$	47.8	44.9	45.5
$=\text{CHCMe}_3$	29.2	32.9	33.1
$\overbrace{\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$	78.4, 69.6	79.7, 70.1	
$\overbrace{\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$	25.5, 24.7	25.7, 24.7	
$\text{C}_2\text{-py}$			153.2, 150.7
$\text{C}_3\text{-py}$			124.6, 124.1
$\text{C}_4\text{-py}$			139.7, 138.6
CONDITIONS	$\text{CDCl}_3, -20^\circ\text{C}$	$\text{CDCl}_3, -30^\circ\text{C}$	$\text{CDCl}_3, 28^\circ\text{C}$

* Shifts are listed in ppm.

The observation of only the cis, mer isomer of 26 seems consistent with the results obtained with different tertiary phosphine ligands. As the basicity of the phosphine decreased, the ratio of the cis, mer isomer to the trans, mer isomer increased.^a Ligands such as pyridine and THF are much less basic than PMe_3 and would be expected to be predominantly (if not exclusively) in the cis, mer configuration. Conversely, NMe_3 is more basic than PMe_3 .⁸⁴ This theory, therefore, would predict that a complex such as " $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{NMe}_3)_2$ "^b would possess predominantly (or exclusively) trans NMe_3 ligands.

E. Reaction of $(\text{Me}_3\text{CCH}_2)_2\text{MX}_3$ with Bidentate Ligands

1. The Preparation and Properties of the $\text{Me}_3\text{CCH}=\text{MX}_3(\text{LL})$ Series

The preparation of six coordinate mononeopentylidene complexes possessing chelating ligands would be interesting for several reasons. First, because of the chelate effect, these complexes would not be expected to have labile or exchanging ligands nor to be in a monomer-dimer equilibrium. Second, because of the "bite" or coordination span ($\sim 90^\circ$) of many chelates, these complexes are all expected to have a coordination geometry similar to the cis, mer isomers seen before.

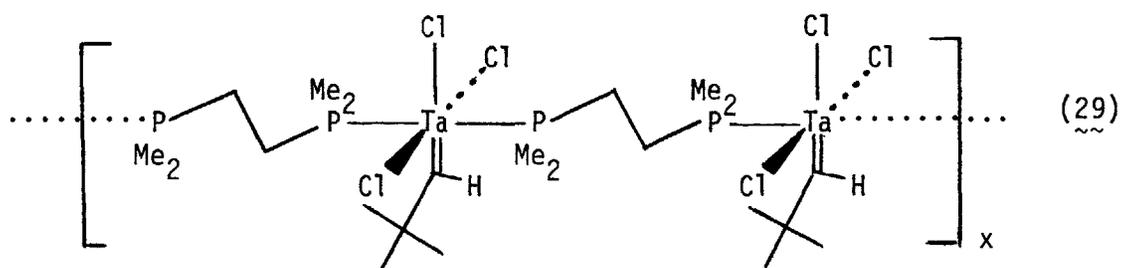
The synthesis of this type of complex, however, has been hindered by complicating factors. The reaction of $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ with dmpe in pentane causes the immediate precipitation of a white, microcrystalline product and leaves the pentane solution colorless. This product is not soluble

^aThe basicity of tertiary phosphines is as follows: $\text{PMe}_3 > \text{PMe}_2\text{Ph} > \text{PPh}_2\text{Me} > \text{PPh}_3$.⁸³

^bThis synthesis has not yet been attempted; it should, however, proceed in good yield.

in any of the normal solvents used in this work.^a The proposed formula is that of a linear polymer, $[\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})]_x$, 29. The proposed structure^b appears in Figure 2.6. This complex, 29, shows the characteristic $\text{C}_\alpha\text{-H}_\alpha$ stretch for the neopentylidene ligand in the infrared at 2498 cm^{-1} .

Figure 2.6. The Proposed Structure of $[\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})]_x$



Several attempts were made to favor the formation of monomeric species. Most of these measures failed to have any effect on the nature of the product.^c In some cases, however, a change in the solvent can produce a dramatic difference in the course of the reaction. Along with pentane,

^aThese include pentane, ether, THF, benzene, toluene, CHCl_3 , CH_2Cl_2 , or acetonitrile. There is a reaction with acetonitrile which causes 29 to turn yellow but the product is also insoluble.

^bA zig-zag structure with cis bridging dmpe ligands cannot be ruled out. This seems unlikely, however, since intermediates to its formation would be expected to produce at least some 30.

^cThese measures included cooling the reaction to low temperatures, changing the order of addition of reagents, and using more dilute solutions.

solvents such as ether or toluene yield only $\underline{29}$. The reaction of dmpe with $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ in either CHCl_3 or CH_2Cl_2 is different and yields a red-purple solution from which $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})$, $\underline{30}$, can be isolated. This complex, $\underline{30}$, is soluble in CHCl_3 , CH_2Cl_2 , benzene, or toluene. It can be recrystallized nicely from toluene-pentane solutions at -30°C . $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})$ is not entirely stable in solution except in CHCl_3 or CH_2Cl_2 . Benzene or toluene solutions of $\underline{30}$ left standing at RT slowly deposit polymeric $\underline{29}$. The addition of ether or other ligands to these solutions accelerates this conversion. For this reason, a ligand exchange reaction between $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$, $\underline{13}$, and dmpe yields only the polymeric $\underline{29}$. One end of the dmpe ligand in $\underline{30}$ must be very weakly bound to the Ta and readily displaced by other ligands or coordinating solvents. The opening of the chelate ring then makes polymerization possible. The polymerization reaction appears to be irreversible. Although $\underline{30}$ is easily converted to $\underline{29}$, there is no method at present by which $\underline{29}$ can be transformed into $\underline{30}$.

The solvent dependencies involved in the formation and stabilization of $\underline{30}$ are difficult to rationalize. Solvents such as toluene which should favor a cis configuration of ligands yield $\underline{29}$ while solvents such as CHCl_3 which favor a trans orientation yield $\underline{30}$. In CHCl_3 or CH_2Cl_2 the faster rate of α -hydrogen abstraction (vide supra) may prevent polymerization of the intermediates which would yield $\underline{29}$. The enhanced stability of $\underline{30}$ in CHCl_3 (vs. that in toluene) is not readily explainable. The loss of one end of the dmpe ligand by the metal must be unfavorable in CHCl_3 or else recoordination is favored over polymerization.

The complexes in this class that have been prepared are included in Table 2.XII. These have all been prepared by reacting the appropriate

Table 2.XII. Several Complexes of the Type $\text{Me}_3\text{CCH}=\text{TaX}_3(\text{LL})$

		Color	$\nu_{\text{C}_\alpha\text{H}_\alpha} (\text{cm}^{-1})$	$J_{\text{C}_\alpha\text{H}_\alpha} (\text{Hz})$
$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})$	(30)	red-purple		72.0
$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{tmeda})$	(31)	purple	2532	79.1
$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{bipy})$	(32)	blue-purple		
$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{diars})$	(33)	red	2490	73.3
$\text{Me}_3\text{CCH}=\text{TaBr}_3(\text{dmpe})$	(34)	blue-purple	2427	71.8
$\text{Me}_3\text{CCH}=\text{TaBr}_3(\text{diphos})$	(35)	green		
$\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{dmpe})$	(36)	green		

dineopentyl metal trihalide with one equivalent of the chelating ligand in CHCl_3 or CH_2Cl_2 . The bromide complex, $\text{Me}_3\text{CCH}=\text{TaBr}_3(\text{dmpe})$, 34, is more stable than 30. The replacement of chloride by bromide decreases the e^- density on the metal. Even though chloride is more electronegative than bromide, bromide is a much poorer $p\pi$ donor than chloride.^a This decrease in the e^- density on the metal^b in 34 causes the metal to bind the chelating

^aFor BX_3 the Lewis acid strength increases as $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$.⁸⁴

^bThe difference in electron density around the metal between chloride and bromide complexes is also observable experimentally in the rate of ligand induced α -hydrogen abstraction for $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ vs. the same rate for $(\text{Me}_3\text{CCH}_2)_2\text{TaBr}_3$. Since the α -hydrogen abstraction process depends on an electron deficient metal center, the rates of reaction are expected to be faster for $(\text{Me}_3\text{CCH}_2)_2\text{TaBr}_3$. This is the observed result. Additionally, intermediates such as $(\text{Me}_3\text{CCH}_2)_2\text{TaBr}_3(\text{PMe}_3)$ are less stable than the chloride analogues.

ligand more tightly which enhances the stability of the complex. The complexes which process the nitrogen donor ligands tmeda or bipy, 31 or 32, respectively, are extremely stable. It appears that the tantalum-nitrogen interaction is much stronger than the tantalum-phosphorus interaction. The solubilities of 31 and 32 are very different. $\text{Me}_3\text{CCH}=\text{TaCl}_3\text{-(tmeda)}$, 31, is the most soluble of all the complexes listed in Table 2.XII. This complex, 31, is even soluble to some extent in pentane and cyclohexane. The complex, $\text{Me}_3\text{CCH}=\text{TaCl}_3\text{(bipy)}$, 32, is almost insoluble. It is soluble, but only sparingly, in CH_2Cl_2 .

2. The Characterization of the $\text{Me}_3\text{CCH}=\text{MX}_3(\text{LL})$ Series

Cyrosopic molecular weight measurements prove that these complexes are monomeric. The measured value for $\text{Me}_3\text{CCH}=\text{TaCl}_3\text{(tmeda)}$, 31, in cyclohexane was 489 (calcd 473.65) and for $\text{Me}_3\text{CCH}=\text{TaBr}_3\text{(dmpe)}$, 34, in benzene was 653 (calcd 640.95).

The ^1H , ^{13}C , and ^{31}P NMR data on these compounds show that they do not exchange ligands on the NMR time scale and that they are a single species in solution unlike the other neopentylidene complexes which possess two monodentate ligands. Tables 2.XIII., 2.XIV., and 2.XV. contain this data.

These complexes possess the low frequency for $\nu_{\text{C}_\alpha\text{H}_\alpha}$ in the IR and the low value for $J_{\text{C}_\alpha\text{H}_\alpha}$ in the ^{13}C NMR which are characteristic of these electron deficient niobium or tantalum neopentylidene complexes. All these values are listed in Table 2.XII. In every case where both values for each complex are available, there appears to be a direct relationship between $\nu_{\text{C}_\alpha\text{H}_\alpha}$ and $J_{\text{C}_\alpha\text{H}_\alpha}$. As $\nu_{\text{C}_\alpha\text{H}_\alpha}$ decreases, $J_{\text{C}_\alpha\text{H}_\alpha}$ also decreases.

Table 2.XIII. The ^1H NMR Data* for the $\text{Me}_3\text{CCH}=\text{MX}_3(\text{LL})$ Series (Conditions: CDCl_3 , 35°C)

	$=\text{CHC}\underline{\text{Me}}_3$	$=\text{CHC}\underline{\text{Me}}_3(\text{J}_{\text{HA}})(\text{J}_{\text{HA}'})$	$-\underline{\text{A}}\underline{\text{Me}}_2(\text{J}_{\text{HA}})$	$-\text{A}'\underline{\text{Me}}_2(\text{J}_{\text{HA}'})$	$-\underline{\text{CH}}_2\underline{\text{A}}\underline{\text{Me}}_2$	$-\underline{\text{CH}}_2\underline{\text{A}}'\underline{\text{Me}}_2$	A
$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})$ (30)	8.77	6.42 (1.0)(5.1)	8.24 (9.4)	8.53 (8.0)	7.70-8.40		P
$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{tmeda})$ (31)	8.84	6.45	6.82	7.29	6.96-7.03	7.16-7.24	N
$\text{Me}_3\text{CCH}=\text{TaBr}_3(\text{dmpe})$ (34)	8.74	6.65 (1.3)(9.6)	8.25 (9.5)	8.36 (8.6)	7.97-8.17		P

*Shifts are listed in τ while coupling constants are listed in Hz.

Table 2.XV. The ^{31}P NMR Data* for the $\text{Me}_3\text{CCH}=\text{MX}_3(\text{LL})$ Series

	$-\underline{\text{P}}\underline{\text{Me}}_2$	$-\underline{\text{P}}'\underline{\text{Me}}_2$	$\text{J}_{\text{pp}'}$
$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})$ (30)	17.32(br)	-3.69(br)	
$\text{Me}_3\text{CCH}=\text{TaBr}_3(\text{dmpe})$ (34)	11.60	-5.70	20

*Shifts are listed in ppm while coupling constants are listed in Hz.

Table 2.XIV. The ^{13}C NMR Data* for the $\text{Me}_3\text{CCH}=\text{MX}_3(\text{LL})$ Series

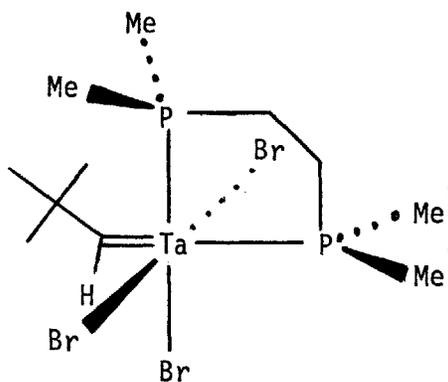
	$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})$ (30)	$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{tmeda})$ (31)	$\text{Me}_3\text{CCH}=\text{TaBr}_3(\text{dmpe})$ (34)
$=\underline{\text{C}}\text{H}\underline{\text{C}}\text{Me}_3(\text{J}_{\text{CA}})(\text{J}_{\text{CA}'})$	243.0	248.4	248.1(13.2)(16.1)
$=\text{CH}\underline{\text{C}}\text{Me}_3(\text{J}_{\text{CA}'})$	46.0	45.8	46.4(14.7)
$=\text{CH}\underline{\text{C}}\text{Me}_3$	33.5	33.6	33.5
$-\text{A}\underline{\text{M}}\text{e}_2(\text{J}_{\text{CA}})$	15.0(31.5)	56.4	17.0(30.8)
$-\text{A}'\underline{\text{M}}\text{e}_2(\text{J}_{\text{CA}'})$	9.0(19.1)	49.6	10.6(19.1)
$-\underline{\text{C}}\text{H}_2\text{A}\text{Me}_3(\text{J}_{\text{CA}})(\text{J}_{\text{CA}'})$	20-32	60.3	28.0(27.1)(12.5)
$-\underline{\text{C}}\text{H}_2\text{A}'\text{Me}_2(\text{J}_{\text{CA}})(\text{J}_{\text{CA}'})$	20-32	57.6	24.3(8.1)(21.3)

* Shifts are listed in ppm while coupling constants are listed in Hz.

Complexes with the smallest ν_{C-H_α} and J_{C-H_α} are expected to have the most perturbation in the $C_\alpha-H_\alpha$ bond due to its interaction with the metal center. These perturbations as pointed out in the structure of $[Me_3CCH=Ta(PMe_3)Cl_3]_2$, 12, include long $C_\alpha-H_\alpha$ distances, short $M-H_\alpha$ distances, and small $M-C_\alpha-H_\alpha$ angles. These distortions are probably much greater in the monomeric neopentylidene complexes (with or without chelating ligands) because ν_{C-H_α} and J_{C-H_α} are significantly smaller in these complexes compared to the values of the two parameters for the dimeric 12.

The 1H , ^{13}C , and ^{31}P NMR spectra indicate that the geometry of each complex is very similar to that of $Me_3CCH=TaCl_3(py)_2$, 26, or to that of the cis, mer isomer of $Me_3CCH=TaCl_3(PMe_3)_2$, 13b. The proposed structure is shown in Figure 2.7 for 34. The ^{31}P NMR clearly shows two nonequivalent phosphorus nuclei with a small coupling constant ($J_{PP}=20$ Hz) which is characteristic of a cis geometry.^a

Figure 2.7. The Structure of $Me_3CCH=TaBr_3(dmpe)$



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^aThe nonequivalent trans PMe_3 ligands in $Ta(PhCH=CH_2)Cl_3(PMe_3)_2$ have a coupling constant of 158 Hz (see Chap. 3).

The ^1H and ^{13}C NMR spectra demonstrate that one phosphorus is trans to the alkylidene ligand while the other is cis. The low field $^{13}\text{C}(^1\text{H})$ resonance of the α -carbon is a double doublet due to coupling to both a trans phosphorus nucleus ($J_{\text{CP}}=16.1\text{Hz}$) and a cis phosphorus nucleus ($J_{\text{CP}}=13.2\text{Hz}$). The same is true for the ^1H resonance of the α -hydrogen ($J_{\text{HP}}=1.3\text{Hz}$, $J_{\text{HP}}=9.6\text{Hz}$). The ^1H and ^{13}C NMR spectra also show that there is a mirror plane containing the tantalum atom, both phosphorus nuclei, and the alkylidene ligand. Each spectra shows two kinds of $-\text{PMe}_2$ groups in which both methyls per phosphorus are equivalent. This is an A_6XYB_6 pattern in the ^1H NMR. These data confirm that 34 is another example of a complex with cis σ -donor ligands in which the carbene ligand prefers to lie in a plane containing a P-Ta-Cl axis rather than in one containing a Cl-Ta-Cl axis.^a The data shown for $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})$, 30, and for $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{tmeda})$, 31, are consistent with the above analysis. Similar data for the remaining complexes in this series indicate that all of the coordination geometries for 30 thru 36 are identical. Exactly why the plane of the alkylidene ligand twists 90° as the σ -donor ligands change from a trans to a cis orientation is not clear. Electronic factors probably play a major role as steric factors should always favor the alignment of the carbene ligand along the Cl-Ta-Cl axis.

^aBoth the dimeric complexes and the monomeric complexes with trans σ -donor ligands possess carbene ligands which lie in the plane containing the Cl-Ta-Cl axis (vide supra).

F. Reactions of R_2TaCl_3 with PMe_3

A large class of neopentylidene complexes of the general formula $[Me_3CCH=MX_3L_y]_z$ have been prepared and discussed where M, X, L, y, and z have varied widely. In all cases, however, the alkylidene ligand has been a neopentylidene moiety. This raises the question of whether neopentyl groups are specifically activated toward ligand induced α -hydrogen abstractions or whether other alkyl groups can also be converted into alkylidene ligands by this process.

Probably the most neopentyl-like alkyl group is the trimethylsilylmethyl group (Me_3SiCH_2-). The reaction of $(Me_3SiCH_2)_2TaCl_3$ ⁸⁵ with PMe_3 in pentane at RT yields only starting materials. The same reaction done in $CHCl_3$, however, produces good yields of green, crystalline $Me_3SiCH=TaCl_3(PMe_3)_2$,³⁷ $\sim\sim$. This indicates that the Me_3SiCH_2- group is less prone to undergo α -hydrogen abstraction than is the neopentyl group. The inductive effect of the silicon (which is replacing the β -carbon of the neopentyl group) must be transmitted through the α -carbon to increase the electron density both on the metal and in the $C_\alpha-H_\alpha$ bond. Increasing the electron density around the metal can cause a decrease in the interaction of the metal with the $C_\alpha-H_\alpha$ bonds of the alkyl group. Increasing the electron density in the $C_\alpha-H_\alpha$ bond strengthens the bond. These two conditions are unfavorable to α -hydrogen abstraction. It is interesting that Wilkinson has isolated $(Me_3SiCH_2)_2TaCl_3(1,10-phen)$.⁸⁵ This indicates how close to the borderline for α -hydrogen abstraction the Me_3SiCH_2- group is. In trimethylsilylmethyl complexes some ligands will promote α -hydrogen abstraction while others only form adducts.

Table 2.XVI. The ^1H and ^{13}C Data* for $\text{Me}_3\text{SiCH}=\text{TaCl}_3(\text{PMe}_3)_2$ (37)

	$=\text{CHSiMe}_3$ (J_{CH})	$=\text{CHSiMe}_3$ ($J_{\text{C}_\alpha\text{H}_\alpha}$)	PMe_3 (J_{CH})	Conditions
^1H NMR	9.70		8.70(br)	C_6D_6 , 35°C
^{13}C NMR	3.2 (119.2)	277.8 (101.1)	15.8(130.9)	CDCl_3 , 28°C

*Shifts are listed in τ or ppm while coupling constants are listed in Hz.

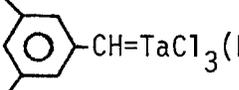
The spectroscopic data for 37 appear in Table 2.XVI. As in the case of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$, 13, this complex, 37, possesses PMe_3 ligands which exchange at RT on the NMR time scale and most likely is a mixture of two isomers.

So far only alkyl groups without β -hydrogen atoms have been studied. The use of an ethyl group, for example, could determine whether β -hydrogen elimination or α -hydrogen abstraction is preferable. The reaction of Et_2TaCl_3 (prepared *in situ*) with PMe_3 in toluene at -78°C yields only $\text{Ta}(\text{C}_2\text{H}_4)\text{Cl}_3(\text{PMe}_3)_2^a$ which is the product expected from β -hydrogen elimination. Although β -hydrogen elimination is very facile,²⁸ the lack of steric crowding in this case contributes toward making the α -hydrogen abstraction process unfavorable.^b

Others have studied systems which are analogous to $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ in that they are derived from sterically crowded alkyl complexes which lack β -hydrogen atoms. J. Fellmann has prepared $\text{PhMe}_2\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$

^aThe preparation and characterization of this compound is fully discussed in Chap. 3 (*vide infra*).

^b $\text{Me}_2\text{TaCl}_3(\text{PMe}_3)_2$ is stable to $>120^\circ\text{C}$.⁶¹

from the reaction of $(\text{PhMe}_2\text{CCH}_2)_2\text{TaCl}_3$ with PMe_3 .⁴⁷ L. Messerle has prepared $\text{PhCH}=\text{TaCl}_3(\text{PMe}_3)_2$ from the reaction of $(\text{PhCH}_2)_2\text{TaCl}_3$ with PMe_3 .⁵⁶ Finally, P. Sharp has prepared  $\text{CH}=\text{TaCl}_3(\text{PMe}_3)_2$ from the decomposition of $(\text{Mes})(\text{Me})\text{TaCl}_3(\text{PMe}_3)_2$ which gives the dimethyl derivative of Messerle's complex through a γ - rather than α -hydrogen abstraction.⁶¹

This series of primary alkylidene complexes can now be expressed as $[\text{RCH}=\text{MX}_3\text{L}_x]_y$. It is highly possible that with the proper choice of alkyl groups complexes of this type which possess secondary alkylidene ligands (i.e., $\text{RR}'\text{C}=\text{}$) may be prepared. It is unfortunate that this ligand induced α -hydrogen abstraction process (which works extremely well for the Group V metals) has not been very useful in either Group IV or VI. Some progress has been made in Group VI^{39,40} although the proper type of starting alkyl compounds are either unknown or unstable towards alternate modes of decomposition. Little progress has occurred in Group IV⁸⁰ since the starting alkyl compounds are very stable (or possibly the desired products are unstable).

Despite a few limitations it is possible to synthesize an immense number of alkylidene complexes by ligand induced α -hydrogen abstraction. The diversity of this set of compounds is important in the study of carbene complexes. With this large class of compounds the effects of changes at and around the carbene ligand or metal center on their properties and reaction chemistry can be studied in detail. Trends can be identified and used as rationales to prepare or determine which complexes might be expected to possess certain desired properties with a high degree of confidence. This type of approach is valuable in that much guesswork and unproductive efforts can be eliminated especially in areas such as the "tailoring" of catalysts.

EXPERIMENTAL ^a1. Preparation of $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3(\text{PMe}_3)$ (11) [VII-12].

PMe_3 (0.36 g) in 2 mL of pentane was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ (2.15 g) in 15 mL of pentane at -30°C . The yellow solution became red as the PMe_3 was added and orange-red needles of 11 precipitated. The product was collected by filtration, rinsed with cold pentane, and dried briefly in vacuo. The yield was 2.20 g (92.7%) of 11 which is thermally unstable and must be stored at -30°C .

^1H NMR ($\#H-018$, τ , $\text{C}_6\text{D}_5\text{CD}_3$, -80°C , 270 MHz): 7.65 (d, 4, $^3J_{\text{HP}}=12.0$ Hz, $-\text{CH}_2\text{CMe}_3$), 8.46 (s, 18, $-\text{CH}_2\text{CMe}_3$), 9.37 (d, 9, $^2J_{\text{HP}}=8.4$ Hz, PMe_3).

^{13}C NMR ($\#C-020$, ppm, $\text{C}_6\text{D}_5\text{CD}_3$, -60°C , 67.89 MHz, ^1H gated decoupled): 96.1 (t, $J_{\text{CH}}=121$ Hz, $-\text{CH}_2\text{CMe}_3$), 45.6 (s, $-\text{CH}_2\text{CMe}_3$), 35.1 (q, $J_{\text{CH}}=124$ Hz, $-\text{CH}_2\text{CMe}_3$), 12.1 (qd, $J_{\text{CH}}=131$ Hz, $J_{\text{CP}}=21$ Hz, PMe_3).

$^{31}\text{P}(^1\text{H})$ NMR ($\#130-A$, ppm, toluene, -50°C , 36.43 MHz): -16.4 (s, PMe_3).

2. Preparation of $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Cl}_3]_2$ (12).

a. from $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3(\text{PMe}_3)$ [VI-14].

A saturated ether solution of $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3(\text{PMe}_3)$ (2.50 g) was allowed to stand at RT for 1 day during which time it decomposed with the loss of one equivalent of CMe_4 per Ta to produce large red crystals of 12. The product was collected by filtration, rinsed with pentane, and dried in vacuo. A second crop can be obtained by reducing the volume of the mother liquor in vacuo. The yield was 2.05 g (95.7%).

^aThe Experimental for Chap. 1 lists general procedures.

b. from $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ and $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ [VI-71].

$(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ (2.58 g) in 5 mL of ether was added dropwise with stirring to $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ (3.06 g) in 20 mL of ether. Large red crystals of 12 were obtained as before (vide supra). The yield was 5.02 g (96.5%).

^1H NMR ($\#253$, τ , C_6H_6 , 35°C , 60 MHz): 4.70 (br s, 1, $=\text{CHCMe}_3$), 8.86 (d, 9, $^2J_{\text{HP}}=9.6$ Hz, PMe_3), 8.90 (s, 9, $=\text{CHCMe}_3$).

^{13}C NMR^a (ppm, C_6D_6 , 28°C , 15 MHz, ^1H gated decoupled): 276.0 (dd, $J_{\text{CH}}=101$ Hz, $^2J_{\text{CP}}=7$ Hz, $=\text{CHCMe}_3$), 46.6 (s, $=\text{CHCMe}_3$), 33.5 (q, $J_{\text{CH}}=126$ Hz, $=\text{CHCMe}_3$), 15.8 (qd, $J_{\text{CH}}=132$ Hz, $J_{\text{CP}}=29$ Hz, PMe_3).

$^{31}\text{P}(^1\text{H})$ NMR ($\#108$, ppm, $\text{C}_6\text{D}_5\text{CD}_3$, -30°C , 36.43 MHz): 5.3 (s, PMe_3).

IR ($\#147$, cm^{-1} , nujol mull, NaCl plates): 2605 (br_w, $\nu_{\text{C}\alpha\text{H}\alpha}$).

MW (VI-20, C_6H_6 , 4.22 mM): calcd 868.0; found 853.

ANAL^a (for $\text{TaC}_8\text{H}_{19}\text{Cl}_3\text{P}$): calcd C 22.17, H 4.41;
found C 22.68, H 4.28.

3. Preparation of $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_2\text{Ph})\text{Cl}_3]_2$ (14) [VI-3].

PMe_2Ph (0.25 g) in 2 mL of pentane was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ (0.86 g) in 10 mL of pentane at -30°C . The color of the solution changed from yellow to red, and after the reaction was warmed to RT a red oil formed. On standing this oil gave red crystals of 14 which

^aPerformed by J. Fellmann.

were collected by filtration, rinsed with pentane, and dried in vacuo.
The yield was 0.88 g (98.6%)

^1H NMR (τ , C_6H_6 , 35°C , 60 MHz): 4.67 (br s, 1, $=\text{CHCMe}_3$),
8.54 (d, 6, $^2J_{\text{HP}}=8.3$ Hz, PMe_2Ph), 8.92 (s, 9, $=\text{CHCMe}_3$).

IR (τ , cm^{-1} , nujol mull, NaCl plates): 2592 (m, $\nu_{\text{C}_\alpha\text{H}_\alpha}$);
1978, 1869, 1795, 1730 (w, Ph combination modes); 1570 (m, Ph C=C).

4. Preparation of $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PPh}_2\text{Me})\text{Cl}_3]_2$ (15) [V-74].

PPh_2Me (0.36 g) in 2 mL of pentane was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ (0.86 g) in 10 mL of pentane at -30°C . The solution changed from yellow to orange and then slowly to red after warming to RT. A red oil formed which gave red crystals of 15 on standing overnight. The product was collected by filtration, rinsed with pentane, and dried in vacuo. The yield was 0.93 g (92.6%).

^1H NMR (τ , C_6H_6 , 35°C , 60 MHz): 4.49 (s, 1, $=\text{CHCMe}_3$),
8.12 (d, 3, $^2J_{\text{HP}}=8.0$ Hz, PPh_2Me), 8.90 (s, 9, $=\text{CHCMe}_3$).

5. Preparation of $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Br}_3]_2$ (16) [VIII-3].

PMe_3 (0.15 g) in 2 mL of ether was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_2\text{TaBr}_3$ (1.13 g) in 5 mL of ether at -30°C . The yellow solution immediately became dark red and was allowed to warm to RT. Overnight red crystals of 16 formed. These were collected by filtration, rinsed with pentane, and dried in vacuo. A second crop was collected from the mother liquor after some of the ether was removed in vacuo. The yield was 1.11 g (97.9%).

^1H NMR (#511, τ , CDCl_3 , 35°C , 60 MHz): 6.16 (br s, 1, $=\text{CHCMe}_3$), 8.22 (d, 9, $^2J_{\text{HP}}=9.0$ Hz, PMe_3), 8.73 (s, 9, $=\text{CHCMe}_3$).

^{13}C NMR (#128, ppm, CDCl_3 , 28°C , 15 MHz, ^1H gated decoupled): 283.0 (dd, $J_{\text{CH}}=86$ Hz, $^2J_{\text{CP}}=10$ Hz, $=\text{CHCMe}_3$), 47.9 (s, $=\text{CHCMe}_3$), 33.3 (q, $J_{\text{CH}}=126$ Hz, $=\text{CHCMe}_3$), 17.7 (qd, $J_{\text{CH}}=131$ Hz, $J_{\text{CP}}=29$ Hz, PMe_3).

$^{31}\text{P}(^1\text{H})$ NMR (#135, ppm, CHCl_3 , -50°C , 36.43 MHz): 6.1 (s, PMe_3).

IR(#149, cm^{-1} , *nujol* mull, NaCl plates): 2519(vw, $\nu_{\text{C}_\alpha\text{H}_\alpha}$).

6. Preparation of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ (13).

a. from $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ [X-46].

PMe_3 (4.68 g) in 10 mL of pentane was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ (12.90 g) in 60 mL of pentane at -30°C . The yellow solution became red and needles of $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3(\text{PMe}_3)$ precipitated. These dissolved to give a dark red solution which became purple after the reaction was warmed to RT. After 3 hrs. at RT the pentane was removed in vacuo to give a purple oil which slowly crystallized at -30°C . The yield was 14.94 g (97.9%) of microcrystalline 13. The product can be recrystallized from ether at -30°C to yield purple fibers of 13.

b. from $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Cl}_3]_2$ [VII-29].

PMe_3 (0.80 g) in 1 mL of ether was added with stirring to $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Cl}_3]_2$ (4.33 g) in 20 mL of ether. The red solution became purple and after 1/2 hr. the ether was removed in vacuo to yield a purple oil from which 13 was isolated as before (vide supra). The yield was 5.01 g (98.4%).

c. from $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{THF})_2$ [IX-34].

PMe_3 (0.94 g) in 2 mL of ether was added with stirring to $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{THF})_2$ (3.01 g) in 10 mL of ether. The red solution became purple and after 1/2 hr. the ether was removed in vacuo to yield a purple oil from which 13 was isolated as before (vide supra). The yield was 2.89 g (94.5%).

^1H NMR (#287-A, τ , $\text{C}_6\text{D}_5\text{CD}_3$, 32°C , 60 MHz): 8.65 (br, 18, PMe_3), 8.80 (s, 9, $=\text{CHCMe}_3$). (^1H -015, τ , $\text{C}_6\text{D}_5\text{CD}_3$, -60°C , 270 MHz): cis, mer isomer: 6.03 (br s, 1, $=\text{CHCMe}_3$), 8.78 (d, 9, $^2\text{J}_{\text{HP}}=8.7$ Hz, PMe_3), 8.87 (s, 9, $=\text{CHCMe}_3$), 8.96 (d, 9 $^2\text{J}_{\text{HP}}=6.9$ Hz, PMe_3'); trans, mer isomer: 3.91 (br s, 1, $=\text{CHCMe}_3$), 8.70 (t, 18, $^2\text{J}_{\text{HP}}\cong 4$ Hz, PMe_3), 8.82 (s, 9, $=\text{CHCMe}_3$).

^{13}C NMR (#C-017, ppm, $\text{C}_6\text{D}_5\text{CD}_3$, -50°C , 67.89 MHz, ^1H gated decoupled): cis, mer isomer: 255.9 (ddd, $\text{J}_{\text{CH}}=96$ Hz, $^2\text{J}_{\text{CP}}=33$ Hz, $^2\text{J}_{\text{CP}}=12$ Hz, $=\text{CHCMe}_3$), 46.8 (d, $^3\text{J}_{\text{CP}}=13$ Hz, $=\text{CHCMe}_3$), 33.2 (q, $\text{J}_{\text{CH}}=127$ Hz, $=\text{CHCMe}_3$), 18.0 (qd, $\text{J}_{\text{CH}}=129$ Hz, $\text{J}_{\text{CP}}=28$ Hz, PMe_3), 12.3 (qd, $\text{J}_{\text{CH}}=132$ Hz, $\text{J}_{\text{CP}}=16$ Hz, PMe_3'); trans, mer isomer: 256.5 (dt, $\text{J}_{\text{CH}}=75$ Hz, $^2\text{J}_{\text{CP}}=12$ Hz, $=\text{CHCMe}_3$), 45.8 (s, $=\text{CHCMe}_3$), 34.5 (q, $\text{J}_{\text{CH}}=125$ Hz, $=\text{CHCMe}_3$), 15.5 (qt, $\text{J}_{\text{CH}}=134$ Hz, $\text{J}_{\text{CP}}=15$ Hz, PMe_3).

$^{31}\text{P}(^1\text{H})$ NMR (#128, ppm, toluene, -70°C , 36.43 MHz): cis, mer isomer: -5.7 (d, $^2\text{J}_{\text{PP}}=7$ Hz, PMe_3), -30.5 (d, $^2\text{J}_{\text{P}'\text{P}}=7$ Hz, PMe_3'); trans, mer isomer: -4.9 (s, PMe_3).

IR(#146, cm^{-1} , nujol mull, NaCl plates): 2510 (m, $\nu_{\text{C}\alpha\text{H}\alpha}$).

MW (VI-16, C_6H_6 , 6.36 mM): calcd 509.6; found 377.

7. Preparation of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_2\text{Ph})_2$ (17) [V-3].

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PMe_2Ph (0.84 g) in 2 mL of pentane was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ (1.29 g) in 20 mL of pentane at -30°C . The yellow solution became red and was allowed to warm to RT. After 1/2 hr. a purple microcrystalline solid formed. The crude product was collected by filtration and recrystallized from toluene-pentane at -30°C . The yield was 1.80 g (94.7%) of red-purple crystalline 17.

^1H NMR (#265, τ , C_6D_6 , 35°C , 90 MHz): 2.45-3.05 (m, 10 PMe_2Ph), 8.48 (br, 12, PMe_2Ph), 8.89 (s, 9, $=\text{CHCMe}_3$). (#H-016, τ , $\text{C}_6\text{D}_5\text{CD}_3$, -50°C , 270 MHz): cis, mer isomer: 2.50-3.05 (m, 10, PMe_2Ph and $\text{PMe}_2\text{Ph}'$), 5.95 (s, 1, $=\text{CHCMe}_3$), 8.65 (d, 6, $^2J_{\text{HP}}=8.4$ Hz, PMe_2Ph), 8.80 (d, 6, $^2J_{\text{HP}'}=5.8$ Hz, $\text{PMe}_2\text{Ph}'$), 8.88 (s, 9, $=\text{CHCMe}_3$); trans, mer isomer: 2.50-3.05 (m, 10, $\text{PMeMe}'\text{Ph}$), 3.94 (s, 1, $=\text{CHCMe}_3$), 8.31 (t, 6, $^2J_{\text{HP}}=3.9$ Hz, $\text{PMeMe}'\text{Ph}$), 8.84 (t, 6, $^2J_{\text{HP}'}=3.9$ Hz, $\text{PMeMe}'\text{Ph}$), 9.29 (s, 9, $=\text{CHCMe}_3$).

^{13}C NMR (#C-004, ppm, C_6D_6 , 35°C , 67.89 MHz, ^1H gated decoupled): 262.2 (br d, $J_{\text{CH}}=88$ Hz, $=\text{CHCMe}_3$), 137.0 (s, ipso Ph), 130.9 (d, $J_{\text{CH}}=162$ Hz, ortho Ph), 129.9 (d, $J_{\text{CH}}=162$ Hz, para Ph), 128.6 (d, $J_{\text{CH}}=160$ Hz, meta Ph), 46.8 (s, $=\text{CHCMe}_3$), 33.2 (q, $J_{\text{CH}}=127$ Hz, $=\text{CHCMe}_3$), 17.1 (q, $J_{\text{CH}}=131$ Hz, PMe_2Ph), 11.1 (q, $J_{\text{CH}}=132$ Hz, PMe_2Ph).

$^{31}\text{P}(^1\text{H})$ NMR (#136, ppm, toluene, -50°C , 36.43 MHz): cis, mer isomer: -0.8 (br s, PMe_2Ph), -25.7 (br s, $\text{PMe}_2\text{Ph}'$); trans, mer isomer: 1.8 (s, PMe_2Ph).

IR (#159, cm^{-1} , nujol mull, NaCl plates): 2518 (m, $\nu_{\text{C}_\alpha\text{H}_\alpha}$); 1967, 1884, 1800, 1728 (w, Ph combination modes); 1565 (m, Ph C=C).

8. Preparation of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PPh}_2\text{Me})_2$ (18) [V-66].

PPh_2Me (1.20 g) in 3 mL of pentane was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ (1.29 g) in 10 mL of pentane at -30°C . The yellow solution became orange and then red on warming to RT. After several hrs. a red oil formed which slowly crystallized. The red-purple crystals of 18 were collected by filtration, rinsed with pentane, and dried in vacuo. The yield was 2.09 g (91.9%).

^1H NMR (#247, τ , C_6D_6 , 35°C , 60 MHz): 2.35-3.10 (m, 20 PPh_2Me), 4.50 (s, 1, $=\text{CHCMe}_3$), 8.34 (br, 6, PPh_2Me), 8.87 (s, 9, $=\text{CHCMe}_3$).

IR (#161, cm^{-1} , nujol mull, NaCl plates): 2535 (vw, $\nu_{\text{C}_\alpha\text{H}_\alpha}$); 1964, 1892, 1805, 1729 (w, Ph combination modes); 1580 (m, Ph C=C).

9. Preparation of $\text{Me}_3\text{CCH}=\text{TaBr}_3(\text{PMe}_3)_2$ (19) [IX-67].

PMe_3 (0.80 g) in 2 mL of pentane was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_2\text{TaBr}_3$ (2.82 g) in 15 mL of pentane at -30°C . The yellow solution became dark red immediately and purple needles, presumably $(\text{Me}_3\text{CCH}_2)_2\text{TaBr}_3(\text{PMe}_3)$, precipitated. These dissolved rapidly to give a blue-purple solution from which blue-purple crystals of 19 formed. The product was collected by filtration, rinsed with pentane, and dried in vacuo. The yield was 3.09 g (96.1%).

^1H NMR (#378, τ , C_6D_6 , 35°C , 60 MHz): 8.54 (br, 18, PMe_3), 8.67 (s, 9, $=\text{CHCMe}_3$).

^{13}C NMR (#133, ppm, CDCl_3 , -20°C , 15 MHz, ^1H gated decoupled): trans, mer isomer: 258.7 (dt, $J_{\text{CH}}=74$ Hz, $^2J_{\text{CP}}=8$ Hz, $=\text{CHCMe}_3$), 45.6 (s, $=\text{CHCMe}_3$),

33.2 (q, $J_{\text{CH}}=125$ Hz, $=\text{CHCMe}_3$), 16.5 (qt, $J_{\text{CH}}=132$ Hz, $J_{\text{CP}}=15$ Hz, PMe_3).

^{31}P (^1H) NMR (#137, ppm, toluene, -50°C , 36.43 MHz): cis, mer isomer: -9.2 (br s, PMe_3), -31.1 (br s, PMe_3'); trans, mer isomer: -4.0 (s, PMe_3).

IR(#150, cm^{-1} , nujol mull, NaCl plates): 2505 (m, $\nu_{\text{C}_\alpha\text{H}_\alpha}$).

10. Preparation of $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_3)_2$ (20).

a. from $(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_3$ [VII-27].

PMe_3 (1.44 g) in 3 mL of pentane was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_3$ (3.08 g) in 50 mL of pentane at -30°C . Red-brown crystals, which may be $(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_3(\text{PMe}_3)$, formed initially from the red solution. These dissolved rapidly to give a purple solution from which a green-brown powder precipitated. The solution was then filtered. The pentane was removed from the purple filtrate to yield blue-purple crystals of 20. The yield was 2.49 g (65.5%).

b. from $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{THF})_2$ [X-48].

PMe_3 (0.32 g) in 3 mL of ether was added dropwise with stirring to $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{THF})_2$ (0.83 g) in 10 mL of ether at -30°C . The purple solution was allowed to warm to RT. After 1/2 hr. the solution was filtered although the solution was still homogeneous. The product, 20, was isolated as before (vide supra). The yield was 0.84 g (99.6%).

^1H NMR(#203, τ , C_6H_6 , 35°C , 60 MHz): 5.43 (br, 1, $=\text{CHCMe}_3$), 8.75 (br, 18, PMe_3), 8.83 (s, 9, $=\text{CHCMe}_3$). (#514-B, τ , CDCl_3 , -30°C , 60 MHz): cis, mer isomer: 5.84 (d, $^3J_{\text{HP}}=6.5$ Hz, $=\text{CHCMe}_3$), 8.31-8.54 (m, 18, PMe_3 and PMe_3'), 8.71 (s, 9, $=\text{CHCMe}_3$); trans, mer isomer: 4.37 (br, 1, $=\text{CHCMe}_3$), 8.31-8.54 (m, 18, PMe_3), 8.71 (s, 9, $=\text{CHCMe}_3$).

^{13}C NMR (#169, ppm, CDCl_3 , -30°C , 15 MHz, ^1H gated decoupled): cis, mer isomer: 252.8 (br d, $J_{\text{CH}}=79$ Hz, $=\text{CHCMe}_3$), 45.9 (s, $=\text{CHCMe}_3$), 29.2 (q, $J_{\text{CH}}=126$ Hz, $=\text{CHCMe}_3$), 16.6 (qd, $J_{\text{CH}}=137$ Hz, $J_{\text{CP}}=25$ Hz, PMe_3), 11.6 (qd, $J_{\text{CH}}=137$ Hz, $J_{\text{CP}}=16$ Hz, PMe_3'); trans, mer isomer: 252.8 (br d, $J_{\text{CH}}=79$ Hz, $=\text{CHCMe}_3$), 46.5 (s, $=\text{CHCMe}_3$), 29.8 (q, $J_{\text{CH}}=126$ Hz, $=\text{CHCMe}_3$), 14.2 (qt, $J_{\text{CH}}=137$ Hz, $J_{\text{CP}}=13$ Hz, PMe_3).

$^{31}\text{P}(^1\text{H})$ NMR (#138, ppm, toluene, -50°C , 36.43 MHz): cis, mer isomer: -10.9 (br s, PMe_3), -26.9 (br s, PMe_3'); trans, mer isomer: -10.0 (s, PMe_3).

IR (#157, cm^{-1} , nujol mull, NaCl plates): 2510 (br m, $\nu_{\text{C}_\alpha\text{H}_\alpha}$).

11. Preparation of $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_2\text{Ph})_2$ (21) [V-7].

PMe_2Ph (1.66 g) in 5 mL of pentane was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_3$ (2.05 g) in 50 mL of pentane at -30°C . After the reaction had warmed to RT, a purple suspension formed in the red solution while a brown tar was deposited on the bottom of the reaction flask. The purple suspension was decanted and filtered. The crude purple powder was dissolved in toluene, filtered, and recrystallized from toluene-pentane at -30°C to give purple crystals of 21. The yield was 2.01 g (61.4%).

^1H NMR (#H-007, τ , C_6D_6 , 35°C , 270 MHz): 2.40-3.00 (m, 10, PMe_2Ph), 5.45 (br s, 1, $=\text{CHCMe}_3$), 8.61 (br, 12, PMe_2Ph), 8.95 (s, 9, $=\text{CHCMe}_3$).

12. Preparation of $[\text{Me}_3\text{CCH}=\text{Nb}(\text{PMe}_3)\text{Cl}_3]_2$ (22).

a. from $(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_3$ [VI-50].

PMe_3 (0.14 g) in 1 mL of pentane was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_3$ (0.68 g) in 5 mL of pentane at -30°C . Red-brown crystals,

which may be $(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_3(\text{PMe}_3)$, formed initially. These dissolved rapidly to give a dark red solution from which a brown powder precipitated. The precipitate was collected by filtration, rinsed with pentane, and dissolved in toluene. The toluene solution was filtered to remove some insoluble brown material. The product was crystallized from the concentrated toluene solution at -30°C with pentane. The red-purple crystals of 22 were collected by filtration, rinsed with pentane, and dried in vacuo. The yield was 0.42 g (67.5%) of 22 which appears to be thermally unstable and must be stored at -30°C .

b. from $(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_3$ and $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_3)_2$ [VI-21].

$\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_3)_2$ (0.42 g) in 5 mL of cold ether was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_3$ (0.34 g) in 5 mL of ether at -30°C . A purple-brown precipitate formed. The product was purified and isolated as before (vide supra). The yield was 0.39 g (56.4%).

^1H NMR (τ , C_6H_6 , 35°C , 60 MHz): 3.64 (br s, 1, $=\text{CHCMe}_3$), 8.92 (d, 9, $^2J_{\text{HP}}=10.3$ Hz, PMe_3), 8.96 (s, 9, $=\text{CHCMe}_3$).

IR (cm^{-1} , nujol mull, NaCl plates): 2595 ($\nu_{\text{C}_\alpha\text{H}_\alpha}$).

13. Preparation of $[\text{Me}_3\text{CCH}=\text{Nb}(\text{PMe}_2\text{Ph})\text{Cl}_3]_2$ (23) [VI-66].

PMe_2Ph (0.25 g) in 2 mL of pentane was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_3$ (0.86 g) in 10 mL of pentane at -30°C . The red solution became dark and a purple-brown powder precipitated. This was collected by filtration, rinsed with pentane, and dissolved in toluene. The toluene solution was filtered to remove some insoluble brown powder. The product

was crystallized from the concentrated toluene solution at -30°C with pentane. The purple crystals of 23 were collected by filtration, rinsed with pentane, and dried in vacuo. The yield was 0.45 g (61.3%) of 23 which appears to be thermally unstable and must be stored at -30°C .

^1H NMR (#314, τ , C_6D_6 , 35°C , 60 MHz): 2.65-3.00 (m, 5, PMe_2Ph), 3.62 (br s, 1, $=\text{CHCMe}_3$), 8.43 (d, 6, $^2J_{\text{HP}}=8.8$ Hz, PMe_2Ph), 8.89 (s, 9, $=\text{CHCMe}_3$).

14. Preparation of $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{THF})_2$ (24) [X-9].

THF (1.44 g) in 2 mL of ether was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_3$ (1.71 g) in 10 mL of ether at -30°C . The red solution was allowed to warm to RT. After 2 hrs. at RT, the solution had become purple. These solutions of 24 were generally used in situ assuming quantitative yield.^a The product can also be obtained as dark-purple crystals from ether at -30°C .

^1H NMR (#513-B, τ , CDCl_3 , -30°C , 60 MHz): 5.50 (m, 4, $\overbrace{\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$), 5.82 (m, 4, $\overbrace{\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2'}$), 6.40 (br s, 1, $=\text{CHCMe}_3$), 7.76 (m, 4, $\overbrace{\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$), 8.01 (m, 4, $\overbrace{\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2'}$), 8.75 (s, 9, $=\text{CHCMe}_3$).

^{13}C NMR (#195, ppm, CDCl_3 , -20°C , 15 MHz, ^1H gated decoupled): 257.0 (d, $J_{\text{CH}}=82$ Hz, $=\text{CHCMe}_3$), 78.4 (t, $J_{\text{CH}}=150$ Hz, $\overbrace{\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$), 69.8 (t, $J_{\text{CH}}=149$ Hz, $\overbrace{\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2'}$), 47.6 (s, $=\text{CHCMe}_3$), 29.0 (q, $J_{\text{CH}}=129$ Hz, CHCMe_3), 25.0 (t, $J_{\text{CH}}=125$ Hz, $\overbrace{\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$), 24.2 (t, $J_{\text{CH}}=125$ Hz, $\overbrace{\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2'}$).

^aThe typical yields of products from subsequent reactions of 24 were 90-95% based on $(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_3$.

15. Preparation of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{THF})_2$ (25) [IX-61].

THF (1.44 g) in 2 mL of ether was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ (2.15 g) in 20 mL of ether at -30°C . The color of the solution changed from yellow to red and then slowly to purple after the solution had warmed to RT. After 8 hrs. at RT the solution was filtered and the volume of the solution was reduced in vacuo. Purple crystals of 25 were collected after cooling the concentrated ether solution to -30°C . The yield was 2.16 g (86.1%).

^1H NMR (#467, τ , CDCl_3 , 35°C , 60 MHz): 5.67 (m, 8, $\overline{\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$), 6.50 (s, 1, $=\text{CHCMe}_3$), 7.89 (m, 8, $\overline{\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$), 8.76 (s, 9, $=\text{CHCMe}_3$).

^{13}C NMR (#168, ppm, CDCl_3 , -30°C , 15 MHz, ^1H gated decoupled): 253.8 (d, $J_{\text{CH}}=79$ Hz, $=\text{CHCMe}_3$), 79.7 (t, $J_{\text{CH}}=152$ Hz, $\overline{\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$), 70.1 (t, $J_{\text{CH}}=150$ Hz, $\overline{\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$), 44.9 (s, $=\text{CHCMe}_3$), 32.8 (q, $J_{\text{CH}}=125$ Hz, $=\text{CHCMe}_3$), 25.7 (t, $J_{\text{CH}}=133$ Hz, $\overline{\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$), 24.7 (t, $J_{\text{CH}}=133$ Hz, $\overline{\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$).

IR (#155, cm^{-1} , nujol mull, NaCl plates): 2540 (w , $\nu_{\text{C}_\alpha\text{H}_\alpha}$).

16. Preparation of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{py})_2$ (26) [VIII-46].

At -30°C , py (0.55 g) in 2 mL of CH_2Cl_2 was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ (1.29 g) in 8 mL of CH_2Cl_2 . The yellow solution became red. The reaction was allowed to warm to RT. After 8 hrs. at RT the solvent was removed in vacuo to yield a red solid which was dissolved in ether. The red solution was filtered. The product was crystallized from the concentrated ether solution with pentane at -30°C to yield red crystals of 26. The yield was 1.47 g (95.0%).

^1H NMR (#418, τ , CDCl_3 , 35°C , 60 MHz): 0.78-2.75 (m, 10, py and py'), 6.37 (s, 1, =CHCMe₃), 8.77 (s, 9, =CHCMe₃).

^{13}C NMR (#148-B, ppm, CDCl_3 , 28°C , 15 MHz, ^1H gated decoupled): 254.7 (d, $J_{\text{CH}}=78$ Hz, =CHCMe₃), 153.1 (dd, $J_{\text{CH}}=182$ Hz, $^2J_{\text{CH}}=9$ Hz, C_2py), 150.7 (dd, $J_{\text{CH}}=179$ Hz, $^2J_{\text{CH}}=7$ Hz, $\text{C}_2\text{py}'$), 139.7 (dt, $J_{\text{CH}}=164$ Hz, $^2J_{\text{CH}}=6$ Hz, C_4py), 138.5 (dt, $J_{\text{CH}}=166$ Hz, $^2J_{\text{CH}}=6$ Hz, $\text{C}_4\text{py}'$), 124.6 (dt, $J_{\text{CH}}=169$ Hz, $^2J_{\text{CH}}=6$ Hz, C_3py), 124.1 (dt, $J_{\text{CH}}=169$ Hz, $^2J_{\text{CH}}=6$ Hz, $\text{C}_3\text{py}'$), 45.5 (s, =CHCMe₃), 33.2 (q, $J_{\text{CH}}=126$ Hz, =CHCMe₃).

17. Preparation of $\text{Me}_3\text{CCH}=\text{TaBr}_3(\text{THF})_2$ (27) [IX-1].

THF (0.16 g) in 1 mL of ether was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_2\text{TaBr}_3$ (0.56 g) in 2 mL of ether at -30°C . The yellow solution became red and then blue-purple as the solution warmed to RT. After 8 hrs. the solution was filtered and the solvent was removed in vacuo to give an oil which crystallized at -30°C . The yield was 0.61 g (96.1%) of blue-purple microcrystalline 27.

^1H NMR (#447, τ , CDCl_3 , 35°C , 60 MHz): 5.53 (m, 8, $\overline{\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$), 7.20 (s, 1, =CHCMe₃), 7.90 (m, 8, $\overline{\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$), 8.63 (s, 9, =CHCMe₃).

18. Preparation of $\text{Me}_3\text{CCH}=\text{TaBr}_3(\text{THT})_2$ (28) [IX-18].

THT (0.10 g) was added to $(\text{Me}_3\text{CCH}_2)_2\text{TaBr}_3$ (0.06 g) in 1/2 mL of CH_2Cl_2 at 0°C . The yellow solution became orange and then red after the solution had warmed to RT. After 3 hrs. the reaction appears to be complete and quantitative by ^1H NMR.

^1H NMR (#451, τ , CH_2Cl_2 , 35°C , 60 MHz): 7.16 (m, 8, $\overline{\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$), 8.08 (m, 8, $\overline{\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$), 8.70 (s, 9, =CHCMe₃).

19. Preparation of $[\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})]_x$ (29).

a. from $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ [X-7].

At -30°C , dmpe (0.30 g) in 2 mL of pentane was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ (0.86 g) in 10 mL of pentane. The yellow solution became colorless as a white microcrystalline solid precipitated. The product, 29, was collected by filtration, rinsed with pentane, and dried in vacuo. The yield was 1.01 g (99.5%).

b. from $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ [VI-57].

At RT, dmpe (0.08 g) in 1 mL of ether was added dropwise with stirring to $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ (0.26 g) in 4 mL of ether. The purple solution became colorless as 29 precipitated. The product was isolated as before (vide supra). The yield was 0.25 g (98.5%).

c. from $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})$ [VIII-4].

An ether solution of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})$ (0.25 g) was allowed to stand at RT. White microcrystalline 29 slowly began to precipitate from the red solution. After 3 days the product was isolated as before (vide supra). The yield was 0.24 g (96.0%).

IR (#145, cm^{-1} , nujol mull, NaCl plates): 2498 ($w, \nu_{\text{C}_\alpha\text{H}_\alpha}$).

20. Preparation of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})$ (30) [VIII-4].

At -30°C , dmpe (0.75 g) in 3 mL of CHCl_3 was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ (2.15 g) in 20 mL of CHCl_3 at -30°C . The yellow solution became red and was allowed to warm to RT. After 8 hrs. the solvent was removed in vacuo to yield a red solid. The crude product was dissolved in toluene, and the solution was filtered. The product was crystallized from the concentrated toluene solution at -30°C with pentane.

The yield was 2.24 g (88.3%) of red-purple crystals of 30.

^1H NMR (#383-A, τ , C_6D_6 , 35°C , 90 MHz): 6.20 (dd, 1, $^3J_{\text{HP}}=5.2$ Hz, $^3J_{\text{HP}}=1.0$ Hz, $=\text{CHCMe}_3$), 8.30-8.90 (m, 4, $\text{Me}_2\text{PCH}_2\text{CH}_2\text{P}'\text{Me}_2$), 8.61 (d, 6, $^2J_{\text{HP}}=9.4$ Hz, $-\text{P}'\text{Me}_2$), 8.81 (d, 6, $^2J_{\text{HP}}=8.0$ Hz, $-\text{P}'\text{Me}_2$), 8.84 (s, 9, $=\text{CHCMe}_3$).

^{13}C NMR (#193, ppm, CDCl_3 , 28°C , 15 MHz, ^1H gated decoupled): 243.0 (ddd, $J_{\text{CH}}=72$ Hz, $^2J_{\text{CP}}=23$ Hz, $^2J_{\text{CP}}=13$ Hz, $=\text{CHCMe}_3$), 46.0 (d, $^3J_{\text{CP}}=13$ Hz, CHCMe_3), 33.5 (q, $J_{\text{CH}}=126$ Hz, $=\text{CHCMe}_3$), 27.5 (m, $J_{\text{CP}}=26$ Hz, $^2J_{\text{CP}}=13$ Hz, $-\text{CH}_2\text{PMe}_2$), 24.0 (m, $J_{\text{CP}}=20$ Hz, $^2J_{\text{CP}}=8$ Hz, $-\text{CH}_2\text{P}'\text{Me}_2$), 15.0 (qd, $J_{\text{CH}}=132$ Hz, $J_{\text{CP}}=32$ Hz, $-\text{P}'\text{Me}_2$), 9.0 (qd, $J_{\text{CH}}=132$ Hz, $J_{\text{CP}}=19$ Hz, $-\text{P}'\text{Me}_2$).

$^{31}\text{P}(^1\text{H})$ NMR (#139, ppm, CHCl_3 , -50°C , 36.43 MHz): 20.5 (br s, $-\text{P}'\text{Me}_2$), 0.6 (br s, $-\text{P}'\text{Me}_2$).

21. Preparation of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{tmeda})$ (31) [VIII-32].

At -30°C , tmeda (0.58 g) in 5 mL of CH_2Cl_2 was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ (2.15 g) in 20 mL of CH_2Cl_2 . The yellow solution immediately became purple. The solution was allowed to warm to RT and after 2 hrs. the solvent was removed in vacuo to give a purple solid. The crude product was dissolved in ether and the solution was filtered. The product was crystallized from the ether solution at -30°C with pentane to give purple crystals of 31. The yield was 2.24 g (94.6%).

^1H NMR (#H-014, τ , CDCl_3 , 35°C , 270 MHz): 6.45 (s, 1, $=\text{CHCMe}_3$), 6.82 (s, 6, $-\text{NMe}_2$), 6.99 (m, 2, $-\text{CH}_2\text{NMe}_2$), 7.20 (m, 2, $-\text{CH}_2\text{N}'\text{Me}_2$), 7.29 (s, 6, $-\text{N}'\text{Me}_2$), 8.84 (s, 9, $=\text{CHCMe}_3$).

^{13}C NMR (#140, ppm, CDCl_3 , 28°C , 15 MHz, ^1H gated decoupled):

248.4 (d, $J_{\text{CH}}=79$ Hz, $=\text{CHCMe}_3$), 60.3 (t, $J_{\text{CH}}=138$ Hz, $-\text{CH}_2\text{NMe}_2$), 57.6 (t, $J_{\text{CH}}=135$ Hz, $-\text{CH}_2\text{N}'\text{Me}_2$), 56.6 (q, $J_{\text{CH}}=139$ Hz, $-\text{NMe}_2$), 49.6 (q, $J_{\text{CH}}=138$ Hz, $-\text{N}'\text{Me}_2$), 45.8 (s, $=\text{CHCMe}_3$), 33.6 (q, $J_{\text{CH}}=126$ Hz, $=\text{CHCMe}_3$).

IR (#156, cm^{-1} nujol mull, NaCl plates): 2532 (m, $\nu_{\text{C}_\alpha\text{H}_\alpha}$).

MW(X-67, cyclohexane, 13.55 mM): calcd 473.7; found 489.

ANAL (IX-12, for Ta $\text{C}_{11}\text{H}_{26}\text{Cl}_3\text{N}_2$): calcd C 27.90, H 5.53, N 5.91;

found C 27.92, H 5.71, N 5.72.

22. Preparation of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{bipy})$ (32) [VIII-28].

At -30°C , bipy (0.78 g) in 10 mL of CH_2Cl_2 was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ (2.15g) in 20 mL of CH_2Cl_2 . The yellow solution immediately became dark blue-purple and dark blue-purple crystals of 32 formed as the solution warmed to RT. The product was collected by filtration, rinsed with pentane, and dried in vacuo. A second crop was obtained by reducing the volume of the mother liquor in vacuo. The yield was 2.52 g (98.2%).

^1H NMR (#395, τ , CH_2Cl_2 , 35°C , 60 MHz): 0.10-2.50 (m, 8, bipy), 6.67 (s, 1, $=\text{CHCMe}_3$), 8.68 (s, 9, $=\text{CHCMe}_3$).

$^{13}\text{C}(^1\text{H})$ NMR (#135, ppm, CDCl_3 , 28°C , 15 MHz): 247.1 (s, $=\text{CHCMe}_3$), 158.6 (s, bipy), 157.0 (s, bipy), 151.2 (s, bipy), 149.9 (s, bipy), 141.1 (s, bipy), 140.2 (s, bipy), 128.2 (s, bipy), 127.0 (s, bipy), 122.9 (s, bipy), 122.9 (s, bipy), 46.4 (s, $=\text{CHCMe}_3$), 33.7 (s, $=\text{CHCMe}_3$).

ANAL (IX-15, for Ta $\text{C}_{15}\text{H}_{18}\text{Cl}_3\text{N}_2$): calcd C 35.08, H 3.53, N 5.46;

found C 35.11, H 3.63, N 5.60.

23. Preparation of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{diars})$ (33) [VII-60].

At -30°C , diars (0.86 g) in 1 mL of CH_2Cl_2 was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ (1.29 g) in 10 mL of CH_2Cl_2 . The color of the solution changed from yellow to red and the solution was allowed to warm to RT. After 8 hrs. the solvent was removed in vacuo to give a red solid. The product was dissolved in toluene, filtered, and crystallized at -30°C with pentane to give red crystals of 33. The yield was 1.82 g (94.3%).

^1H NMR (#339, τ , CDCl_3 , 35°C , 60 MHz): 2.47 (m, 4, C_6H_4), 6.52 (s, 1, $=\text{CHCMe}_3$), 8.54 (s, 6, $-\text{AsMe}_2$), 8.73 (s, 6, $-\text{As}'\text{Me}_2$), 8.77 (s, 9, $=\text{CHCMe}_3$).

^{13}C NMR (#118, ppm, CDCl_3 , 28°C , 15 MHz, ^1H gated decoupled): 247.4 (d, $J_{\text{CH}}=73$ Hz, $=\text{CHCMe}_3$), 142.6 (s, $\text{As}-\text{C}_{\text{ipso}}$), 141.4 (s, $\text{As}'-\text{C}_{\text{ipso}}$), 132.3 (d, $J_{\text{CH}}=161$ Hz, $\text{C}_6\text{H}_4(1)$), 131.6 (d, $J_{\text{CH}}=161$ Hz, $\text{C}_6\text{H}_4(3)$), 46.3 (s, $=\text{CHCMe}_3$), 33.5 (q, $J_{\text{CH}}=126$ Hz, $=\text{CHCMe}_3$), 14.9 (q, $J_{\text{CH}}=136$ Hz, $-\text{AsMe}_2$), 8.9 (q, $J_{\text{CH}}=136$ Hz, $-\text{As}'\text{Me}_2$).

IR(#148, cm^{-1} , nujol mull, NaCl plates): 2490 (m, $\nu_{\text{C}_\alpha\text{H}_\alpha}$).

24. Preparation of $\text{Me}_3\text{CCH}=\text{TaBr}_3(\text{dmpe})$ (34) [IX-13].

At -30°C , dmpe (0.61 g) in 2 mL of CH_2Cl_2 was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_2\text{TaBr}_3$ (2.25 g) in 10 mL of CH_2Cl_2 . The yellow solution became purple and the solution was allowed to warm to RT. After 8 hrs. the solvent was removed in vacuo to give a purple solid. The crude product was dissolved in toluene, and the solution was filtered. The

product was crystallized from the concentrated toluene solution at -30°C with pentane. The yield was 2.48 g (96.7%) of blue-purple crystals of 34.

^1H NMR (τ , CDCl_3 , 35°C , 270 MHz): 6.65 (dd, 1, $^3J_{\text{HP}}=9.6$ Hz, $^3J_{\text{HP}}=1.3$ Hz, $=\text{CHCMe}_3$), 7.97-8.17 (m, 4, $\text{Me}_2\text{PCH}_2\text{CH}_2\text{P}'\text{Me}_2$), 8.25 (d, 6, $^2J_{\text{HP}}=9.5$ Hz, $-\text{P}'\text{Me}_2$), 8.36 (d, 6, $^2J_{\text{HP}}=8.6$ Hz, $-\text{P}'\text{Me}_2$), 8.74 (s, 9, $=\text{CHCMe}_3$).

^{13}C NMR (τ , ppm, CDCl_3 , 15 MHz, ^1H gated decoupled): 248.3 (ddd, $J_{\text{CH}}=72$ Hz, $^2J_{\text{CP}}=16$ Hz, $^2J_{\text{CP}}=13$ Hz, $=\text{CHCMe}_3$), 46.5 (s, $=\text{CHCMe}_3$), 33.4 (q, $J_{\text{CH}}=125$ Hz, $=\text{CHCMe}_3$), 28.0 (m, $J_{\text{CP}}=27$ Hz, $^2J_{\text{CP}}=13$ Hz, $-\text{CH}_2\text{P}'\text{Me}_2$), 24.3 (m, $J_{\text{CP}}=21$ Hz, $^2J_{\text{CP}}=8$ Hz, $-\text{CH}_2\text{P}'\text{Me}_2$), 19.1 (qd, $J_{\text{CH}}=126$ Hz, $J_{\text{CP}}=31$ Hz, $-\text{P}'\text{Me}_2$), 10.6 (qd, $J_{\text{CH}}=130$ Hz, $J_{\text{CP}}=19$ Hz, $-\text{P}'\text{Me}_2$).

^{31}P (^1H) NMR (τ , ppm, toluene, -30°C , 36.43 MHz): 13.7 (d, $J_{\text{PP}}=18$ Hz, $-\text{P}'\text{Me}_2$), -3.1 (d, $J_{\text{PP}}=18$ Hz, $-\text{P}'\text{Me}_2$).

IR (τ , cm^{-1} , nujol mull, NaCl plates): 2427 (m, $\nu_{\text{C-H}}$).

MW (X-74, C_6H_6 , 6.12 mM): calcd 641.0; found 653.

ANAL (IX-13, for $\text{TaC}_{11}\text{H}_{26}\text{Br}_3\text{P}_2$): calcd C 20.62, H 4.09;

found C 21.02, H 4.24.

25. Preparation of $\text{Me}_3\text{CCH}=\text{TaBr}_3(\text{diphos})$ (35) [IX-14].

At -30°C , diphos (1.59 g) in 5 mL of CH_2Cl_2 was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_2\text{TaBr}_3$ (2.25 g) in 10 mL of CH_2Cl_2 . The yellow solution became dark red and the solution was allowed to warm to RT. After 8 hrs. the solvent was removed in vacuo to give a dark solid. The product was dissolved in ether and the solution was filtered. The product was

crystallized from the concentrated ether solution at -30°C with pentane to give green crystals of 35. The yield was 3.24 g (91.1%).

^1H NMR (#432, τ , CDCl_3 , 35°C , 60 MHz): 1.87-2.93 (m, 20, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}'\text{Ph}_2$), 6.35 (s, 1, $=\text{CHCMe}_3$), 6.74-6.95 (m, 4, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}'\text{Ph}_2$), 8.57 (s, 9, $=\text{CHCMe}_3$).

$^{13}\text{C}(^1\text{H})$ NMR (#145, ppm, CDCl_3 , 28°C , 15 MHz): 263.1 (dd, $^2J_{\text{CP}}=28$ Hz, $^2J_{\text{CP}}=10$ Hz, $=\text{CHCMe}_3$), 137.5-125.1 (m, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}'\text{Ph}_2$), 48.2 (d, $^3J_{\text{CP}}=12$ Hz, $=\text{CHCMe}_3$), 32.9 (s, $=\text{CHCMe}_3$), 23.0 (dd, $J_{\text{CP}}=24$ Hz, $^2J_{\text{CP}}=12$ Hz, $-\text{CH}_2\text{PPh}_2$), 20.7 (dd, $J_{\text{CP}}=18$ Hz, $^2J_{\text{CP}}=9$ Hz, $-\text{CH}_2\text{P}'\text{Ph}_2$).

26. Preparation of $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{dmpe})$ (36) [X-73].

At -30°C , dmpe (0.15 g) in 1 mL of CHCl_3 was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_2\text{NbCl}_3$ (0.34 g) in 5 mL of CHCl_3 . The red solution immediately became dark. The solution was allowed to warm to RT, and the solvent was removed in vacuo to give a green solid. The crude product was dissolved in toluene and the solution was filtered. The toluene was removed in vacuo to give green crystalline 36. The yield was 0.26 g (62.0%)

^1H NMR (#508, τ , CDCl_3 , 35°C , 60 MHz): 6.21 (br d, 1, $^3J_{\text{HP}}=11$ Hz, $=\text{CHCMe}_3$), 7.95 (m, 4, $\text{Me}_2\text{PCH}_2\text{CH}_2\text{P}'\text{Me}_2$), 8.60 (m, 12, $\text{Me}_2\text{PCH}_2\text{CH}_2\text{P}'\text{Me}_2$), 8.89 (s, 9, $=\text{CHCMe}_3$).

27. Preparation of $\text{Me}_3\text{SiCH}=\text{TaCl}_3(\text{PMe}_3)_2$ (37) [VIII-9].

PMe_3 (0.95 g) in 3 mL of CHCl_3 was added dropwise with stirring to $(\text{Me}_3\text{SiCH}_2)_2\text{TaCl}_3$ (2.31 g) in 15 mL of CHCl_3 at RT. The yellow solution slowly became red-green. After 8 hrs. the solvent was removed in vacuo to give a green solid. This was dissolved in ether and the solution was filtered. The product was crystallized from the concentrated ether solution at -30°C with pentane to give green crystals of 37. The yield was 2.44 g (92.8%).

^1H NMR (#385, τ , C_6D_6 , 35°C , 60 MHz): 8.70 (br, 18, PMe_3), 9.70 (s, 9, $=\text{CHSiMe}_3$).

^{13}C NMR (#124, ppm, CDCl_3 , 28°C , 15 MHz, ^1H gated decoupled): 277.8 (d, $J_{\text{CH}}=101$ Hz, $=\text{CHSiMe}_3$), 15.8 (q, $J_{\text{CH}}=131$ Hz, PMe_3), 3.2 (q, $J_{\text{CH}}=119$ Hz, $=\text{CHSiMe}_3$).

Chapter 3

The Reactions of
Monoalkylidene Complexes of Niobium and Tantalum

INTRODUCTION

The new class of monoalkylidene complexes, $\text{Me}_3\text{CCH}=\text{MX}_3\text{L}_n$, whose synthesis and characterization was described in Chapter 2, are extremely reactive molecules. An outline of some of the reaction chemistry of these complexes is presented in this chapter.

These new complexes contain nucleophilic alkylidene ligands. The reaction of these complexes with unsaturated molecules such as CO or MeCN yields ketene or imido complexes, respectively. This type of behavior is unknown in the chemistry of electrophilic Fischer carbene complexes³ which are stable in the presence of CO and MeCN and even contain these molecules as ligands in many cases. Because these new monoalkylidene complexes are nucleophilic, they react as "super-Wittig" reagents with organic carbonyl compounds. Because of their high reactivity these complexes even act as alkylidene transfer reagents with other transition metal complexes.⁸⁰

In addition to the reactive alkylidene ligand, these complexes possess three replaceable halide ligands as well as two labile and exchangeable neutral ligands. By means of various replacement reactions, then, it is possible to diversify this already large class of monoalkylidene complexes even further. This scheme has been useful in developing alternate or improved routes to previously known alkylidene complexes such as $\text{Nb}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ ²⁹ or $\text{CpNb}(\text{CHCMe}_3)\text{Cl}_2$.⁴² More importantly, a number of new alkylidene complexes which are inaccessible by other means have been prepared from the monoalkylidene complexes. These new complexes include $\text{Cp}^*\text{Nb}(\text{CHCMe}_3)\text{Cl}_2$ and $\text{Me}_3\text{CCH}=\text{Ta}(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$. Thus, it has

become apparent that complexes of the type $\text{Me}_3\text{CCH}=\text{MX}_3\text{L}_n$ are extremely useful from a synthetic standpoint as starting materials for many other types of alkylidene complexes.

These monoalkylidene complexes of tantalum and niobium also react with olefins. In the case of tantalum, the products are new Ta(III) olefin complexes while the niobium analogues yield reduced Nb(III) complexes which do not contain olefin ligands. This reaction provides a route to numerous Ta(III) olefin complexes which is important since complexes of this type are not common. Some of the derivatized monoalkylidene complexes such as $\text{Me}_3\text{CCH}=\text{Ta}(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$, on the other hand, react catalytically with olefins. These catalytic processes include selective olefin dimerization and olefin metathesis.

Even though the reaction chemistry discussed here is extensive, it represents only a small part of the potential reaction chemistry of these monoalkylidene complexes which may someday be developed.

RESULTS AND DISCUSSION

A. Reactions of Mononeopentylidene Complexes with Small Molecules

The mononeopentylidene complexes such as $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$, 13, react exothermically with a number of small molecules (e.g. HCl , $\text{Me}_2\text{C}=\text{O}$, MeCN , and CO). The products of these reactions indicate that the α -carbon of the neopentylidene ligand is nucleophilic. As in the case of the bisneopentylidene complexes, $\text{M}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PR}_3)_2$ (see Chap. 1), the mononeopentylidene complexes possess an electrophilic metal center as well as a nucleophilic neopentylidene ligand. This polarized metal-to-carbon double bond is responsible for the high reactivity of these complexes.

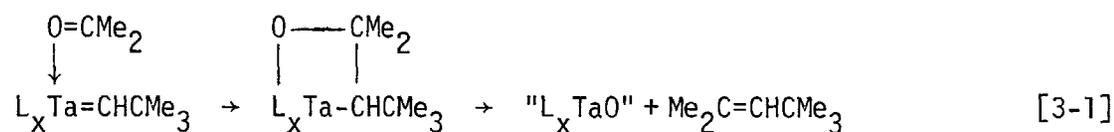
The reaction of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$, 13, with one equivalent of HCl in ether at -78°C gives an 89% yield of $(\text{Me}_3\text{CCH}_2)\text{TaCl}_4(\text{PMe}_3)_2$, 38.^a This selective reaction indicates that the neopentylidene ligand of 13 is significantly more reactive with HCl than the neopentyl group of the product, 38. One equivalent of neopentane, per Ta is evolved, however, from the reaction of 13 with two equivalents of HCl at -78°C as expected. The inorganic product of this second reaction is a bright yellow, sparingly soluble complex which is believed to be $\text{TaCl}_5(\text{PMe}_3)_2$, 39.

Acetone reacts vigorously with the mononeopentylidene complexes to yield one equivalent of free 2,4,4-trimethyl-2-pentene per Ta and an insoluble tantalum oxide in a Wittig type reaction. Other nucleophilic

^aThe reaction of $(\text{Me}_3\text{CCH}_2)\text{TaCl}_4$ in pentane with two equivalents of PMe_3 yields an identical complex.

^bThe reaction of TaCl_5 in ether with two equivalents of PMe_3 yields an identical complex.

neopentylidene complexes are known to react in a similar manner with aldehydes and ketones.^{56,58} In this reaction the tantalum in $\underline{13}$ can coordinate acetone either in an η^2 fashion^{41,86} or through the electro-negative oxygen atom by loss of PMe_3 . The carbonyl carbon is then in a position to be attacked by the nucleophilic alkylidene (Eq. 3-1). The proposed cyclic intermediate then cleaves to yield the reaction products.

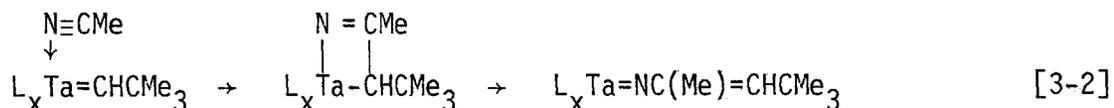


The reaction discussed above is also useful in providing a means of measuring the deuterium isotope effect (K_H/K_D) in the formation of partially deuterated $\underline{13}$ from $(\text{Me}_3\text{CCHD})_2\text{TaCl}_3$. The reaction of the partially labelled mononeopentylidene complex, $\underline{13}$, with acetone produces one equivalent of 2,4,4-trimethyl-2-pentene per Ta with a d_1/d_0 ratio of 4-5. This is the value of the deuterium isotope effect for the α -hydrogen abstraction process in the formation of $\underline{13}$.

The polymeric mononeopentylidene complex, $[\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})]_x$, $\underline{29}$, also reacts with acetone. This reaction which is not rapid (as opposed to the reaction of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$, $\underline{13}$, with acetone) must be carried out in a sealed tube at 100°C . Even under these forcing conditions, the yield of 2,4,4-trimethyl-2-pentene is only 0.50 equivalents per Ta. Side reactions which may involve protonation of the neopentylidene by the solvent, the excess acetone, or even the dmpe ligands produce 0.34 equivalents of neopentane per Ta.

The strength and versatility of the monoalkylidene complexes as carbene transfer reagents has been demonstrated by Wengrovius in the reaction of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PEt}_3)_2$ with $\text{W}(\text{O})(\text{OCMe}_3)_4$ to yield $\text{Ta}(\text{OCMe}_3)_4\text{Cl}$ and a tungsten alkylidene complex, $\text{Me}_3\text{CCH}=\text{W}(\text{O})\text{Cl}_2(\text{PEt}_3)_2$.⁸⁰

The reaction of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$, 13, with acetonitrile is rapid and exothermic at RT. This reaction yields a red-orange imido complex in which the MeCN has been inserted into the $\text{Ta}=\text{C}_\alpha$ bond. This complex, $\text{Me}_3\text{CCH}=\text{C}(\text{Me})\text{N}=\text{TaCl}_3(\text{PMe}_3)_2$, 40, can be isolated as a thermally stable, red-orange oil from solution. The niobium analogue of 40, which is $\text{Me}_3\text{CCH}=\text{C}(\text{Me})\text{N}=\text{NbCl}_3(\text{PMe}_3)_2$, 41, can be prepared in an analogous manner. Similar imido complexes have been prepared by this type of reaction from other nucleophilic neopentylidene complexes and a variety of nitriles.^{18,42} It is likely that the reaction of 13 with MeCN proceeds in the same manner as the reaction of 13 with acetone. The metal can coordinate the acetonitrile through the electronegative nitrogen atom while the nucleophilic α -carbon of the neopentylidene ligand attacks the nitrile carbon (Eq. 3-2). In this case, however, rearrangement of the proposed cyclic intermediate is not accompanied by cleavage of an organic fragment from the metal.



The product, the imido complex, 40, from the reaction discussed above is a mixture of two isomers since the carbon-carbon double bond of the imido ligand can possess either the E or the Z configuration. The olefinic protons for the two isomers appear in the ^1H NMR spectrum of 40 at 5.63 τ (E isomer, 40a, 33%) and 4.90 τ (Z isomer, 40b, 67%). This

isomer assignment is based on the relative chemical shifts of the two kinds of methyl groups in the imido ligand and on the E/Z ratio compared to those values for the E and Z isomers of $\text{Me}_3\text{CCH}=\text{C}(\text{Me})\text{N}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$.¹⁸ The complete ^1H NMR spectral data for the mixture of $\underline{\underline{40a}}$ and $\underline{\underline{40b}}$ are listed in Table 3.I. The E and Z isomers, $\underline{\underline{40a}}$ and $\underline{\underline{40b}}$, do not interconvert on the NMR time scale at RT. The PMe_3 resonances for $\underline{\underline{40a}}$ and

Table 3.I. ^1H NMR Spectral Data* for $\text{Me}_3\text{CCH}=\text{C}(\text{Me})\text{N}=\text{TaCl}_3(\text{PMe}_3)_2$

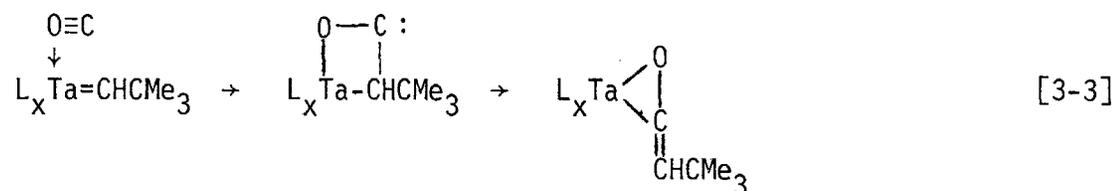
	E isomer ($\underline{\underline{40a}}$)	Z isomer ($\underline{\underline{40b}}$)
$\underline{\text{Me}}_3\text{CCH}=\text{C}(\text{Me})\text{N}=\underline{\underline{\hspace{1cm}}}$	8.66	8.98
$\text{Me}_3\text{CCH}=\text{C}(\underline{\text{Me}})\text{N}=\underline{\underline{\hspace{1cm}}}$	5.63	4.90
$\text{Me}_3\text{CCH}=\text{C}(\text{Me})\text{N}=\underline{\underline{\hspace{1cm}}}$	8.19	8.22
$\underline{\text{PMe}}_3$	8.63 (br)	8.73 (br)

* Shifts are listed in τ .

$\underline{\underline{40b}}$ are broad as in the case of the starting material, $\underline{\underline{13}}$. It is conceivable, therefore, that $\underline{\underline{40a}}$ and $\underline{\underline{40b}}$ each possess a trans, mer and a cis, mer isomer which interconvert rapidly by PMe_3 exchange as in $\underline{\underline{13}}$. This possibility was not investigated further.

The mononeopentylidene complex, $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$, $\underline{\underline{13}}$, also reacts smoothly and rapidly at RT with carbon monoxide to yield a deep purple ketene complex, $\text{Ta}(\eta^2\text{-O}=\text{C}=\text{CHCMe}_3)\text{Cl}_3(\text{PMe}_3)_2$, $\underline{\underline{42}}$. The green niobium analogue of $\underline{\underline{42}}$, which is $\text{Nb}(\eta^2\text{-O}=\text{C}=\text{CHCMe}_3)\text{Cl}_3(\text{PMe}_3)_2$, $\underline{\underline{43}}$, can be prepared in a similar manner. Other nucleophilic neopentylidene complexes of

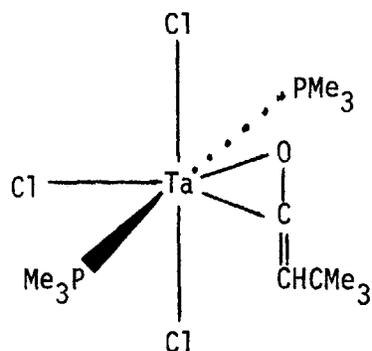
tantalum are also known to react with CO to form ketene complexes.⁵⁶ The reaction of 13 with CO is believed to proceed in a manner similar to reactions of 13 with acetone and acetonitrile. The tantalum coordinates CO through the oxygen atom while the neopentylidene ligand attacks the carbon atom to give a cyclic intermediate which rearranges to give the product (Eq. 3-3).



The tert-butylketene appears to be tightly bound to the tantalum through the carbonyl group. The IR spectrum of 42 does not contain any ketene carbonyl stretching absorptions^a but does possess a weak carbon-carbon double bond absorption at 1605 cm⁻¹. The ¹H and ¹³C NMR spectra of 42 indicate that there is only one isomer of the ketene complex. The PMe₃ ligands are equivalent, are nonlabile at RT, and are virtually coupled. In the ketene ligand the carbon atom originally derived from CO has a shift of 200.7 ppm in the ¹³C NMR spectrum and is a virtual triplet due to phosphorus coupling. The carbon atom of the ketene ligand which was initially C_α of the neopentylidene ligand of 13 has a shift of 100.5 ppm in the ¹³C NMR spectrum and is a doublet with a normal sp² J_{CH} value of 158 Hz. The proposed structure of 42 based on the above data is shown in Figure 3.1.

^aThe normal ketene carbonyl absorption occurs at 2150 cm⁻¹.⁴⁶

Figure 3.1 The Proposed Structure of $\text{Ta}(\eta^2\text{-O=C=CHCMe}_3)\text{Cl}_3(\text{PMe}_3)_2$



The tantalum in 42 firmly binds the tert-butylketene ligand. The ketene cannot be released from the metal by either ligand substitution or thermal decomposition in vacuum. This may be due to a strong tantalum-oxygen interaction. Finally, the complex $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})$, 30, reacts with CO but more slowly than 13 to give an orange product. This has been tentatively identified as $\text{Ta}(\eta^2\text{-O=C=CHCMe}_3)\text{Cl}_3(\text{dmpe})$, 44. Other neopentylidene complexes with chelating ligands such as tmeda are inert under a CO atmosphere.

The reaction of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$, 13, with H_2 is extremely slow. Purple toluene solutions of 13 become green after 3 days at RT under 50 PSIG of H_2 . One equivalent of neopentane per Ta is produced in this reaction. The product appears to contain at least one unstable tantalum

hydride complex. A broad hydride resonance appears at 12.6 τ in the ^1H NMR spectrum of the product which may contain $\text{H}_2\text{TaCl}_3(\text{PMe}_3)_2$. This resonance disappears with time from samples kept in solution or in the solid state at -30°C . The reaction of $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_3)_2$, 20, with H_2 yields one-half equivalent of purple, insoluble $[\text{Nb}(\text{PMe}_3)_2\text{Cl}_3]_2^a$ and CMe_4 . The mononeopentylidene complexes, $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{LL})$, which possess chelating ligands such as dmpe or tmeda are inert under a H_2 atmosphere.

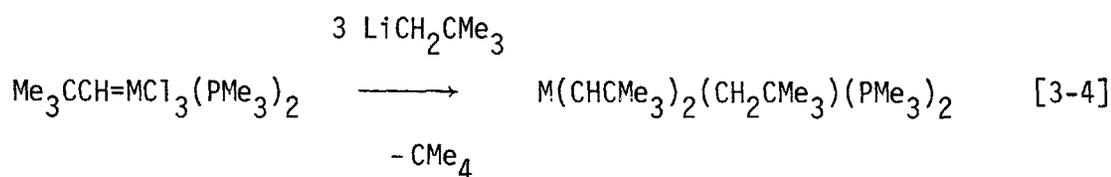
B. Reaction of Mononeopentylidene Complexes involving Halide Replacement

A number of reagents will react with the mononeopentylidene complexes of niobium and tantalum, $\text{Me}_3\text{CCH}=\text{MX}_3\text{L}_2$, to replace the halide ligands with other groups. It is possible, therefore, to synthesize almost any known Nb(V) or Ta(V) neopentylidene complex by means of halide replacement in the appropriate $\text{Me}_3\text{CCH}=\text{MX}_3\text{L}_2$ complex. In addition, a number of complexes which are inaccessible by other routes can also be prepared by this method. This makes the mononeopentylidene complexes extremely useful from a synthetic standpoint. Since these mononeopentylidene complexes possess three replaceable halides and two exchangeable neutral ligands per metal, the number of different neopentylidene complexes that could be prepared from a $\text{Me}_3\text{CCH}=\text{MX}_3\text{L}_2$ complex appears limited only by elucidation of the proper reaction conditions and by the stability of the final product.

One of the primary reasons for investigating the reaction of $(\text{Me}_3\text{CCH}_2)_2\text{MX}_3$ with tertiary phosphines (which led to the discovery of the mononeopentylidene complexes described in Chap. 2) was to determine if

^aThis same dimeric complex is also produced in the reaction of 20 with ethylene (vide infra).

alternate syntheses could be developed for the preparation of the bis-alkylidene complexes, $M(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PR}_3)_2$ ($\underline{3}$, $\underline{4}$, $\underline{6}$, and $\underline{7}$),²⁹ described in Chap. 1. The reaction of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$, $\underline{13}$, or $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_3)_2$, $\underline{20}$, with three equivalents of $\text{LiCH}_2\text{CMe}_3$ does produce $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$, $\underline{3}$, or $\text{Nb}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$, $\underline{6}$, respectively in good yields (Eq. 3-4). The bisalkylidene complexes

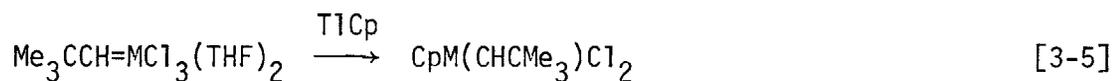


prepared in this manner are identical to authentic samples prepared from $\text{Me}_3\text{CCH}=\text{M}(\text{CH}_2\text{CMe}_3)_3$. The original synthesis of the tantalum bisneopentylidene complex, $\underline{3}$, is the most convenient of the two preparations available. The niobium bisneopentylidene complex, $\underline{6}$, however, can be prepared with less difficulty and with increased purity and yield (92%) of product in the alternate synthesis from $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_3)_2$, $\underline{20}$.

Whether this new synthesis of the bisalkylidene complexes from $\text{Me}_3\text{CCH}=\text{MCl}_3(\text{PR}_3)_2$ proceeds through an intermediate which contains phosphine ligands or through $\text{Me}_3\text{CCH}=\text{M}(\text{CH}_2\text{CMe}_3)_3$ was not determined. If the phosphines do remain bound to the metal throughout the reaction, then it might be possible to utilize this route for the preparation of bisneopentylidene complexes which possess chelating ligands or ligands other than tertiary phosphines. Complexes of this type are inaccessible via the original synthesis through $\text{Me}_3\text{CCH}=\text{M}(\text{CH}_2\text{CMe}_3)_3$; however, this type of reaction was not investigated. Additionally, Fellmann has cleanly prepared the known $\text{M}(\text{CHCMe}_3)_2\text{Cl}(\text{PR}_3)_2$ complexes from the reaction of

one equivalent of $\text{Mg}(\text{CH}_2\text{CMe}_3)_2$ (diox) with one equivalent of either 13 or 20.⁴⁷

A number of neopentylidene complexes which contain cyclopentadienyl ligands have been prepared by the reaction of $(\text{Me}_3\text{CCH}_2)_2\text{MX}_3$ with cyclopentadienide reagents. The reaction of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{THF})_2$, 25, and $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{THF})_2$, 24, with TiCp in ether yields the known complexes $\text{CpTa}(\text{CHCMe}_3)\text{Cl}_2$, 45, and $\text{CpNb}(\text{CHCMe}_3)\text{Cl}_2$, 46,^{41,42} respectively, (Eq.3-5).



The preparation of these complexes from $(\text{Me}_3\text{CCH}_2)_2\text{MCl}_3$ and TiCp is more direct, but for the niobium complex, 46, the yield is only 7-15%. The synthesis of 46 via $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{THF})_2$ gives the product in 78% yield which is a 5-10 fold increase over the yield in the original preparation of 46.

The reactions of 25 and 24 with LiCp'' or TiCp'' are analogous to Eq. 3-5 and yield $\text{Cp}''\text{Ta}(\text{CHCMe}_3)\text{Cl}_2$, 47, and $\text{Cp}''\text{Nb}(\text{CHCMe}_3)\text{Cl}_2$, 48, respectively. The tantalum complex, 47, has been prepared previously from $\text{Cp}''\text{Ta}(\text{CH}_2\text{CMe}_3)(\text{CH}_2\text{Ph})\text{Cl}_2$ with difficulty in low yield.^{41,42} $\text{Cp}''\text{Nb}(\text{CHCMe}_3)\text{Cl}_2$, 48, has been synthesized only via $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{THF})_2$, however. LiCp'' can be used in the preparation of 47 or 48. The yield of $\text{Cp}''\text{Nb}(\text{CHCMe}_3)\text{Cl}_2$, 48, is low by this method because of side reactions. Therefore the reaction of $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{THF})_2$ with TiCp'' was investigated. This reaction is very clean. The yield of purple crystalline 48, which can be sublimed, is 88%.

This new complex, 48, is entirely similar to the three previous cyclopentadienyl neopentylidene complexes of Ta and Nb (45, 46, and 47). The IR spectrum of 48 possesses a $C_{\alpha}-H_{\alpha}$ stretch at 2455 cm^{-1} . The H_{α} resonance in the ^1H NMR spectrum of 48 occurs at 4.26τ . The C_{α} resonance for 48 is a doublet at 250.2 ppm with a $J_{C_{\alpha}H_{\alpha}}$ value of 91 Hz in the ^{13}C NMR spectrum. The values of these parameters correspond quite well with those recorded for 45, 46, and 47.^{41,42} The complete ^1H and ^{13}C NMR spectral data for 48 are listed in Table 3.II.

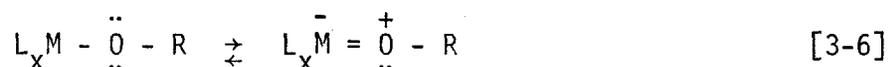
Table 3.II. ^1H and ^{13}C NMR Spectral Data for $\text{Cp}^*\text{Nb}(\text{CHCMe}_3)\text{Cl}_2$

	^1H NMR*	^{13}C NMR**
C_5Me_5	8.05	13.0(127)
\underline{C}_5Me_5		121.1
$=\underline{\text{CH}}\text{CMe}_3$	4.26	250.2 (91)
$=\text{CH}\underline{\text{C}}\text{Me}_3$		48.8
$=\text{CHC}\underline{\text{M}}\text{e}_3$	8.88	31.6 (126)

*Shifts are listed in τ .
 **Shifts are listed in ppm while coupling constants are listed in Hz.

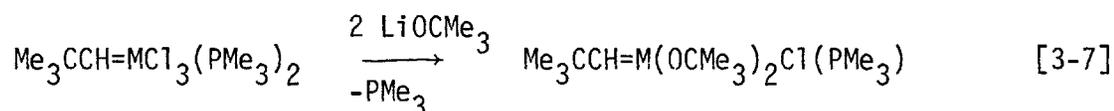
Attempts to prepare neopentylidene complexes from neopentyl complexes containing alkoxide groups is difficult at best. The introduction of even one alkoxide group into a neopentyl complex significantly reduces the tendency toward α -hydrogen abstraction.⁴⁷ The presence of two alkoxide groups in a neopentyl complex seems to suppress α -hydrogen abstraction completely.⁴⁷ These observations indicate that alkoxide

groups can increase the electron density around the metal center and/or can be arranged in the coordination sphere to reduce steric crowding.^a The electron density at a metal center can be increased by an alkoxide ligand through interaction of the electrophilic metal with the nonbonding electron pairs of the oxygen atom (Eq. 3-6). The theory that alkoxides are less sterically demanding than alkyl groups is supported by the



stability of Ta(OCMe₃)₅⁸⁷ while its alkyl analogue "Ta(CH₂CMe₃)₅"¹⁸ is unknown. The preparation of neopentylidene complexes with alkoxide groups could be achieved, however, by attaching alkoxide groups to complexes which already possess a neopentylidene ligand.

The reaction of Me₃CCH=TaCl₃(PMe₃)₂, 13, or Me₃CCH=NbCl₃(PMe₃)₂, 20, with two equivalents of LiOCMe₃ yields Me₃CCH=Ta(OCMe₃)₂Cl(PMe₃), 49, and Me₃CCH=Nb(OCMe₃)₂Cl(PMe₃), 50, respectively in good yield. (Eq. 3-7).



The preparation of other complexes in which either one or three halides have been replaced by alkoxides are not as straightforward. The reaction of 31 with one equivalent of LiOCMe₃ produces a mixture containing some Me₃CCH=Ta(OCMe₃)Cl₂(PMe₃)₂^b along with equal amounts of 13 and 49. A milder tert-butoxide reagent might improve this reaction, however.

^aAny increase in electron density or decrease in steric crowding will reduce the tendency toward α-hydrogen abstraction. 47

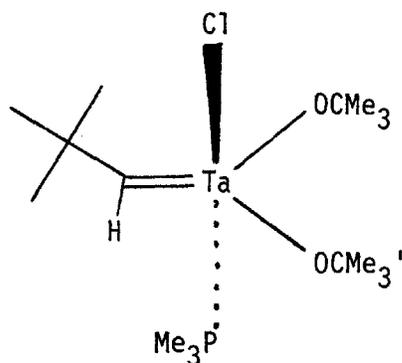
^bThis complex has been prepared by an alternate route by Fellmann.

The reaction of $\underline{\underline{13}}$ with three equivalents of LiOCMe_3 (or KOCMe_3) produces $\underline{\underline{49}}$ as the primary product and only traces (if any) of $\text{Me}_3\text{CCH}=\text{Ta}(\text{OCMe}_3)_3$.^a

The complexes, $\text{Me}_3\text{CCH}=\text{Ta}(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$, $\underline{\underline{49}}$, and $\text{Me}_3\text{CCH}=\text{Nb}(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$, $\underline{\underline{50}}$, are yellow crystalline, pentane soluble compounds which are thermally stable and monomeric. The effect of the tert-butoxide ligands on the electron density around the metal in these formally $12 e^-$ complexes is evident in the values of $J_{\text{C}_\alpha\text{H}_\alpha}$ and $\nu_{\text{C}_\alpha\text{H}_\alpha}$ for $\underline{\underline{49}}$. As the tantalum increases its interaction with the nonbonded oxygen electrons, it decreases its interaction with the electrons in the $\text{C}_\alpha\text{-H}_\alpha$ bond. The values of $J_{\text{C}_\alpha\text{H}_\alpha}$ and $\nu_{\text{C}_\alpha\text{H}_\alpha}$ (which were 75 Hz and 2510 cm^{-1} , respectively for $\underline{\underline{13}}$, the starting material) are increased to 114 Hz and 2720 cm^{-1} , respectively, for $\underline{\underline{49}}$. The ^1H and ^{13}C NMR spectral data show that there is only one isomer of $\underline{\underline{49}}$ in solution at RT. The complex possesses nonequivalent tert-butoxide groups and a nonlabile PMe_3 ligand at RT. The proposed structure of $\underline{\underline{49}}$ which is consistent with this data is shown in Figure 3.2.

It has been shown that the incorporation of alkoxide ligands into the mononeopentylidene complexes can be readily accomplished. It is therefore reasonable to believe that similar groups such as mercaptides ($-\text{SR}$), dialkylamides ($-\text{NR}_2$), or dialkylphosphides ($-\text{PR}_2$) might also be introduced into these mononeopentylidene complexes under the appropriate conditions. Reactions of this type were not investigated, however.

^aThis complex has been prepared by an alternate route by Rocklage.⁷⁹

Figure 3.2. The Proposed Structure of $\text{Me}_3\text{CCH}=\text{Ta}(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ 

The mononeopentylidene complexes, $\text{Me}_3\text{CCH}=\text{MX}_3\text{L}_2$, in which the halide is bromide have significantly less electron density around the metal than those in which the halide is chloride (see Chap. 2). In order to investigate this trend further, the preparation of " $\text{Me}_3\text{CCH}=\text{TaI}_3(\text{PMe}_3)_2$ " was attempted. Since $(\text{Me}_3\text{CCH}_2)_2\text{TaI}_3$ cannot be readily prepared from TaI_5 , the possibility of a Cl^-/I^- exchange reaction in $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$, 13, was examined. The reaction of 13 with a large excess of NaI in THF gave only a paramagnetic, red-brown tar. Similar reactions with $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Cl}_3]_2$, 12, and $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{THF})_2$, 25, also failed to yield tractable products. It appears that the starting alkylidene complexes or the desired products are not stable under these conditions.

Through the halide replacement reaction scheme, it is possible to prepare a large number of new or previously characterized alkylidene

complexes from the already diverse set of mononeopentylidene complexes, $\text{Me}_3\text{CCH}=\text{MX}_3\text{L}_2$ (vide supra). The reactions investigated in this scheme represent only a few of the possible transformations which might be achieved by this method.

C. Reactions of Mononeopentylidene Complexes with Olefins

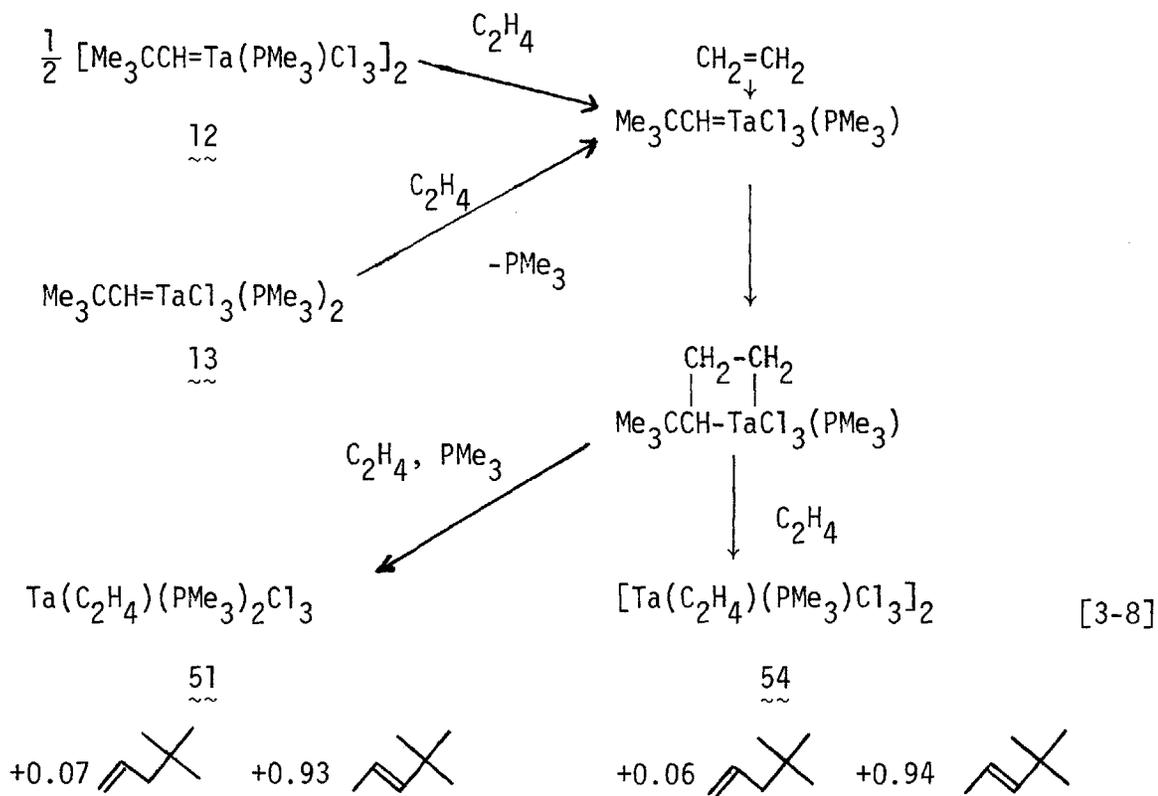
The mononeopentylidene complexes, $\text{Me}_3\text{CCH}=\text{MX}_3\text{L}_2$, react rapidly with simple olefins. Some of these reactions involve cleavage of the neopentylidene ligand from the metal by the olefin through β -hydrogen elimination from an intermediate metallocyclobutane complex. This process yields a Ta(III) or Nb(III) product. This type of reaction is well known for other nucleophilic alkylidene complexes.^{55,56} In other cases the olefins are disproportionated in a metathesis reaction which is catalyzed by the mononeopentylidene complex. This type of reaction, however, is the first example of its kind for nucleophilic neopentylidene complexes. In fact while some isolable carbene complexes are known to cause stoichiometric metathesis of simple olefins⁸⁸ or catalytic metathesis of activated olefins,⁸⁹ few (if any) catalytically metathesize simple olefins.⁹⁰

The reaction of either the monomeric or the dimeric mononeopentylidene complexes, $\text{Me}_3\text{CCH}=\text{TaX}_3(\text{PR}_3)_2$ or $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PR}_3)\text{X}_3]_2$, respectively, with olefins is fast. After a few minutes at RT the reaction is complete. The reaction of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$, 13, with ethylene yields $\text{Ta}(\text{C}_2\text{H}_4)(\text{PMe}_3)_2\text{Cl}_3$, 51, along with 0.066 equivalents of 4,4-dimethyl-1-pentene and 0.922 equivalents of trans-4,4-dimethyl-2-pentene per Ta.^a

^a These products were identified by comparison with authentic samples. The relative yields are unaffected by the presence of added 4,4-dimethyl-1-pentene and are independent of ethylene pressure.

Similarly, the reaction of $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Cl}_3]_2$, 12, produces $[\text{Ta}(\text{C}_2\text{H}_4)(\text{PMe}_3)\text{Cl}_3]_2$, 54, as well as 0.059 equivalents of 4,4-dimethyl-1-pentene and 0.933 equivalents of trans-4,4-dimethyl-2-pentene per Ta.^a These results as well as the results of the reactions of other $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PR}_3)_2$ or $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PR}_3)\text{Cl}_3]_2$ complexes with ethylene are listed in Table 3.III.

This reaction is believed to proceed through coordination of ethylene in the monomer, 13, by the loss of PMe_3 and in the dimer, 12, by cleavage of the halide bridge. In either case this gives an intermediate ethylene neopentylidene complex which then forms a metallocyclobutane complex (Eq. 3-8). The metallocyclobutane complex decomposes by



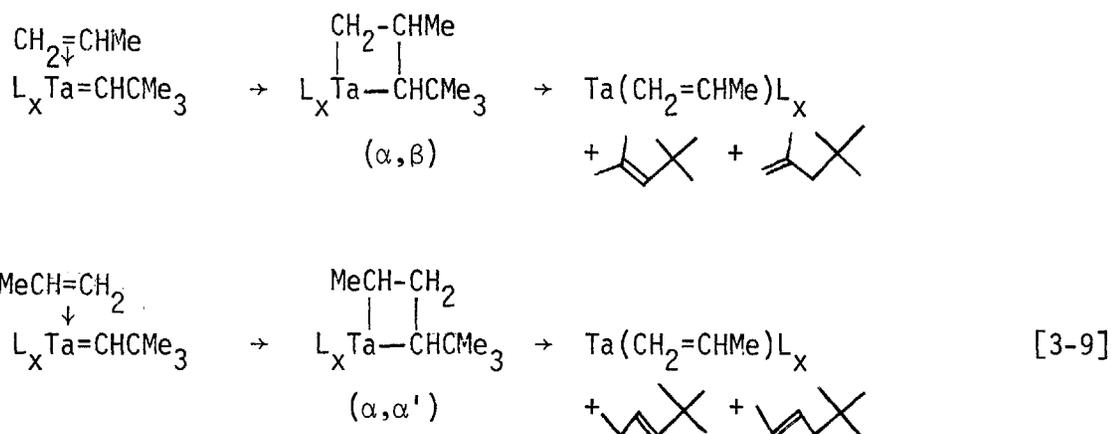
^aThese products were identified by comparison with authentic samples.

β - hydrogen elimination to yield the ethylene complexes, 51 and 54, and the two olefinic cleavage products. The similarity in the ratio of the two olefinic cleavage products seem to indicate that both 12 and 13 react through the same intermediates.

The mononeopentylidene complexes of niobium, $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_3)_2$, 20, and $[\text{Me}_3\text{CCH}=\text{Nb}(\text{PMe}_3)\text{Cl}_3]_2$, 22, also react with ethylene rapidly. In this case as with the tantalum analogues, there are two olefinic cleavage products: 4,4-dimethyl-1-pentene and trans-4,4-dimethyl-2-pentene (see Table 3.III.)^a The inorganic products, however, are not olefin complexes. The product derived from 20 is the purple, paramagnetic $[\text{Nb}(\text{PMe}_3)_2\text{Cl}_3]_2$ while 22 is believed to yield $[\text{Nb}(\text{PMe}_3)\text{Cl}_3]_x$. Apparently, Nb(III) complexes of this type do not coordinate olefins. Other cases are also known where Nb(III) olefin complexes fail to form.^{53,54,55}

The reaction of 12 and 13 with propylene yield dimeric and monomeric Ta(III) propylene complexes as expected. In this case, however, there are four olefinic cleavage products formed in the reaction instead of two as in the reactions with ethylene. This occurs because propylene can interact with the neopentylidene ligand of 12 or 13 in two orientations which would lead to the formation of two different metallocyclobutanes (Eq. 3-9). One metallocycle is substituted in the α and β positions while the other metallocycle is α,α' substituted. The α,β substituted metallocycle decomposes to give one pair of olefins while the α,α' substituted metallocycle yields the other pair of olefins on decomposition. The reaction of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$, 13, with propylene produces

^aThese products were identified by comparison with authentic samples.



0.412 equivalents of 2,4,4-trimethyl-2-pentene and 0.082 equivalents of 2,4,4-trimethyl-1-pentene per Ta from the α, β substituted metallocyclobutane as well as 0.420 equivalents of trans-2,2-dimethyl-3-hexene and 0.072 equivalents of trans-4,4-dimethyl-2-hexene per Ta from the α, α' substituted metallocyclobutane.^a

These results indicate that either metallocycle has a 50% chance of being produced. Either both metallocycles are energetically equivalent which seems unlikely based on the results of other systems^b or the propylene reacts with the neopentylidene ligand faster than it can reorientate. The organometallic product of this reaction is blue, crystalline $\text{Ta}(\text{CH}_2=\text{CHMe})(\text{PMe}_3)_2\text{Cl}_3$, 60. Table 3.IV. lists these results as well as the results of the reactions of other $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PR}_3)_2$ and $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PR}_3)\text{Cl}_3]_2$ complexes with propylene.

The reaction of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$, 13, with styrene is similar to that of 13 with propylene in that four olefinic cleavage products are

^aThese four products were identified by comparison with authentic samples.
^bOther neopentylidene complexes yield products from reaction with propylene which can be formed only from the α, β substituted metallocyclobutane.^{53,54}

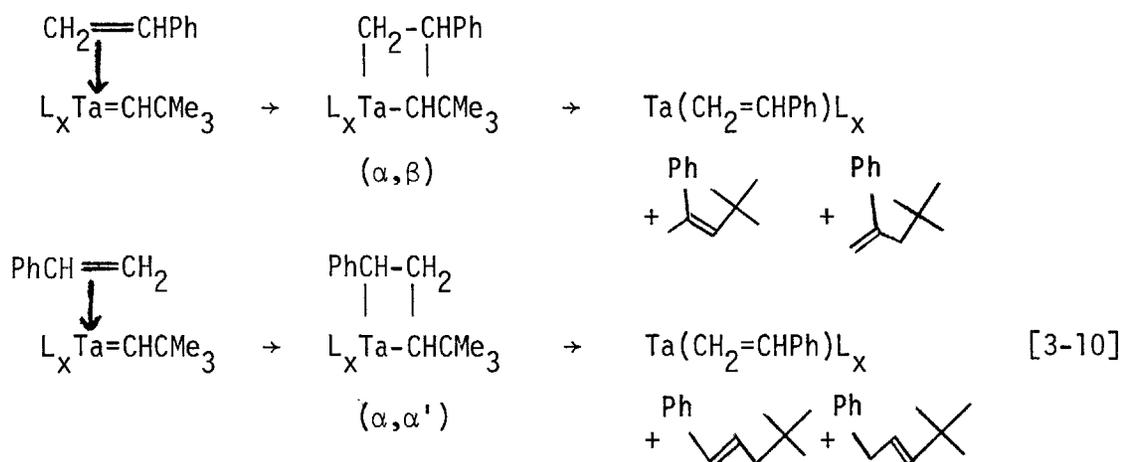
Table 3.III. Reactions of Mononeopentylidene Complexes with Ethylene

$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PR}_3)_2 \rightarrow \text{Ta}(\text{C}_2\text{H}_4)(\text{PR}_3)_2\text{Cl}_3$				PR_3
<u>13</u>	<u>51</u>	0.066	0.922	PMe_3
<u>17</u>	<u>52</u>	0.071	0.874	PMe_2Ph
<u>18</u>	<u>53</u>	0.113	0.860	PPh_2Me
$[\text{Me}_3\text{CCH}=\text{Ta}(\text{PR}_3)\text{Cl}_3]_2 \rightarrow [\text{Ta}(\text{C}_2\text{H}_4)(\text{PR}_3)\text{Cl}_3]_2$				PR_3
<u>12</u>	<u>54</u>	0.059	0.933	PMe_3
<u>14</u>	<u>55</u>	0.053	0.914	PMe_2Ph
<u>15</u>	<u>56</u>	0.112	0.891	PPh_2Me
$\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PR}_3)_2 \rightarrow [\text{Nb}(\text{PR}_3)_2\text{Cl}_3]_2$				PR_3
<u>20</u>	<u>57</u>	0.028	0.907	PMe_3
<u>21</u>	<u>58</u>	0.051	0.925	PMe_2Ph
$[\text{Me}_3\text{CCH}=\text{Nb}(\text{PR}_3)\text{Cl}_3]_2 \rightarrow [\text{Nb}(\text{PR}_3)\text{Cl}_3]_x$				PR_3
<u>22</u>	<u>59</u>	0.027	0.945	PMe_3

Table 3.IV. Reactions of Mononeopentylidene Complexes with Propylene

$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PR}_3)_2 \rightarrow \text{Ta}(\text{CH}_2=\text{CHMe})(\text{PR}_3)_2\text{Cl}_3$				PR_3
<u>13</u>	<u>60</u>	0.412	0.574	PMe_3
<u>17</u>	<u>61</u>	0.443	0.543	PMe_2Ph
<u>18</u>	<u>62</u>	0.472	0.458	PPh_2Me
$[\text{Me}_3\text{CCH}=\text{Ta}(\text{PR}_3)\text{Cl}_3]_2 \rightarrow [\text{Ta}(\text{CH}_2=\text{CHMe})(\text{PR}_3)\text{Cl}_3]_2$				PR_3
<u>12</u>	<u>63</u>	0.449	0.539	PMe_3
<u>14</u>	<u>64</u>	0.409	0.527	PMe_2Ph
<u>15</u>	<u>65</u>	0.565	0.413	PPh_2Me

formed. These four products (in relative amounts) are 0.286 equivalents of trans-1-phenyl-4,4-dimethyl-2-pentene, and 0.299 equivalents of trans-1-phenyl,-4,4-dimethyl-1-pentene from an α,α' metallocycle as well as 0.352 equivalents of cis-2-phenyl-4,4-dimethyl-2-pentene and 0.064 equivalents of 2-phenyl-4,4-dimethyl-1-pentene from an α,β metallocycle (Eq. 3-10).^a

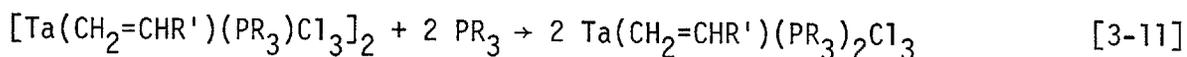


The distribution of olefinic cleavage products indicates that in this case the α,α' metallocycle is more favorable than the α,β metallocycle by a 3/2 ratio. Since this reaction is somewhat slower than the previous reactions, the styrene may be able to orient itself in the favored manner to some extent before the metallocyclobutane forms. The organometallic product of this reaction is blue-green, crystalline, $\text{Ta}(\text{CH}_2=\text{CHPh})(\text{PMe}_3)_2\text{Cl}_3$, 66.

The Ta(III) olefin complexes are blue to blue-green crystalline compounds. Those complexes with one PR_3 ligand per Ta are dimeric and are

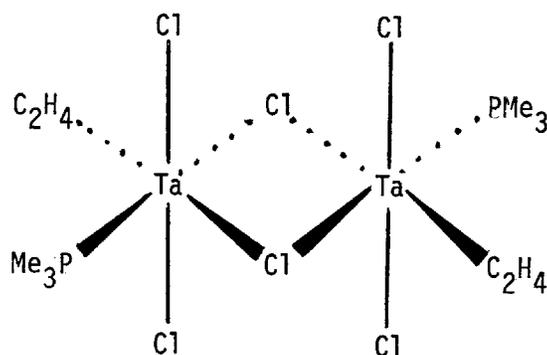
^aThe first and third products were identified by comparison with authentic samples; the identity of the second and fourth products are based on the results of the propylene reaction with 13 and the results of other systems. 56

insoluble. Those complexes with two PR_3 ligands per Ta are monomeric and are soluble in ether, benzene, and chloroform. The addition of two equivalents of PR_3 to a dimeric Ta(III) olefin complex converts it to the analogous monomeric Ta(III) olefin complex (Eq. 3-11).

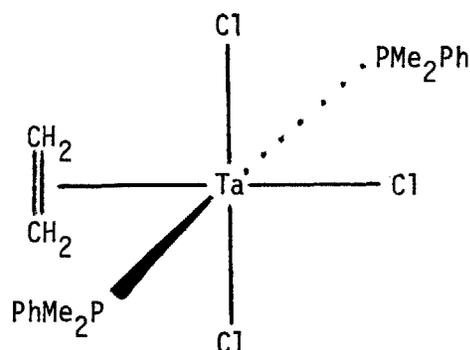


The structure of the dimeric olefin complexes is believed to be similar to that of the dimeric neopentylidene complexes from which they are derived but in which the olefin replaces the neopentylidene ligand (see Figure 3.3.)

Figure 3.3. The Proposed Structure of $[\text{Ta}(\text{C}_2\text{H}_4)(\text{PMe}_3)\text{Cl}_3]_2$.



The structure of the monomeric olefin complexes is similar to the trans,mer isomer of the monoalkylidene complexes from which they are prepared. Again, the olefin occupies the position of the alkylidene

Figure 3.4. The Structure of $\text{Ta}(\text{C}_2\text{H}_4)(\text{PMe}_2\text{Ph})_2\text{Cl}_3$ 

The ^1H NMR spectrum of $\text{Ta}(\text{C}_2\text{H}_4)(\text{PMe}_3)_2\text{Cl}_3$, 51, has a virtual triplet for the PMe_3 ligands at 8.53 τ and a virtual triplet for the C_2H_4 ligand at 7.12 τ . This indicates that the PMe_3 ligands are equivalent. The ^1H NMR spectrum of $\text{Ta}(\text{C}_2\text{H}_4)(\text{PMe}_2\text{Ph})_2\text{Cl}_3$, 52, is similar. This confirms that the phosphine ligands are trans since this is the only geometry in which all four methyl groups are equivalent.^a The ^1H NMR data for these two complexes appear in Table 3.V.

Table 3.V. The ^1H NMR Data* for $\text{Ta}(\text{C}_2\text{H}_4)(\text{PR}_3)_2\text{Cl}_3$

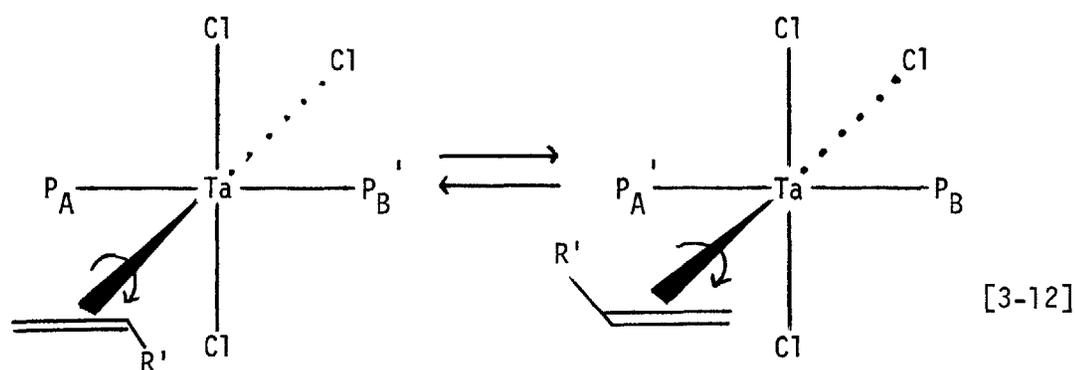
	$\text{C}_2\text{H}_4(\text{J}_{\text{HP}})$	$\text{PMe}(\text{J}_{\text{HP}})$	PPh
$\text{Ta}(\text{C}_2\text{H}_4)(\text{PMe}_3)\text{Cl}_3$ (<u>51</u>)	7.12 (2.4)	8.53 (4.3)	
$\text{Ta}(\text{C}_2\text{H}_4)(\text{PMe}_2\text{Ph})\text{Cl}_3$ (<u>52</u>)	7.48 (2.0)	8.22 (4.1)	2.73-3.04

* Shifts are listed in τ while coupling constants are listed in Hz.

^aA cis orientation of the phosphine ligands would have two diastereotopic pairs of methyl groups.

The propylene complex, $\text{Ta}(\text{CH}_2=\text{CHMe})(\text{PMe}_3)_2\text{Cl}_3$, $\underline{60}$, and the styrene complex, $\text{Ta}(\text{CH}_2=\text{CHPh})(\text{PMe}_3)_2\text{Cl}_3$, $\underline{66}$, are believed to have the same structure as the ethylene complex, $\text{Ta}(\text{C}_2\text{H}_4)(\text{PMe}_3)_2\text{Cl}_3$, $\underline{51}$. The substituted olefins, propylene and styrene, reduce the symmetry of the molecule, however, and the PMe_3 ligands are no longer equivalent. The large coupling between the phosphorus nuclei ($J_{\text{PP}}=158$ Hz) in the $^{31}\text{P}(\text{}^1\text{H})$ NMR spectrum of $\text{Ta}(\text{CH}_2=\text{CHPh})(\text{PMe}_3)_2\text{Cl}_3$, $\underline{66}$, indicates that the PMe_3 ligands are still trans.^a The PMe_3 ligands do not give rise to a typical A_9KLX_9 pattern in the ^1H NMR spectrum of $\underline{66}$ (see Figure 3.5.). The pattern is strongly field dependent as expected but the intensity ratios are incorrect.

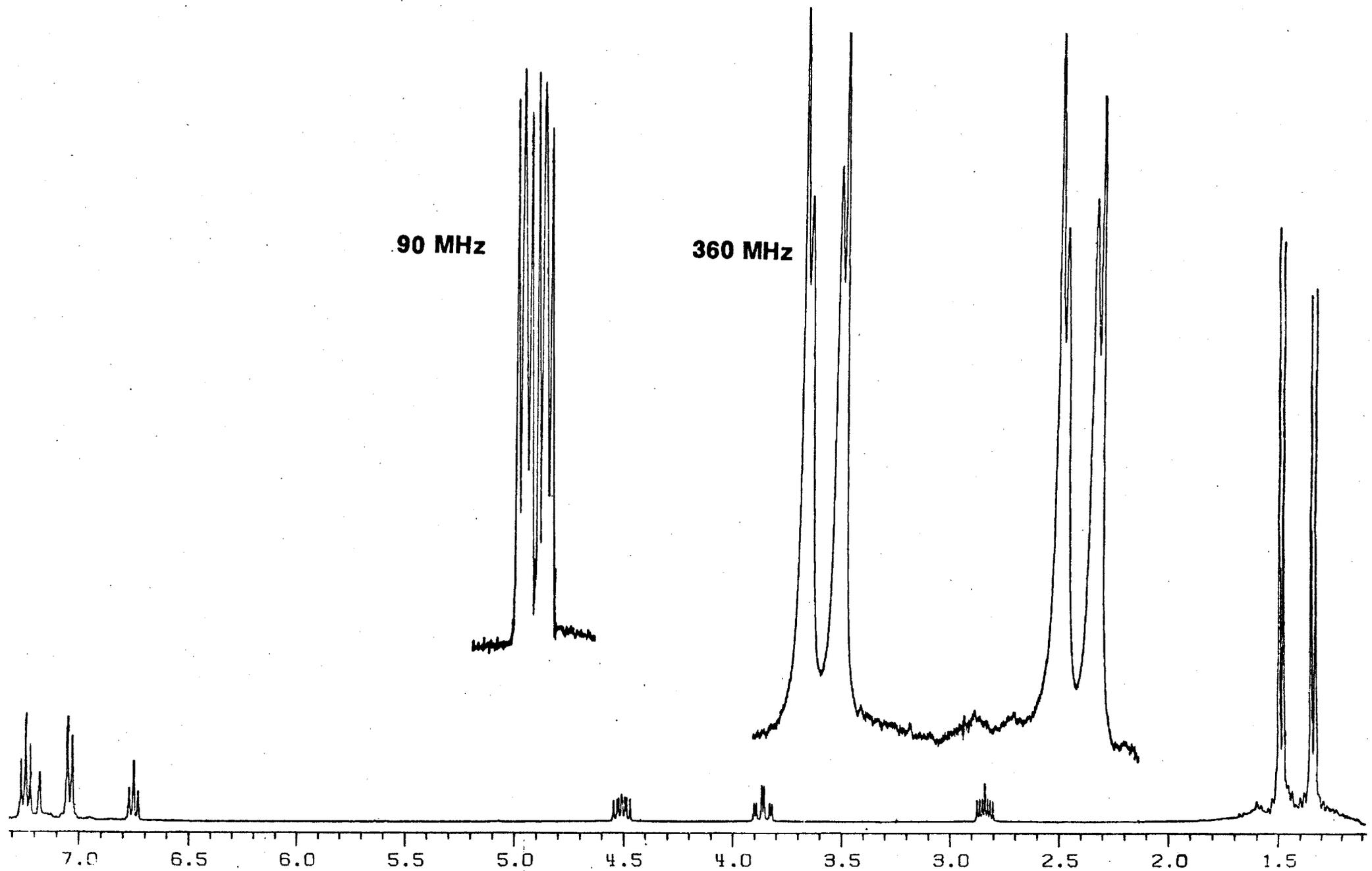
This unusual behavior is believed to be due to rotation of the olefin ligand. This rotation exchanges the environments of the PMe_3 ligands (Eq. 3-12). The PMe_3 ligands which are nonlabile



on the NMR time scale at RT, however, do not exchange. In the high field limit the PMe_3 region of the spectrum approaches a double doublet (for each PMe_3 ligand) due to both short and long range coupling to the

^aThe value of J_{PP} for the inequivalent cis ^{31}P in $\text{Me}_3\text{CCH}=\text{TaBr}_3(\text{dmpe})$ is 20 Hz.

Figure 3.5.
The ^1H NMR Spectrum of
 $\text{Ta}(\text{CH}_2=\text{CHPh})(\text{PMe}_3)_2\text{Cl}_3$



phosphorus nuclei. Presumably, if the rotation of the olefin were slowed enough at low temperature two double doublets would also be seen. The complex, $\text{Ta}(\text{CH}_2=\text{CHMe})(\text{PMe}_3)_2\text{Cl}_3$, 60, exhibits the same behavior.

The monomeric olefin complexes are remarkably stable toward thermal decomposition and are inert toward ligand substitution. The complex, $\text{Ta}(\text{C}_2\text{H}_4)(\text{PMe}_3)_2\text{Cl}_3$, 51, can be sublimed at 80°C at $0.01 \mu\text{Hg}$ without any decomposition. Additionally, 51 can be recovered intact after treatment with excess CO , C_2H_4 , or PMe_3 either thermally at 80°C or photochemically.

Those mononeopentylidene complexes with chelating ligands are much less reactive with ethylene because it is difficult for the olefin to enter the coordination sphere. The reaction of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})$, 30, with C_2H_4 is extremely slow at RT. However, 30 reacts with C_2H_4 at 80°C in 1 hr. to yield 0.775 equivalents of 4,4-dimethyl-1-pentene and 0.150 equivalents of trans-4,4-dimethyl-2-pentene. The initial olefinic cleavage product is primarily the internal olefin as in other reactions; however, this is isomerized to give the terminal olefin as the major product as the reaction proceeds. The inorganic product is an insoluble white powder which may be polymeric with dmpe ligands bridging the Ta centers. A small amount of a soluble blue complex is also produced. This may be $\text{Ta}(\text{C}_2\text{H}_4)(\text{dmpe})\text{Cl}_3$ but there is not enough of it produced to characterize.

The polymeric analogue of 30 which is $[\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})]_x$, 29, also reacts with C_2H_4 but only under forcing conditions. After 1 day at 100°C , the reaction of 29 with C_2H_4 yields 0.310 equivalents of 4,4-dimethyl-1-pentene, 0.559 equivalents of trans-4,4-dimethyl-2-pentene, 0.047 equivalents of neopentane, and 0.012 equivalents of cis-4,4-dimethyl-2-pentene. The organometallic product is an insoluble white powder as is the

starting material, 29.

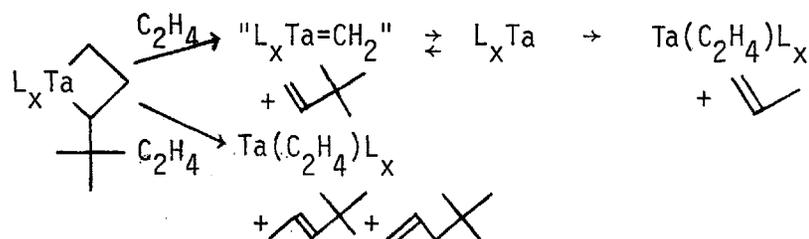
The complex, $\text{Cp}^*\text{Nb}(\text{CHCMe}_3)\text{Cl}_2$, 48, also reacts with olefins but more slowly than the mononeopentylidene complexes without cyclopentadienyl rings. The reaction of 48 with ethylene yields 4,4-dimethyl-1-pentene and trans-4,4-dimethyl-2-pentene while the reaction of 48 with propylene yields 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene.^a The organometallic products, which are soluble, green complexes, are apparently paramagnetic and have not been identified.

In brief summary, the organometallic products from the olefin reactions discussed above in the case of tantalum are six coordinate Ta(III) olefin complexes. For niobium, the organometallic products are generally paramagnetic complexes of Nb(III) which do not contain olefins. These olefin reactions, however, are all characterized by the formation of one equivalent of various olefinic cleavage products which are produced from the coupling of the neopentylidene ligand and the added olefin via a metallocyclobutane complex. In these reactions no products from cyclopropanation, metathesis, dimerization, or isomerization of the added olefins are ever observed.

However, when $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{THF})_2$, 25, is allowed to react with ethylene, 0.178 equivalents of 4,4-dimethyl-1-pentene and 0.753 equivalents of trans-4,4-dimethyl-2-pentene as well as 0.059 equivalents of 3,3-dimethyl-1-butene per Ta are produced. This last product, 3,3-dimethyl-1-butene, is the product expected from the metathesis of a neopentylidene ligand and ethylene. In this case the metallocyclobutane complex does not yield

^aThese products were identified by comparison with authentic samples.

olefinic cleavage products by β -hydrogen elimination. Instead the metallocyclobutane splits by breaking a carbon-carbon bond to form a methylene complex and the organic metathesis product (Eq. 3-13). The newly formed methylene complex can then react with more ethylene



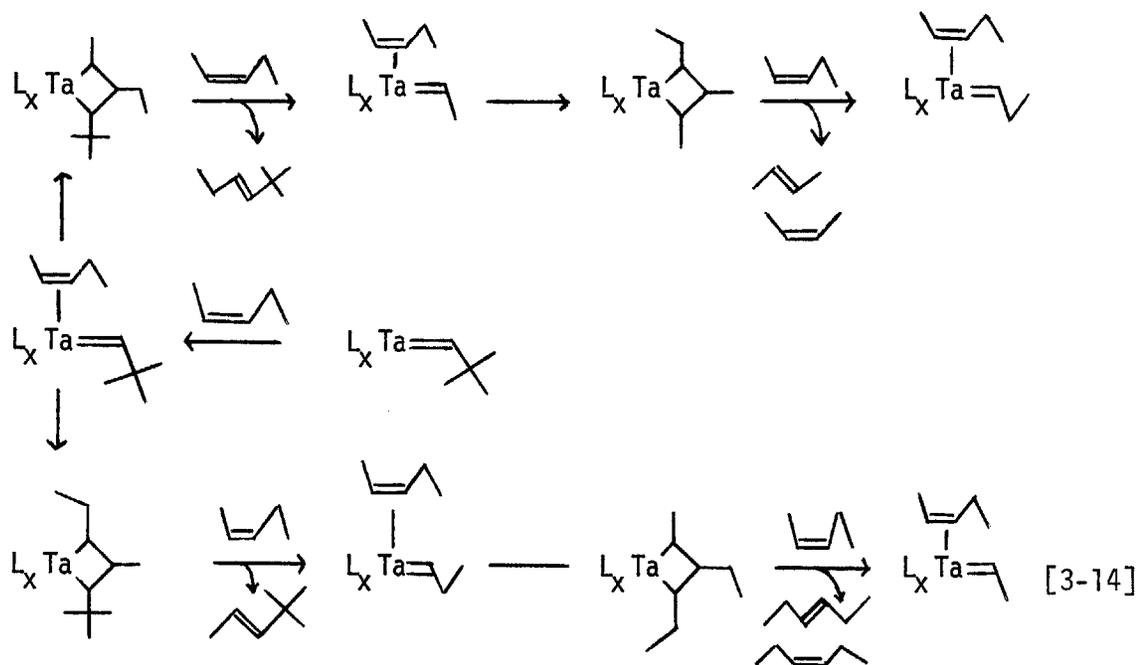
[3-13]

to form an unsubstituted metallocyclobutane complex. This can undergo degenerate metathesis by methylene exchange until it decomposes by β -hydrogen elimination to yield propylene which is found in small amounts in the reaction solution. Additionally, 1-butene is produced very slowly in this reaction. This probably occurs by dimerization of ethylene. The organometallic product which is $[\text{Ta}(\text{C}_2\text{H}_4)(\text{THF})\text{Cl}_3]_2$ (THF) is very unstable but has been isolated by Fellmann.⁴⁷

The reaction of $\text{Me}_3\text{CCH}=\text{Ta}(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$, 49, with ethylene yields 0.026 equivalents of 4,4-dimethyl-1-pentene and 0.039 equivalents of trans-4,4-dimethyl-2-pentene as well as 0.899 equivalents of 3,3-dimethyl-1-butene, the metathesis product, per Ta. Again the newly formed methylene complex is believed to react with ethylene to give propylene of which approximately 0.7 equivalents per Ta is present (Eq. 3-13). In this case, the system is also a very good dimerization catalyst for ethylene. 1-Butene is produced selectively at a rate of $0.07 \text{ Ta}^{-1} \text{ min}^{-1}$ at RT. This

dimerization system may proceed by a mechanism involving a metallo-cyclopentane complex as does the system based on Cp^*TaCl_2 (olefin).⁵³ The organometallic products include 0.5 equivalents of $\text{Ta}(\text{C}_2\text{H}_4)(\text{PMe}_3)_2(\text{OCMe}_3)_2\text{Cl}$, **67**, which is inert under ethylene, and 0.5 equivalents of an unknown Ta(III) complex.

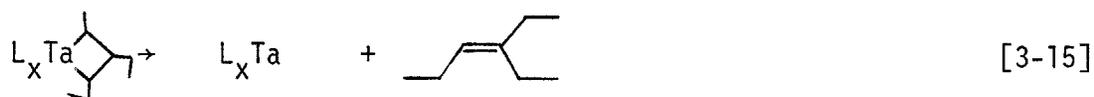
The reaction of $\text{Me}_3\text{CCH}=\text{Ta}(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ with cis-2-pentene at RT yields 0.574 equivalents of trans-4,4-dimethyl-2-pentene and 0.443 equivalents of trans-2,2-dimethyl-3-hexene as products of the stoichiometric metathesis of the neopentylidene complex (Eq. 3-14). The



subsequent catalytic metathesis by the proposed ethylidene and propylidene "chain-carrying" alkylidene complexes yields 19 equivalents each of 2-butenes and 3-hexenes per Ta from the cis-2-pentene which is metathesized. The metathesis reaction stops in less than 5 mins. because of the short life of the catalyst. Presumably the actual rate of metathesis is much faster than the observed rate of $8 \text{ Ta}^{-1}\text{min}^{-1}$. This difference occurs

because the catalyst is active for only part of the initial 5 mins., because reverse reactions can consume the 2-butenes and 3-hexenes, and because isomerization of cis-2-pentene to trans-2-pentene (of which 22 equivalents per Ta is produced) as well as degenerate metathesis can occur instead of productive metathesis. A better substrate for a rate measurement experiment might be cis,cis-2,8-decadiene which on metathesis would yield 2-butenes and cyclohexene.⁹¹ Cyclohexene does not reenter the metathesis cycle so reverse metathesis and degenerate metathesis are eliminated for the most part. The niobium analogue of 49, which is $\text{Me}_3\text{CCH}=\text{Nb}(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$, is a much faster metathesis catalyst but has a shorter lifetime.

The metathesis catalyst can decompose in a number of ways. The most probable is β -hydrogen elimination in the intermediate metallocyclobutane to yield cleavage products (Eq. 3-15). Evidence that this is possible has been seen in the reaction of 49 with ethylene to yield first 3,3-dimethyl-1-butene and then propylene. An alternate possibility is β -hydrogen elimination from the "chain-carrying" alkylidene to yield an olefin (Eq. 3-16). Another decomposition mechanism involves the intermolecular coupling of the "chain-carrying" alkylidenes to yield olefins (Eq. 3-17). Exact determination of the decomposition pathway which requires further research could lead to a longer lived catalyst.



Why $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{THF})_2$ and $\text{Me}_3\text{CCH}=\text{Ta}(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ should metathesize olefins (while other mononeopentylidene complexes will not) is not clear. It may be that oxygen donor ligands such as THF and $-\text{OCMe}_3$ in the coordination sphere help to stabilize intermediate metallocyclobutanes toward β -hydrogen elimination by increasing the electron density on the metal. These longer lived metallocyclobutanes can then undergo the carbon-carbon bond breaking reaction which is necessary for metathesis and which possibly is slower than β -hydrogen elimination.

This system is uniquely suited for the study of the catalytic metathesis of simple olefins for a number of reasons. The starting alkylidene complex, which is easily prepared, is a thermally stable, isolable, diamagnetic, soluble complex which has been well characterized. The catalytic system is homogeneous and does not require cocatalysts. The substrates are simple olefins which is convenient, but functionalized⁹² olefins which are incompatible with most systems should be readily metathesized as well by this system. Finally, under the right conditions, it may even be possible to isolate both the "chain-carrying" alkylidenes and the intermediate metallocyclobutanes of the metathesis reaction.

D. Thermolysis Reactions of Mononeopentylidene Complexes

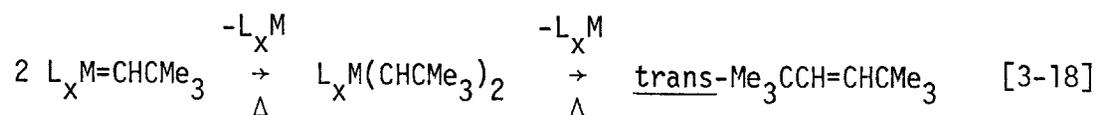
The mononeopentylidene complexes, $\text{Me}_3\text{CCH}=\text{MX}_3\text{L}_2$, are stable in solution or in the solid state at RT. These complexes, however, begin to decompose slowly when heated to approximately 100°C . In order to study this decomposition more closely, a number of mononeopentylidene complexes were thermolyzed and the organic products from these reactions were analyzed.

A sample of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$, 13, was dissolved in ether and sealed in a glass tube. The solution was heated to 90°C for 2 days. The sample appeared to be unchanged for the most part. The solution was then heated to 130°C for 1 day. After this, the tube contained a large amount of insoluble material, but the solution was still purple which indicated that a significant amount of 13 was still present. Analysis of the volatiles by GLC showed that the solution contained 0.40 equivalents of neopentane and 0.03 equivalents of trans-2,2,5,5-tetramethyl-3-hexene per Ta. There were also traces of some unknown high boiling products.

In a similar reaction, a sample of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{THF})_2$, 25, was dissolved in ether, sealed in a glass tube, and heated to 90°C for 2 days. The solution became dark and a large amount of insoluble material formed. Analysis of the volatiles by GLC showed that the solution contained 0.39 equivalents of neopentane and 0.11 equivalents of trans-2,2,5,5-tetramethyl-3-hexene per Ta. There were also traces of some unknown high boiling products.

In these decompositions, the neopentane can be produced by protonation of the neopentylidene by either the solvent or the ligands. The trans-2,2,5,5-tetramethyl-3-hexene could be formed by the coupling of two neopentylidene groups. One mechanism for this process could involve an intermolecular reaction in which a neopentylidene ligand is transferred from one metal center to another.^a This would yield an intermediate bisneopentylidene complex in which the neopentylidene ligands couple on decomposition and form trans-2,2,5,5-tetramethyl-3-hexene (Eq. 3-18).

^aThis type of mechanism is postulated to occur in the decomposition of electrophilic carbene complexes.⁹³



These reactions indicate that the most stable mononeopentylidene complexes are those containing strong ligands such as PMe_3 . Complexes which possess weak ligands such as THF decompose under less strenuous conditions and yield more of the neopentylidene coupling product, trans-2,2,5,5-tetramethyl-3-hexene. In either case, however, the major mode of decomposition appears to be protonation of the neopentylidene ligand to yield neopentane. Thermolysis reactions in other solvents such as mesitylene or in the solid state were not investigated.

EXPERIMENTAL^a1. Preparation of $(\text{Me}_3\text{CCH}_2)\text{TaCl}_4(\text{PMe}_3)_2$ (38).a. from $(\text{Me}_3\text{CCH}_2)\text{TaCl}_4$ [VI-25].

PMe_3 (0.23 g, 3 mmol, 50% excess) in 2 mL of pentane was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)\text{TaCl}_4$ (0.39 g, 1 mmol) in 15 mL of pentane at -30°C . The yellow solution became red-brown as the PMe_3 was added. The pentane was removed in vacuo to give red-brown crystals of 38 which were rinsed with cold pentane and dried in vacuo. The yield was 0.52 g (95%).

b. from $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ [VI-13].

Anhydrous gaseous HCl (22.4 mL, 1 mmol) was added by syringe with stirring to $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ (0.51 g, 1 mmol) in 50 mL of ether at -78°C . The purple solution became red-brown as the HCl was injected. The reaction mixture was allowed to warm to RT and was filtered. The ether was removed in vacuo to give red-brown crystals of 38 which were rinsed with cold pentane and dried in vacuo. The yield was 0.49 g (89%).

$^1\text{H NMR}$ (τ , C_6H_6 , 35°C , 60 MHz): 6.80 (br s, 2, $-\text{CH}_2\text{CMe}_3$), 8.63 (s, 9, $-\text{CH}_2\text{CMe}_3$), 8.85 (br d, 18, $^2J_{\text{HP}}=6.9$ Hz, PMe_3).

2. Preparation of $\text{TaCl}_5(\text{PMe}_3)_2$ (39)a. from TaCl_5 [VI-59].

TaCl_5 (1.07 g, 3.0 mmol) was dissolved in 50 mL of ether and filtered. Then PMe_3 (0.46 g, 6.0 mmol) in 2 mL of ether was added dropwise with stirring to the pale yellow solution. The solution became colorless as a bright yellow precipitate formed. After 20 mins. the microcrystalline product was collected by filtration, rinsed with ether,

^a The Experimental for Chap. 1 lists general procedures.

and dried in vacuo. The yield of 39 was 1.49 g (97%).

b. from $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ [VI-57].

$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ (0.51 g, 1.0 mmol) and n-heptane (0.1005 g, 1.003 mmol, for use as an internal standard) were dissolved in 50 mL of ether and cooled to -78°C . Then anhydrous gaseous HCl (45 mL, 2.0 mmol) was added by syringe slowly with stirring. The purple solution became brown and then slowly colorless as a yellow precipitate formed. After warming to RT, the microcrystalline product was collected by filtration, rinsed with ether, and dried in vacuo. The yield of 39 was 0.50 g (98%). A sample of the reaction solution which was analyzed by GLC contained 0.96 equivalents of neopentane per Ta.

IR (#141-B, cm^{-1} , nujol mull, NaCl plates): 938 (s, ν_{CP}).

3. Reaction of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ with Acetone [IX-68].

$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ (0.090 g, 0.18 mmol) and n-octane (0.020 g, 0.175 mmol, for use as an internal standard) were dissolved in 5 mL of ether and cooled to -30°C . Then dry acetone (0.031 g, 0.54 mmol, 2-fold excess) was added dropwise with stirring. The reaction was immediate and vigorous. The purple solution was decolorized as a white solid precipitated. The supernatant was analyzed by GLC and it contained 0.92 equivalents of $\text{Me}_2\text{C}=\text{CHCMe}_3$ per Ta. NOTE: Other $\text{Me}_3\text{CCH}=\text{MX}_3(\text{PR}_3)_2$ complexes react in a similar fashion with acetone.

4. Reaction of $[\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})]_x$ with Acetone [X-1].

$[\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})]_x$ (0.070 g, 0.138 mmol) and n-octane (0.0173 g, 0.151 mmol, for use as an internal standard) were placed in 1.5 mL of mesitylene. Then dry acetone (0.04 g, 0.69 mmol, 4-fold excess) was added to the white suspension. The reaction mixture was placed in a glass

tube and frozen in a liquid nitrogen bath. The tube was evacuated and sealed. The reaction mixture was heated to 100°C. There was no visible change in the white suspension. After 2 days at 100°C, an aliquot of the supernatant was analyzed by GLC. The sample contained 0.50 equivalents of 2,4,4-trimethyl-2-pentene and 0.34 equivalents of neopentane per Ta. NOTE: This reaction does not proceed at all at RT.

5. Preparation of $\text{Me}_3\text{CCH}=\text{C}(\text{Me})\text{N}=\text{TaCl}_3(\text{PMe}_3)_2$ (40) [X-2].

$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ (1.02 g, 2 mmol) was dissolved in 10 mL of ether and cooled to -30°C. Then MeCN (0.16 g, 4 mmol, 100% excess) was dissolved in 2 mL of ether and added dropwise with stirring. The purple solution rapidly became red-orange. The ether and acetonitrile were removed in vacuo to give 40 as a red-orange oil which was a mixture of two isomers for which the E/Z ratio was 1/2. The yield was 1.03 g (94%). NOTE: The niobium analogue, $\text{Me}_3\text{CCH}=\text{C}(\text{Me})\text{N}=\text{NbCl}_3(\text{PMe}_3)_2$, which is a red oil can be prepared similarly from $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_3)_2$.

^1H NMR (τ , C_6D_6 , 35°C, 60 MHz): E isomer: 5.63 (m, 1, $=\text{NC}(\text{Me})=\text{CHCMe}_3$), 8.19 (br s, 3, $=\text{NC}(\text{Me})=\text{CHCMe}_3$), 8.63 (br, 18, PMe_3), 8.66 (s, 9, $=\text{NC}(\text{Me})=\text{CHCMe}_3$); Z isomer: 4.90 (m, 1, $=\text{NC}(\text{Me})=\text{CHCMe}_3$), 8.22 (br s, 3, $=\text{NC}(\text{Me})=\text{CHCMe}_3$), 8.73 (br, 18, PMe_3), 8.98 (s, 9, $=\text{NC}(\text{Me})=\text{CHCMe}_3$).

6. Preparation of $\text{Ta}(\eta^2\text{-O}=\text{C}=\text{CHCMe}_3)\text{Cl}_3(\text{PMe}_3)_2$ (42) [VI-28].

$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ (1.80 g, 3.53 mmol) was dissolved in 10 mL of ether, placed in a pressure bottle, and stirred at RT for 3 hrs. under 40 PSIG of CO. The purple solution became a darker shade of purple as the ketene complex was produced. The solution was filtered and the solvent was removed in vacuo to yield purple microcrystalline 42. The yield was 1.86 g (98%). The product can be recrystallized from pentane at -30°C

if desired. NOTE: The niobium analogue, $\text{Nb}(\eta^2\text{-O=C=CHCMe}_3)\text{Cl}_3(\text{PMe}_3)_2$, which is green can be prepared similarly from $\text{Me}_3\text{CCH=NbCl}_3(\text{PMe}_3)_2$.

^1H NMR (#293, τ , C_6D_6 , 35°C , 90 MHz): 4.74 (s, 1, O=C=CHCMe_3), 8.43 (s, 9, O=C=CHCMe_3), 8.56 (t, 18, $^2J_{\text{HP}}=4.6$ Hz, PMe_3).

^{13}C NMR (#101, ppm, C_6D_6 , 28°C , 15 MHz, ^1H gated decoupled): 200.7 (t, $^2J_{\text{CP}}=10$ Hz, O=C=CHCMe_3), 100.5 (d, $J_{\text{CH}}=158$ Hz, O=C=CHCMe_3), 34.3 (s, O=C=CHCMe_3), 31.0 (q, $J_{\text{CH}}=125$ Hz, O=C=CHCMe_3), 14.0 (qt, $J_{\text{CH}}=136$ Hz, $J_{\text{CP}}=13$ Hz, PMe_3).

IR (#139, cm^{-1} , nujol mull, NaCl plates): 1605 (w, $\nu_{\text{C=C}}$).

7. Preparation of $\text{Ta}(\eta^2\text{-O=C=CHCMe}_3)\text{Cl}_3(\text{dmpe})(44)$ [VIII-52].

$\text{Me}_3\text{CCH=TaCl}_3(\text{dmpe})$ (0.51 g, 1.00 mmol) was dissolved in 5 mL of toluene, placed in a pressure bottle, and stirred at RT for 4 hrs. under 50 PSIG of CO. The red-purple solution slowly became orange and an orange precipitate formed. The microcrystalline product was collected by filtration and the toluene was removed from the filtrate in vacuo to give a second crop of 44. The yield was 0.49 g (92%). NOTE: Other $\text{Me}_3\text{CCH=TaX}_3(\text{LL})$ complexes in which the chelating ligand is bound more tightly to the metal are much less reactive with CO.

^1H NMR (#428, τ , CHCl_3 , 35°C , 60 MHz): 5.03 (br s, 1, O=C=CHCMe_3), 7.71 (m, 4, $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$), 8.15 (d, 6, $J_{\text{HP}}=10.0$ Hz, $-\text{PMe}_2$), 8.30 (d, 6, $J_{\text{HP}}=8.3$ Hz, $-\text{PMe}_2$), 8.73 (s, 9, O=C=CHCMe_3).

8. Reaction of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ with H_2 [V-42].

$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ (0.17 g, 0.33 mmol) and *n*-heptane (0.0335 g, 0.334 mmol, for use as an internal standard) were dissolved in 3 mL of toluene, placed in a pressure bottle, and stirred at RT for 3 days under 50 PSIG of H_2 . The purple solution slowly became red and then green. An aliquot of the sample was quenched with acetone and was analyzed by GLC. The sample contained 0.87 equivalents of CMe_4 per Ta but no $\text{Me}_2\text{C}=\text{CHCMe}_3$ (which indicated that the reaction was complete). The toluene was removed from the reaction solution in vacuo to yield a microcrystalline green solid. The crude product appeared to contain one or more tantalum hydride complexes by ^1H NMR (#243). The product was unstable in solution and in the solid state even at -30°C to loss of the hydride resonance.

^1H NMR (#243, τ , C_6H_6 , 35°C , 60 MHz): 8.63 (m, 18, PMe_3), 12.60 (br, 2, Ta-H).

9. Reaction of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})$ with H_2 [VIII-34].

$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})$ (0.17 g, 0.34 mmol) was dissolved in 5 mL of benzene, placed in a pressure bottle, and stirred at RT for 3 days under 50 PSIG of H_2 . The starting material was recovered unchanged except for a small amount which had polymerized into the white, insoluble $[\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})]_x$. NOTE: Other $\text{Me}_3\text{CCH}=\text{TaX}_3(\text{LL})$ complexes in which the chelating ligand is bound more tightly to the metal are also unreactive with H_2 .

10. Preparation of $\text{Nb}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ (6) [IV-71].

$\text{LiCH}_2\text{CMe}_3$ (0.12 g, 1.5 mmol) in 3 mL of benzene was added dropwise with stirring to $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_3)_2$ (0.21 g, 0.5 mmol) in 5 mL of benzene. The purple solution slowly became yellow as LiCl precipitated. After 1 hr. the LiCl (0.06 g, 95%) was removed by filtration. The filtrate was treated with activated charcoal and was refiltered. The benzene was removed in vacuo to give yellow crystals of 6. The yield was 0.21 g (92%). The $^1\text{H NMR}$ (#210) was identical to that of an authentic sample of 6.

NOTE: The analogous tantalum bisalkylidene, $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$, can be prepared in a similar fashion from $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$.

11. Preparation of $\text{CpNb}(\text{CHCMe}_3)\text{Cl}_2$ (46) [X-10].

$\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{THF})_2$ (2.07 g, 5.00 mmol) was dissolved in 25 mL of 80/20 ether/THF and cooled to -30°C . Then sublimed TiCp (1.35 g, 5.00 mmol) was added with stirring to the solution which was allowed to warm slowly to RT. The reaction mixture stayed purple as the TiCp dissolved and reacted while TiCl precipitated. After 1 1/2 hrs. at RT the reaction was filtered to remove TiCl (1.25 g, 104%) and the solvent was removed in vacuo to give a crude purple solid. The crude product was dissolved in pentane, filtered, and crystallized at -30°C . A second recrystallization from toluene/pentane at -30°C gave purple crystals of 46. The yield was 1.17 g (78%). NOTE: The tantalum analogue, $\text{CpTa}(\text{CHCMe}_3)\text{Cl}_2$, which is red can be prepared similarly from $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{THF})_2$.

$^1\text{H NMR}$ (#479, τ , C_6D_6 , 35°C , 60 MHz): 2.76 (br s, 1, $=\text{CHCMe}_3$), 4.23 (s, 5, C_5H_5), 9.10 (s, 9, $=\text{CHCMe}_3$).

12. Preparation of $\text{Cp}^{\text{''}}\text{Nb}(\text{CHCMe}_3)\text{Cl}_2$ (48) [X-44].

$\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{THF})_2$ (1.24 g, 3.00 mmol) was dissolved in 15 mL of cold benzene. Then $\text{TlCp}^{\text{''}}$ (1.02 g, 3.00 mmol) in 5 mL of cold benzene was added dropwise with stirring. As the reaction mixture warmed to RT, TlCl began to precipitate from the purple solution. The reaction was stirred for 1 hr. at RT and the mixture was filtered to remove TlCl (0.71 g, 98%). The solvent was removed from the filtrate in vacuo to give 1.06 g of 48 as a purple oil. This oil was sublimed at 65°C and 0.01 μ Hg onto a 0°C probe to give purple microcrystalline 48. The yield was 0.97 g (88%). (Addition of a small amount of pentane to the purple oil at -30°C gave purple crystals of 48 in low yield.) NOTE: The tantalum analogue, $\text{Cp}^{\text{''}}\text{Ta}(\text{CHCMe}_3)\text{Cl}_2$, which is a red oil can be prepared similarly from $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{THF})_2$.

^1H NMR (#500, τ , C_6D_6 , 35°C, 60 MHz): 4.26 (br s, 1, $=\text{CHCMe}_3$), 8.05 (s, 15, C_5Me_5), 8.88 (s, 9, $=\text{CHCMe}_3$).

^{13}C NMR (#188, ppm, $\text{C}_6\text{D}_5\text{CD}_3$, -30°C, 15 MHz, ^1H gated decoupled): 250.2 (br d, $J_{\text{CH}}=91$ Hz, $=\text{CHCMe}_3$), 121.1 (s, C_5Me_5), 48.8 (s, $=\text{CHCMe}_3$), 31.6 (q, $J_{\text{CH}}=126$ Hz, $=\text{CHCMe}_3$), 13.0 (q, $J_{\text{CH}}=127$ Hz, C_5Me_5).

IR (#154, cm^{-1} , nujol mull, NaCl plates): 2455 (m, $\nu_{\text{C}_\alpha\text{H}_\alpha}$).

13. Preparation of $\text{Me}_3\text{CCH}=\text{Ta}(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ (49) [X-61].

LiOCMe_3 (0.80 g, 10 mmol) in 10 mL of ether was added dropwise with stirring to $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ (2.55 g, 5 mmol) in 20 mL of ether at -30°C . As the purple reaction mixture was allowed to warm to RT, LiCl precipitated and the solution became yellow. After 2 hrs. at RT, the mixture was filtered to remove LiCl (0.41 g, 97%) and the ether was removed in vacuo to give a crude yellow solid. The crude product was dissolved in pentane, treated with activated charcoal, and filtered. The pentane was removed in vacuo to give light yellow crystals of 49. The yield was 2.44 g (96%). The product can be recrystallized from pentane at -30°C if desired. NOTE: The niobium analogue, $\text{Me}_3\text{CCH}=\text{Nb}(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$, which is dark yellow can be prepared similarly from $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_3)_2$.

^1H NMR (#457, τ , C_6D_6 , 35°C , 60 MHz): 0.56 (d, 1, $^3J_{\text{HP}}=4.0$ Hz, $=\text{CHCMe}_3$), 8.56 (s, 9, $-\text{OCMe}_3$), 8.61 (s, 9, $-\text{OCMe}_3$), 8.70 (s, 9, $=\text{CHCMe}_3$), 8.95 (d, 9, $^2J_{\text{HP}}=7.9$ Hz, PMe_3).

^{13}C NMR (#116, ppm, C_6D_6 , 28°C , 15 MHz, ^1H gated decoupled): 273.3 (dd, $J_{\text{CH}}=114$ Hz, $^2J_{\text{CP}}=6$ Hz, $=\text{CHCMe}_3$), 81.1 (s, $-\text{OCMe}_3$), 80.7 (s, $-\text{OCMe}_3$), 41.6 (s, $=\text{CHCMe}_3$), 35.0 (q, $J_{\text{CH}}=127$ Hz, $=\text{CHCMe}_3$), 32.4 (q, $J_{\text{CH}}=126$ Hz, $-\text{OCMe}_3$), 32.3 (q, $J_{\text{CH}}=126$ Hz, $-\text{OCMe}_3$), 17.0 (q d, $J_{\text{CH}}=131$ Hz, $J_{\text{CP}}=22$ Hz, PMe_3).

^{31}P (^1H) NMR (#109, ppm, toluene, -30°C , 36.43 MHz): -1.6 (s, PMe_3).

IR(#152, cm^{-1} , nujol mull, NaCl plates): 2720 (vw, $\nu_{\text{C-H}}$).

MW(X-62, cyclohexane, 15.33 mM): calcd. 508.8; found 493.

ANAL (X-72, for $\text{TaC}_{16}\text{H}_{37}\text{O}_2\text{ClP}$): calcd C 37.77, H 7.33;
found C 37.84, H 7.45.

14. Preparation of $\text{Ta}(\text{C}_2\text{H}_4)(\text{PMe}_3)_2\text{Cl}_3$ (51).

a. from $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ [V-19].

$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ (2.04 g, 4.00 mmol) and *n*-heptane (0.1005 g, 1.003 mmol, for use as an internal standard) were dissolved in 10 mL of ether, placed in a pressure bottle, and stirred at RT for 3 hrs. under 50 PSIG of ethylene. The purple solution quickly became blue. The volatiles were collected by trap-to-trap distillation under vacuum. The crude product was purified either by sublimation at 80°C and 0.01 μ Hg to give microcrystalline 51 or by recrystallization from ether/pentane at -30°C to give long blue needles of 51. The yield was 1.82 g (97%). A sample of the volatiles which was analyzed by GLC contained 0.066 equivalents of 4,4-dimethyl-1-pentene and 0.922 equivalents of *trans*-4,4-dimethyl-2-pentene per Ta. NOTE: Other $\text{Ta}(\text{C}_2\text{H}_4)(\text{PR}_3)_2\text{Cl}_3$ complexes were synthesized from the appropriate neopentylidene complex, $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PR}_3)_2$, in the same fashion and with similar yields for both the organic and organometallic products (see Table 3. III.).

b. from $[\text{Ta}(\text{C}_2\text{H}_4)(\text{PMe}_3)\text{Cl}_3]_2$ [VI-4].

$[\text{Ta}(\text{C}_2\text{H}_4)(\text{PMe}_3)\text{Cl}_3]_2$ (1.56 g, 2 mmol) was suspended in 10 ml of benzene. Then PMe_3 (0.16 g, 2.1 mmol, 5% excess) was added to the stirred suspension to give a blue solution. The solution was filtered. The benzene and excess PMe_3 were removed *in vacuo* to give blue needles of 51. The yield was 1.84 g (98%). NOTE: Other $\text{Ta}(\text{C}_2\text{H}_4)(\text{PR}_3)_2\text{Cl}_3$ complexes were synthesized from the appropriate dimeric olefin complex, $[\text{Ta}(\text{C}_2\text{H}_4)(\text{PR}_3)\text{Cl}_3]_2$, in the same fashion and with similar yields.

c. from TaCl_5 [VI-29].

TaCl_5 (1.94 g, 5.4 mmol) was suspended in 200 mL of ether at -78°C . PMe_3 (1.23 g, 16.2 mmol, 50% excess) in 10 mL of ether was added to give a yellow suspension of $\text{TaCl}_5(\text{PMe}_3)_2$. Then ZnEt_2 (0.74 g, 6.0 mmol, 11% excess) in 10 mL of ether was added dropwise with stirring to the reaction mixture. The mixture became dark as it was allowed to warm slowly to RT. The mixture was filtered and the insoluble residue was washed with more ether. The solvent was removed from the combined filtrates in vacuo to yield the crude product. This was sublimed at 80°C and $0.01 \mu \text{ Hg}$ to give blue microcrystalline 51. The yield was 1.39 g (55%).

^1H NMR (#262, τ , C_6D_6 , 35°C , 90 MHz): 7.12 (t, 4, $^3J_{\text{HP}}=2.4$ Hz, C_2H_4), 8.53 (t, 18, $^2J_{\text{HP}}=4.3$ Hz, PMe_3).

$^{13}\text{C}(^1\text{H})$ NMR(#129, ppm, C_6D_6 , 28°C , 15 MHz): 59.0 (t, $^2J_{\text{CP}}=3$ Hz, C_2H_4), 14.4 (t, $J_{\text{CP}}=13$ Hz, PMe_3).

$^{31}\text{P}(^1\text{H})$ NMR (#142, ppm, toluene, -30°C , 36.43 MHz): -4.1 (s, PMe_3).

IR (#137, cm^{-1} , nujol mull, NaCl plates): 947 (s, ν_{CP}).

UV-VIS (#001, nm (ϵ), pentane): 243 (4200), 317 (3400), 605 (53).

ANAL (V-71, for $\text{TaC}_8\text{H}_{22}\text{Cl}_3\text{P}_2$): calcd C 20.56, H 4.74, P 13.24;

found C 20.64, H 4.08, P 13.44.

15. Preparation of $[\text{Ta}(\text{C}_2\text{H}_4)(\text{PMe}_3)\text{Cl}_3]_2$ (54) [VI-41].

$[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Cl}_3]_2$ (2.17 g, 2.51 mmol) and *n*-heptane (0.1005 g, 1.003 mmol, for use as an internal standard) were dissolved in 40 mL of ether, placed in a pressure bottle, and allowed to stand without stirring^a at RT for 1 day under 50 PSIG of C_2H_4 . The red solution slowly became blue. Small clusters of very dark blue crystals of 54 formed to leave a colorless solution. The product was collected by filtration, rinsed with ether, and dried in vacuo. The yield was 1.95 g (99%). A sample of the reaction solution which was analyzed by GLC contained 0.059 equivalents of 4,4-dimethyl-1-pentene and 0.933 equivalents of trans-4,4-dimethyl-2-pentene per Ta. NOTE: Other $[\text{Ta}(\text{C}_2\text{H}_4)(\text{PR}_3)\text{Cl}_3]_2$ complexes were synthesized from the appropriate dimeric neopentylidene complex, $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PR}_3)\text{Cl}_3]_2$, in the same fashion and with similar yields for both the organic and organometallic products (see Table 3.III.).

16. Preparation of $[\text{Nb}(\text{PMe}_3)_2\text{Cl}_3]_2$ (57) [V-33].

$\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PMe}_3)_2$ (0.15 g, 0.36 mmol) and *n*-heptane (0.0335 g, 0.334 mmol, for use as an internal standard) were dissolved in 5 mL of ether, placed in a pressure bottle, and allowed to stand without stirring^a at RT for 8 hrs. under 50 PSIG of ethylene. The blue-purple solution became colorless as purple crystals of 57 formed. The product was collected by filtration, rinsed with ether, and dried in vacuo. The yield was 0.12 g (95%). A sample of the reaction solution which was analyzed by GLC contained 0.028 equivalents of 4,4-dimethyl-1-

^aIf the reaction is stirred the product comes out of solution in a very finely divided microcrystalline form.

pentene and 0.907 equivalents of trans-4,4-dimethyl-2-pentene per Nb.

NOTE: Other $[\text{Nb}(\text{PR}_3)_2\text{Cl}_3]_2$ complexes were synthesized from the appropriate neopentylidene complex, $\text{Me}_3\text{CCH}=\text{NbCl}_3(\text{PR}_3)_2$, in the same fashion and with similar yields of both the organic and organometallic products (see Table 3.III.).

IR ($\#138$, cm^{-1} , nujol mull, NaCl plates): 956 (s, ν_{CP}).

17. Preparation of " $[\text{Nb}(\text{PMe}_3)\text{Cl}_3]_x$ " (59) [VI-33].

$[\text{Me}_3\text{CCH}=\text{Nb}(\text{PMe}_3)\text{Cl}_3]_2$ (0.12 g, 0.17 mmol) and n-heptane (0.0335 g, 0.334 mmol, for use as an internal standard) were dissolved in 5 mL of ether, placed in a pressure bottle, and stirred at RT for 4 hrs. under 50 PSIG of ethylene. The purple solution became colorless as a dark microcrystalline product, which is believed to be 59, formed. The product was collected by filtration, rinsed with ether, and dried in vacuo. The yield was 0.09 g (93%). A sample of the reaction solution which was analyzed by GLC contained 0.027 equivalents of 4,4-dimethyl-1-pentene and 0.945 equivalents of trans-4,4-dimethyl-2-pentene per Nb (see Table 3.III.).

18. Preparation of $\text{Ta}(\text{CH}_2=\text{CHMe})(\text{PMe}_3)_2\text{Cl}_3$ (60) [VIII-63].

$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ (1.53 g, 3.00 mmol) and n-octane (0.0344 g, 0.301 mmol, for use as an internal standard) were dissolved in 15 mL of ether, placed in a pressure bottle, and stirred at RT for 8 hrs. under 50 PSIG of propylene. The purple solution quickly became blue. The volatiles were collected by trap-to-trap distillation under vacuum. The crude product was recrystallized from ether/pentane at -30°C to give blue crystals of 60. The yield was 1.36 g (94%). A sample of the volatiles which was analyzed by GLC contained 0.082 equivalents of 2,4,4-

trimethyl-1-pentene, 0.420 equivalents of trans-5,5-dimethyl-3-hexene, 0.072 equivalents of trans-5,5-dimethyl-2-hexene, and 0.412 equivalents of 2,4,4-trimethyl-2-pentene per Ta. NOTE: Other $\text{Ta}(\text{CH}_2=\text{CHMe})(\text{PR}_3)_2\text{Cl}_3$ complexes were synthesized from the appropriate neopentylidene complex, $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PR}_3)_2$, in the same fashion and with similar yields for both the organic and organometallic products (see Table 3.IV.).

^1H NMR (#356-A, τ , C_6D_6 , 35°C , 90 MHz): 6.41 (m, 1, $\text{CH}_2=\underline{\text{CHMe}}$), 6.72 (m, 2, $\underline{\text{CH}_2}=\text{CHMe}$), 8.45 (m, 9, $\underline{\text{PMe}_3}$), 8.54 (m, 9, $\underline{\text{PMe}_3}'$), 8.88 (m, 3, $\text{CH}_2=\underline{\text{CHMe}}$).

19. Preparation of $[\text{Ta}(\text{CH}_2=\text{CHMe})(\text{PMe}_3)\text{Cl}_3]_2$ (63) [VI-52].

$[\text{Me}_3\text{CCH}=\text{Ta}(\text{PMe}_3)\text{Cl}_3]_2$ (1.41 g, 1.63 mmol) and n-octane (0.0344 g, 0.301 mmol, for use as an internal standard) were dissolved in 30 mL of ether, placed in a pressure bottle, and allowed to stand without stirring^a at RT for 1 day under 50 PSIG of propylene. The red solution slowly became blue. The solution became colorless as dark blue crystals of 63 formed. The product was collected by filtration, rinsed with ether, and dried in vacuo. The yield was 1.26 g (95%). A sample of the reaction solution which was analyzed by GLC contained 0.449 equivalents of 2,4,4-trimethyl-2-pentene and 0.539 equivalents of the other three propylene cleavage products per Ta (vide supra). NOTE: Other $[\text{Ta}(\text{CH}_2=\text{CHMe})(\text{PR}_3)\text{Cl}_3]_2$ complexes were synthesized from the appropriate dimeric neopentylidene complex, $[\text{Me}_3\text{CCH}=\text{Ta}(\text{PR}_3)\text{Cl}_3]_2$, in the same fashion and with similar yields for both the organic and organometallic products (see Table 3.IV.).

^aIf the reaction is stirred, the product comes out of solution in a finely divided microcrystalline form.

20. Preparation of $\text{Ta}(\text{CH}_2=\text{CHPh})(\text{PMe}_3)_2\text{Cl}_3$ (66) [VII-33].

$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ (1.53 g, 3.00 mmol) and *n*-heptane (0.0670 g, 0.668 mmol, for use as an internal standard) were dissolved in 10 mL of ether. Then styrene (1.25 g, 12 mmol, 100% excess) was added dropwise with stirring. The purple solution slowly became blue-green. The reaction was allowed to stand at RT for 8 hrs. and then the volatiles were collected by trap-to-trap distillation under vacuum. The crude product was recrystallized from toluene/pentane at -30°C to give blue-green crystals of 66. The yield was 1.52 g (93%). A sample of the volatiles which was analyzed by GLC contained four styrene cleavage products which included 0.352 equivalents of *cis*-2-phenyl-4,4-dimethyl-2-pentene, 0.286 equivalents of *trans*-1-phenyl-4,4-dimethyl-2-pentene, 0.299 equivalents of *trans*-1-phenyl-4,4-dimethyl-1-pentene, and 0.064 equivalents of 2-phenyl-4,4-dimethyl-1-pentene.

^1H NMR ($\#241$, τ , C_6D_6 , 35°C , 60 MHz): 2.65-3.35 (m, 5, $\text{CH}_2=\text{CHPh}$), 5.45 (m, 1, $\text{CH}_2=\text{CHPh}$), 6.14 (m, 1, $\text{CH}_2=\text{CHPh}$), 7.18 (m, 1, $\text{CH}_2=\text{CHPh}$), 8.52 (m, 18, PMe_3 and PMe_3'). ($\#354\text{-A}$, τ , C_6D_6 , 35°C , 90 MHz): 2.71-3.40 (m, 5, $\text{CH}_2=\text{CHPh}$), 5.50 (m, 1, $\text{CH}_2=\text{CHPh}$), 6.18 (m, 1, $\text{CH}_2=\text{CHPh}$), 7.20 (m, 1, $\text{CH}_2=\text{CHPh}$), 8.54 (m, 9, PMe_3), 8.67 (m, 9, PMe_3'). ($\#H\text{-010}$, τ , C_6D_6 , 35°C , 270 MHz): 2.69-3.38 (m, 5, $\text{CH}_2=\text{CHPh}$), 5.51 (m, 1, $\text{CH}_2=\text{CHPh}$), 6.16 (m, 1, $\text{CH}_2=\text{CHPh}$), 7.19 (m, 1, $\text{CH}_2=\text{CHPh}$), 8.54 (dd, 9, $J_{\text{HP}}=7.5$ Hz, $J_{\text{HP}}=1.2$ Hz, PMe_3), 8.67 (dd, 9, $J_{\text{HP}}=7.5$ Hz, $J_{\text{HP}}=1.1$ Hz, PMe_3').

21. Reaction of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})$ with C_2H_4 [VIII-29].

$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})$ (0.17 g, 0.34 mmol) and *n*-heptane (0.0335 g, 0.334 mmol, for use as an internal standard) were dissolved in 5 mL of toluene, placed in a pressure bottle, and stirred at 80°C for 1 hr. under 50 PSIG of C_2H_4 . The red-purple solution became pale blue and a large amount of white precipitate formed. A sample of the reaction solution which was analyzed by GLC contained 0.775 equivalents of 4,4-dimethyl-1-pentene and 0.150 equivalents of trans-4,4-dimethyl-2-pentene. The reaction solution was filtered to remove 0.11 g of white, microcrystalline precipitate from the pale blue filtrate. The toluene was removed from the filtrate in vacuo to give <0.01 g of blue crystals which may be $\text{Ta}(\text{C}_2\text{H}_4)(\text{dmpe})\text{Cl}_3$. NOTE: Other $\text{Me}_3\text{CCH}=\text{TaX}_3(\text{LL})$ complexes in which the chelating ligand is bound more tightly to the metal are less reactive with ethylene.

22. Reaction of $\text{Cp}^*\text{Nb}(\text{CHCMe}_3)\text{Cl}_2$ with Propylene [X-30].

$\text{Cp}^*\text{Nb}(\text{CHCMe}_3)\text{Cl}_2$ (0.08 g, 0.22 mmol) was dissolved in 1/2 mL of C_6D_6 and was placed in a NMR tube. Excess propylene was injected into the purple solution by syringe. The solution became green very slowly. The amount of starting material decreased as the reaction was monitored by ^1H and ^{13}C NMR, but no new organometallic species could be observed. After the reaction was complete, an aliquot was analyzed by GLC. The sample contained the expected propylene cleavage products: 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene in a 7:2 ratio, respectively. A small amount of neopentane was present but there were

no propylene dimers in the sample even though an excess of propylene was present. NOTE: $\text{Cp}^*\text{Nb}(\text{CHCMe}_3)\text{Cl}_2$ reacts with ethylene in a similar manner to yield ethylene cleavage products but no 1-butene.

23. Reaction of $\text{Me}_3\text{CCH}=\text{Ta}(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ with C_2H_4 [X-49].

$\text{Me}_3\text{CCH}=\text{Ta}(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ (0.17 g, 0.33 mmol) and *n*-heptane (0.0335 g, 0.334 mmol, for use as an internal standard) were dissolved in 5 mL of toluene, placed in a pressure bottle, and stirred at RT for 1/2 hr. under 50 PSIG of C_2H_4 . The yellow solution became a slightly darker shade of yellow. An aliquot of the reaction mixture was quenched with H_2O and was analyzed by GLC. The sample contained 0.899 equivalents of 3,3-dimethyl-1-butene, 0.026 equivalents of 4,4-dimethyl-1-pentene, and 0.039 equivalents of trans-4,4-dimethyl-2-pentene per Ta. Approximately 0.7 equivalents of propylene per Ta were present. The sample also contained a large amount of 1-butene which was produced catalytically at the rate of $\sim 0.07 \text{ Ta}^{-1} \text{ min}^{-1}$. As the concentration of 1-butene increased over a period of 10 hrs. two unidentified hexenes were also produced catalytically. One organometallic product of this reaction is $\text{Ta}(\text{C}_2\text{H}_4)(\text{PMe}_3)_2(\text{OCMe}_3)_2\text{Cl}$ which can be isolated as yellow crystals; the other product is an uncharacterized Ta(III) complex.

24. Preparation of $\text{Ta}(\text{C}_2\text{H}_4)(\text{PMe}_3)_2(\text{OCMe}_3)_2\text{Cl}$ (67) [X-26].

$\text{Me}_3\text{CCH}=\text{Ta}(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ (0.26 g, 0.51 mmol) and PMe_3 (0.08 g, 1.05 mmol, 100% excess) were dissolved in 5 mL of ether, placed in a pressure bottle, and stirred at RT for 4 hrs. under 50 PSIG of C_2H_4 . The solvent was removed in vacuo to yield 0.26 g (95%) of yellow microcrystalline 67 which can be recrystallized from ether at -30°C .

NOTE: Without the presence of additional PMe_3 , the reaction of $\text{Me}_3\text{CCH}=\text{Ta}(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ with C_2H_4 yields 0.5 equivalents of 67 and 0.5 equivalents of an unidentified Ta(III) complex.

^1H NMR (#453, τ , C_6D_6 , 35°C , 90 MHz): 8.55 (m, 22, PMe_3 and C_2H_4), 9.18 (s, 18, $-\text{OCMe}_3$).

^{13}C NMR (#152, ppm, C_6D_6 , 28°C , 15 MHz, ^1H gated decoupled): 76.9 (s, $-\text{OCMe}_3$), 38.7 (t, $J_{\text{CH}}=149$ Hz, C_2H_4), 31.7 (q, $J_{\text{CH}}=125$ Hz, $-\text{OCMe}_3$), 15.0 (q t, $J_{\text{CH}}=127$ Hz, $J_{\text{CP}}=10$ Hz, PMe_3).

25. Reaction of $\text{Me}_3\text{CCH}=\text{Ta}(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ with cis-2-Pentene [X-53].

$\text{Me}_3\text{CCH}=\text{Ta}(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$ (0.051 g, 0.10 mmol) and n-heptane (0.0111 g, 0.110 mmol, for use as an internal standard) were dissolved in 2 mL of cis-2-pentene at RT. Samples of the reaction mixture which were analyzed by GLC showed that the neopentylidene complex rapidly caused the cis-2-pentene to disproportionate. After 5 mins. the reaction was complete. The products of the initial stoichiometric metathesis reaction were 0.574 equivalents of trans-4,4-dimethyl-2-pentene and 0.443 equivalents of trans-2,2-dimethyl-3-hexene per Ta. The products of the catalytic metathesis reaction were 19 equivalents of 2-butenes and 19 equivalents of 3-hexenes per Ta. In addition 22 equivalents of trans-2-pentene per Ta were produced. NOTE: The niobium analogue, $\text{Me}_3\text{CCH}=\text{Nb}(\text{OCMe}_3)_2\text{Cl}(\text{PMe}_3)$, disproportionates olefins in a similar manner but at a faster rate with a shorter catalyst lifetime.

26. Reaction of $[\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})]_x$ with C_2H_4 [IX-73].

$[\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{dmpe})]_x$ (0.075 g, 0.148 mmol) and n-octane (0.0173 g, 0.151 mmol, for use as an internal standard) were added to 5 mL of mesitylene, placed in a pressure bottle, and stirred at 100°C for 1 day under 50 PSIG of ethylene. The only visible change in the reaction was that the supernatant slowly became a faint blue. An aliquot of the supernatant was analyzed by GLC. The sample contained 0.310 equivalents of 4,4-dimethyl-1-pentene, 0.559 equivalents of trans-4,4-dimethyl-2-pentene, 0.012 equivalents of cis-4,4-dimethyl-2-pentene, and 0.047 equivalents of neopentane per Ta.

27. Thermolysis of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ [X-39].

$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$ (0.17 g, 0.33 mmol) and n-heptane (0.0335 g, 0.334 mmol, for use as an internal standard) were dissolved in 1.5 mL of ether. The reaction mixture was placed in a glass tube and frozen in a liquid nitrogen bath. The tube was evacuated and sealed. The reaction mixture was heated to 90°C for 2 days and then to 130°C for 1 day. Although the solution had darkened and solids were present there still was starting material present. The volatiles were collected by trap-to-trap distillation and an aliquot was analyzed by GLC. The sample contained 0.03 equivalents of trans-2,2,5,5-tetramethyl-3-hexene and 0.40 equivalents of neopentane per Ta as well as traces of several unknowns.

28. Thermolysis of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{THF})_2$ [X-38].

$\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{THF})_2$ (0.16 g, 0.33 mmol) and *n*-heptane (0.0335 g, 0.334 mmol, for use as an internal standard) were dissolved in 1.5 mL of ether. The reaction mixture was placed in a glass tube and frozen in a liquid nitrogen bath. The tube was evacuated and sealed. The reaction mixture was heated to 90°C for 2 days. The solution darkened and a large quantity of solids formed. The volatiles were collected by trap-to-trap distillation and an aliquot was analyzed by GLC. The sample contained 0.11 equivalents of trans-2,2,5,5-tetramethyl-3-hexene and 0.39 equivalents of neopentane per Ta as well as traces of several unknowns.

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APPENDIX I

The Organization of Research Notebooks

The experimental data described in this text were recorded in eleven notebooks (I-XI) from January, 1976 through August, 1979. The notebooks are arranged chronologically in increasing numerical order. Each experiment is identified by a notebook number and page number (e.g. VI-29) and references the spectral data recorded for that experiment.

Spectral data as well as other auxiliary data are organized chronologically in separate folders or binders (listed below) by type of spectrum or measurement. All spectra, traces, or plots in each set are numbered sequentially, are dated, and are referenced with a notebook number and page number. These data are organized and collected in the following groups:

1. 60 MHz and 90 MHz ^1H NMR spectra (#000). These were recorded on the T-60, R-20B, R-22B, and FX-60Q.
2. 270 MHz ^1H NMR spectra (#H-000). These were recorded on the HFX-270.
3. 15.00 MHz ^{13}C NMR spectra (#000). These were recorded on the FX-60Q.
4. 67.89 MHz ^{13}C NMR spectra (#C-000). These were recorded on the HFX-270.
5. 36.43 MHz ^{31}P NMR spectra (#000). These were recorded on the HFX-90.
6. 109.3 MHz ^{31}P NMR spectra (#P-000). These were recorded on the HFX-270.

7. IR spectra (#000). These were recorded on the Perkin-Elmer 567.
8. UV-VIS spectra (#000). These were recorded on the Cary 17.
9. GC and GC-MS traces. These were recorded on the Hewlett-Packard 3380A and 5990A, respectively.
10. MW plots.

APPENDIX II

The Preparation of $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{PMe}_2)\text{Br}_2(\text{PMe}_3)_2$ Introduction

As described in the preceding text dineopentyl trihalide complexes of Nb and Ta react with a variety of ligands to yield alkylidene complexes of the type $\text{Me}_3\text{CCH}=\text{MX}_3\text{L}_n$ through a mechanism which involves ligand induced α -hydrogen abstraction (see Chap. 2). Additionally, complexes of the type $\text{Me}_3\text{CCH}=\text{M}(\text{CH}_2\text{CMe}_3)_3$ react with tertiary phosphines by a similar ligand induced α -hydrogen abstraction mechanism to yield bisalkylidene complexes, $\text{M}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PR}_3)_2$, in preference to the tautomeric alkylidyne complexes, $\text{Me}_3\text{CC}\equiv\text{M}(\text{CH}_2\text{CMe}_3)_2(\text{PR}_3)_2$ (see Chap. 1). In an attempt to employ ligand induced α -hydrogen abstraction in the preparation of alkylidyne complexes,^a the reaction of trineopentyl dihalide complexes of Nb and Ta with several different ligands was studied.^b This appendix describes the results of that investigation.

Results and Discussion

$(\text{Me}_3\text{CCH}_2)_3\text{TaCl}_2$ ¹⁸ is very inert towards reaction with PMe_3 . The addition of excess PMe_3 to $(\text{Me}_3\text{CCH}_2)_3\text{TaCl}_2$ in pentane or even in methylene chloride^c did not cause any evolution of neopentane from the yellow solution either on standing at RT or on heating the sample. The inertness

^aOne successful example of this type is the preparation of $\text{CpTa}(\text{CCMe}_3)_2\text{Cl}(\text{PMe}_3)_2$ from $\text{CpTa}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)\text{Cl}$ and PMe_3 .^{26,41}

^bIn this case two consecutive ligand induced α -hydrogen abstractions would be required to synthesize the alkylidyne complexes.

^cIn the systems described previously (see Chap. 2) and in other systems^{41,42} the rate of ligand induced α -hydrogen abstraction is fastest in methylene chloride.

of $(\text{Me}_3\text{CCH}_2)_3\text{TaCl}_2$ is most likely due to the crowded coordination sphere of the complex. Because of this it is difficult for PMe_3 to coordinate to the metal or to remain coordinated for any appreciable amount of time. It also is extremely doubtful that a second PMe_3 could coordinate to " $(\text{Me}_3\text{CCH}_2)_3\text{TaCl}_2(\text{PMe}_3)$ ". This would require that the α -hydrogen abstraction occur in a six coordinate species which may be less facile than in the five or seven coordinate intermediates in the mechanisms proposed for the bisalkylidenes (see Chap. 1) or the monoalkylidenes (see Chap. 2).

Since ligand induced α -hydrogen abstraction in $(\text{Me}_3\text{CCH}_2)_3\text{TaCl}_2$ did not take place even with the most active ligand and in the best solvent, a more reactive starting material, $(\text{Me}_3\text{CCH}_2)_3\text{TaBr}_2$,^a was employed. The addition of excess PMe_3 to $(\text{Me}_3\text{CCH}_2)_3\text{TaBr}_2$ in CH_2Cl_2 did cause the slow evolution of neopentane from the yellow solution. As the reaction proceeded the yellow color of the initial solution gradually faded to yield a very pale yellow to colorless solution. After one day at RT ^b the reaction was complete. Two equivalents of neopentane per Ta had been given off during the course of the reaction. Removal of the methylene chloride in vacuo gave an off-white, crystalline product in 96% yield.^c This complex was slightly soluble in pentane and very soluble in ether, benzene, toluene, methylene chloride, and chloroform. The product was stable in the solid

^aThe decreased electron density around the metal in the bromide complex⁸⁴ (compared to the chloride complex) should enhance its ability to coordinate PMe_3 .

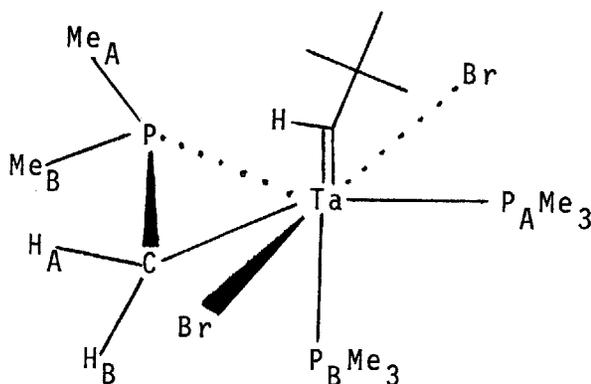
^bThis reaction is very slow compared to similar reactions with $(\text{Me}_3\text{CCH}_2)_2\text{TaCl}_3$ (see Chap. 2).

^cThis yield is based on the assumed formula $\text{Me}_3\text{CC}\equiv\text{TaBr}_2(\text{PMe}_3)_3$.

state but decomposed in solution at RT over a period of one day (much more rapidly in chloroform) unless excess PMe_3 was present. The complex was recrystallized conveniently from ether/pentane or toluene/pentane at -30°C .

The off-white, crystalline complex was thought to be $\text{Me}_3\text{CC}\equiv\text{TaBr}_2(\text{PMe}_3)_3$. Analysis of the spectral data, however, indicated that the complex did not contain an alkylidyne moiety. The spectra in fact were quite complex but clearly showed that the product was a tantalum alkylidene complex. The product was identified as $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{PMe}_2)\text{Br}_2(\text{PMe}_3)_2$, **68**. The proposed structure of **68** appears in Figure AII.1.

Figure AII.1. The Proposed Structure of $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{PMe}_2)\text{Br}_2(\text{PMe}_3)_2$.



The ^1H NMR spectrum of **68** (Figure AII.2,) shows the presence of one ^tBu group resonance and one H_α resonance which is a multiplet due to phosphorus coupling. The P-Me region is complex. Two non-equivalent *cis* PMe_3 ligands each exhibit a doublet while the $-\text{PMe}_2$ group which contains

Figure AII.2.
The ^1H NMR Spectrum of
 $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{PMe}_2)\text{Br}_2(\text{PMe}_3)_2$

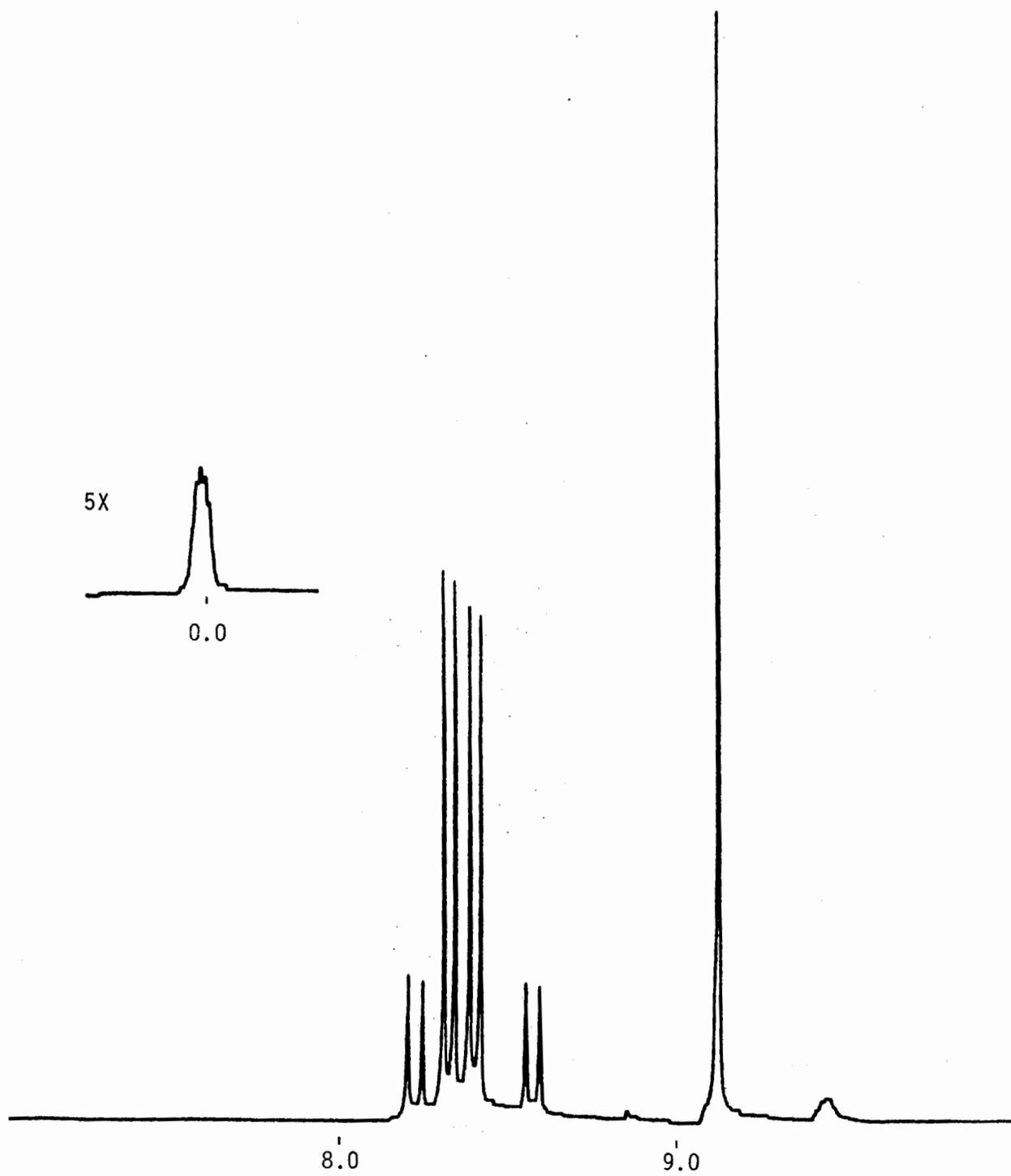


Figure AII,3.
The ^{13}C (^1H) NMR Spectrum of
 $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{PMe}_2)\text{Br}_2(\text{PMe}_3)_2$

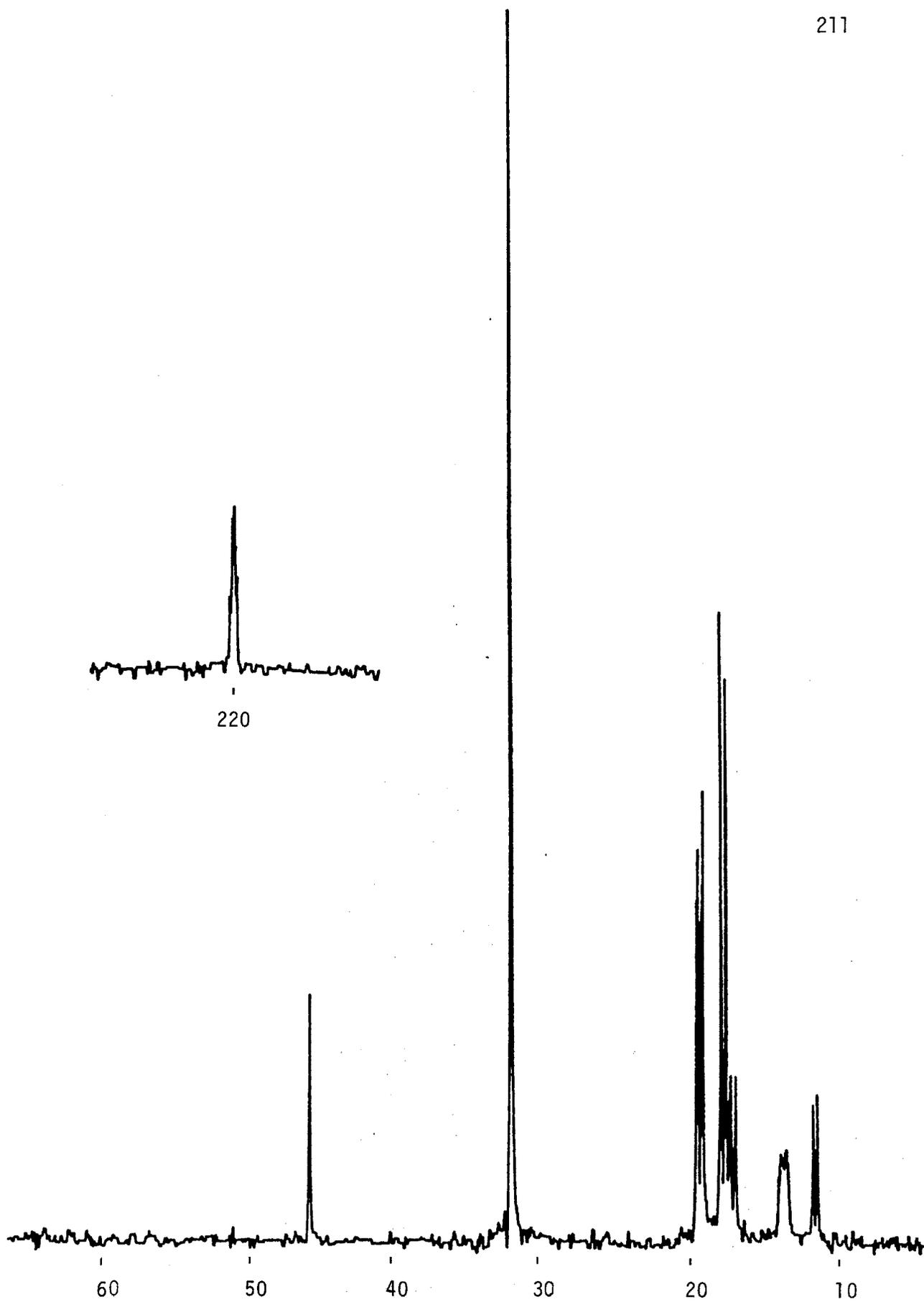
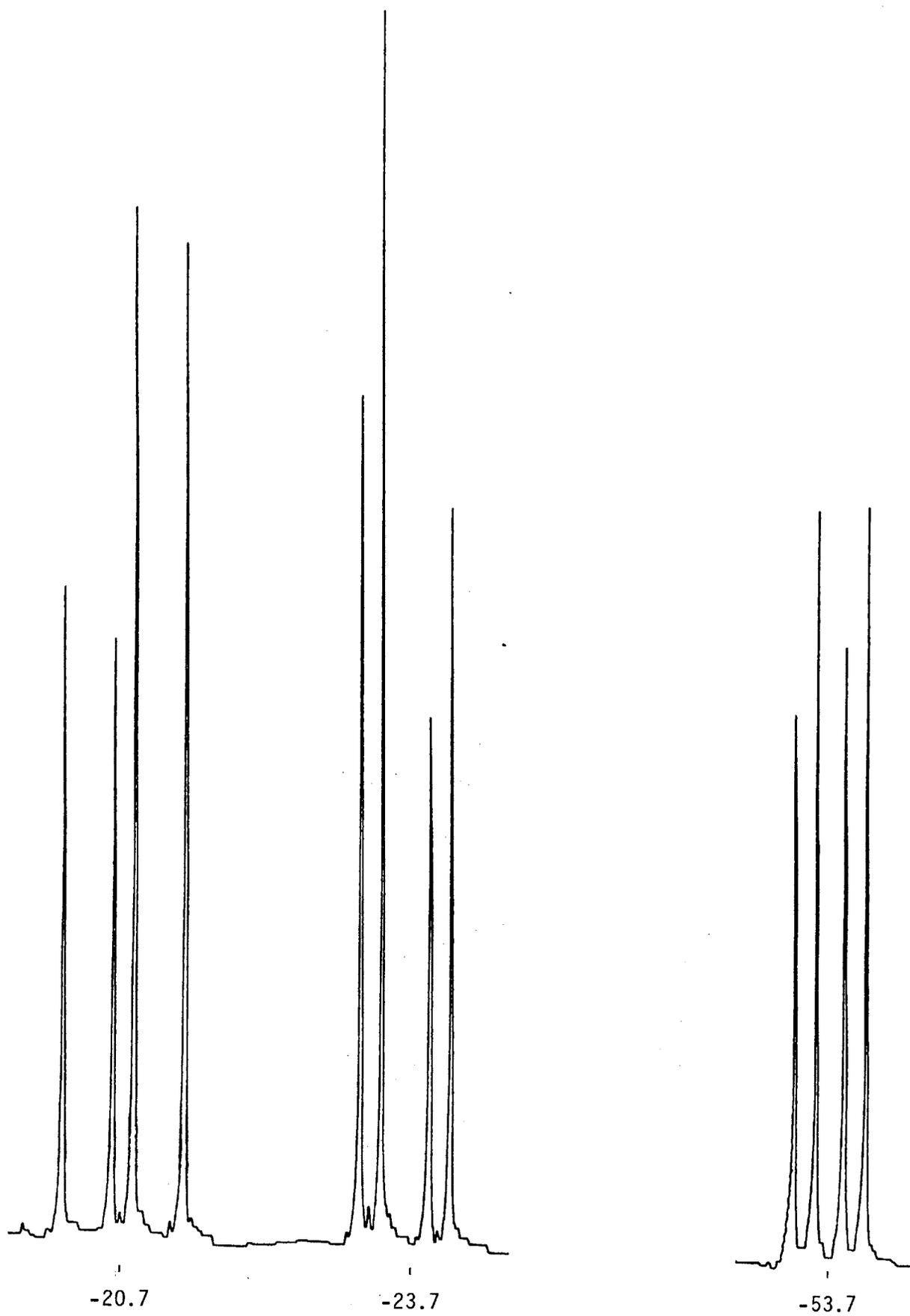


Figure AII.4,
The $^{31}\text{P}(^1\text{H})$ NMR Spectrum of
 $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{PMe}_2)\text{Br}_2(\text{PMe}_3)_2$



diastereotopic methyl groups appears as a double doublet. The PCH_2 - group which possesses diastereotopic protons gives a broad resonance due to phosphorus coupling. Ligand exchange, if it occurs, is slow on the NMR time scale at RT since the rest of the spectrum is sharp.

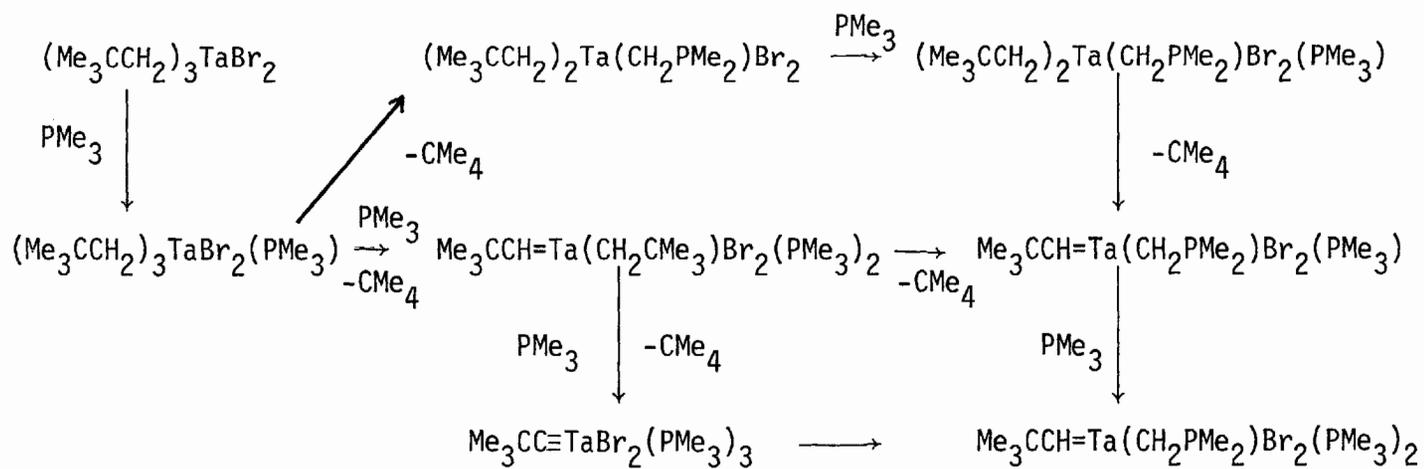
The ^{13}C NMR spectrum of 68 (Figure AII.3.) is similar to the ^1H NMR spectrum in that it shows the presence of one ^tBu group and one C_α which appears at 220.1 ppm and for which $J_{\text{C}_\alpha\text{H}_\alpha}$ is only 69 Hz. The rest of the spectrum also agrees with the proposed structure. There are the proper resonances for two non-equivalent cis PMe_3 ligands as well as the expected resonances for the $-\text{CH}_A\text{H}_B\text{PMe}_A\text{Me}_B$ group.

The $^{31}\text{P}(^1\text{H})$ NMR spectrum of 68 (Figure AII.4.) is a standard ABX pattern.⁹⁴ The shifts for P_A , P_B , and P_X are -20.7, -23.7, and -53.7 ppm, respectively. The coupling constants, J_{AB} , J_{AX} , and J_{BX} , are 83 Hz, 58 Hz, and 26 Hz, respectively. These values indicate that P_A and P_B are coordinated to the metal while P_X which appears to be trans to P_A may or may not be coordinated.^{57g, 72b}

The IR spectrum of 68 shows clearly that this complex is an alkylidene complex. The spectrum contains a very strong $\nu_{\text{C}_\alpha\text{H}_\alpha}$ stretch at 2419 cm^{-1} .

The formation of $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{PMe}_2)\text{Br}_2(\text{PMe}_3)_2$, 68, is an example of a ligand induced α -hydrogen abstraction and a ligand hydrogen abstraction²⁸ rather than the intended double α -hydrogen abstraction.^a The reaction mechanism (which was not investigated) may proceed through a number of different intermediates depending on whether α -hydrogen abstraction

^aIf the neopentylidene and neopentyl groups are trans in one of the intermediates, then α -hydrogen abstraction becomes impossible. It seems unlikely that a proton from a PMe_3 ligand could be more susceptible to abstraction than H_α with a $J_{\text{C}_\alpha\text{H}_\alpha}$ value of 69 Hz. It is likely therefore that this is a kinetic rather than thermodynamic result.



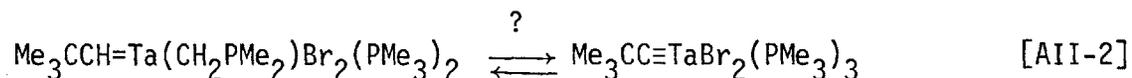
68
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[AII-1]

occurs before or after ligand hydrogen abstraction. It is possible that the desired product, $\text{Me}_3\text{CC}\equiv\text{TaBr}_2(\text{PMe}_3)_3$, may even be one of the reaction intermediates in the formation of $\underline{68}$. Several possible mechanisms for the formation of $\underline{68}$ are shown in Eq. AII-1.

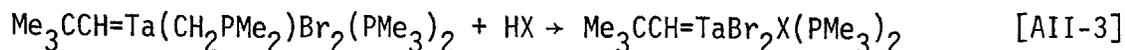
In an effort to determine if this was a general reaction, the reaction of $(\text{Me}_3\text{CCH}_2)_3\text{TaBr}_2$ with other ligands was investigated. There was no reaction between $(\text{Me}_3\text{CCH}_2)_3\text{TaBr}_2$ and ligands such as THF. The reaction of $(\text{Me}_3\text{CCH}_2)_3\text{TaBr}_2$ and ligands such as tmeda gave uncharacterizable mixtures which also contained insoluble material.

The reaction chemistry of $\underline{68}$ which should be interesting because of the presence of the $-\text{CH}_2\text{PMe}_2$ ligand has unfortunately not yet been investigated. Of primary importance would be the question of whether the equilibrium between the alkylidene and the alkylidyne exists and if so under what conditions the equilibrium can be shifted to the alkylidyne complex (Eq. AII-2). Concerning these questions, it has been noticed

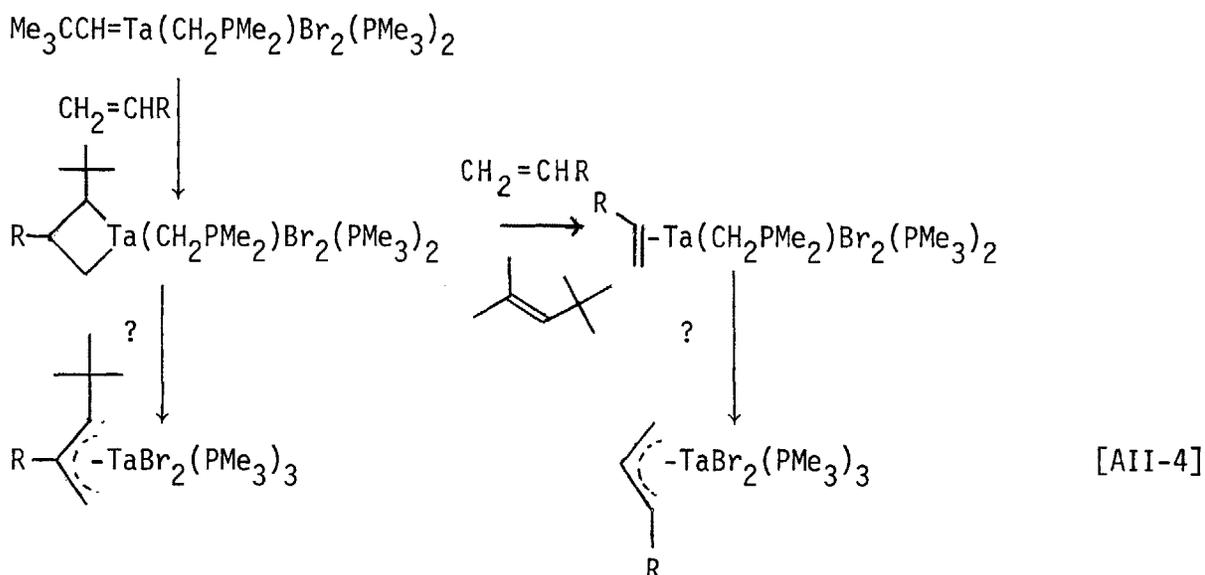


that under some conditions the various NMR spectra of $\underline{68}$ show the presence of traces of other isomers of $\underline{68}$. This may be a result of PMe_3 exchange as in the trans, mer to cis, mer isomerization of $\text{Me}_3\text{CCH}=\text{TaCl}_3(\text{PMe}_3)_2$, $\underline{13a}$ and $\underline{13b}$, or it may be due to the postulated alkylidene-alkylidyne equilibrium. Additionally, the solution "decomposition" of $\underline{68}$ has not been explained and may be involved in this equilibrium.

The reaction of $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{PMe}_2)\text{Br}_2(\text{PMe}_3)_2$, $\underline{68}$, with other molecules should be interesting since the $-\text{CH}_2\text{PMe}_2$ ligand can function in a number of ways including as a proton trap (Eq. AII-3). The reaction of $\underline{68}$ with



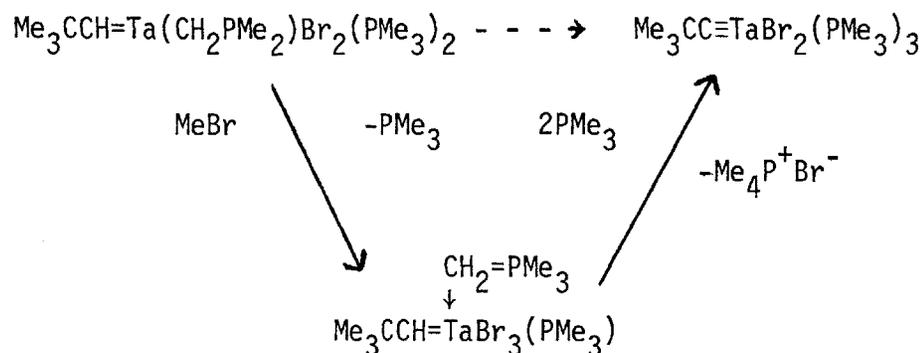
olefins^a could yield either an olefin complex, an allyl complex, or a mixture of both depending on the rates of proton transfer from the tantalum to the various ligands (Eq. AII-4). Any allyl complexes of Ta would be



interesting in themselves and might also function as olefin hydrogenation catalysts.

The reaction of 68 with MeBr under the proper conditions might alkylate the $-\text{CH}_2\text{PMe}_2$ ligand selectively (rather than the neopentylidene ligand) to yield a coordinated phosphorane complex.^{57g} This complex could further react and might even provide a method for converting the alkylidene to the alkylidyne as long as the conversion is thermodynamically feasible (Eq. AII-5).

^aBecause the low values of $J_{\text{C}\alpha\text{H}}$ and $\nu_{\text{C}\alpha\text{H}\alpha}$ indicate that the Ta in 68 is very electron deficient, it is unlikely that 68 would function as an olefin metathesis catalyst.



[AII-5]

Experimental

The Preparation of $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{PMe}_2)\text{Br}_2(\text{PMe}_3)_2$ (68) [VIII-74].

PMe_3 (0.61 g, 8 mmol, 33% excess) in 2 mL of CH_2Cl_2 was added dropwise with stirring to $(\text{Me}_3\text{CCH}_2)_3\text{TaBr}_2$ (1.11 g, 2 mmol) in 10 mL of CH_2Cl_2 at -30°C . The solution was allowed to warm and stand at RT for one day. The solution was filtered and the CH_2Cl_2 was removed in vacuo to yield 1.23 g of off-white, crystalline 68. The yield was 96%. The product was recrystallized from ether/pentane at -30°C .

^1H NMR ($^{\#}\text{H-011}$, τ , C_6D_6 , 6°C , 270 MHz): -0.02 (m, 1, $=\text{CHCMe}_3$), 8.28 (d, 3, $^2J_{\text{HP}}=11.0$ Hz, $-\text{PMe}_A\text{Me}_B$), 8.38 (d, 9, $^2J_{\text{HP}}=8.0$ Hz, P_AMe_3), 8.45 (d, 9, $^2J_{\text{HP}}=7.7$ Hz, P_BMe_3), 8.61 (d, 3, $^2J_{\text{HP}}=10.7$ Hz, $-\text{PMe}_A\text{Me}_B$), 9.12 (s, 9, $=\text{CHCMe}_3$), 9.45 (br, 2, $-\text{CH}_A\text{H}_B\text{PMe}_A\text{Me}_B$).

^{13}C NMR ($^{\#}\text{C-016}$, ppm, C_6D_6 , 6°C , 67.89 MHz, ^1H gated decoupled): 220.1 (d, $J_{\text{CH}}=69$ Hz, $=\text{CHCMe}_3$), 46.8 (s, $=\text{CHCMe}_3$), 32.4 (q, $J_{\text{CH}}=126$ Hz, $=\text{CHCMe}_3$), 18.8 (qdd, $J_{\text{CH}}=131$ Hz, $J_{\text{CP}}=24$ Hz, $^3J_{\text{CP}}=5$ Hz, P_AMe_3), 17.2 (q d, $J_{\text{CH}}=131$ Hz, $J_{\text{CP}}=24$ Hz, P_BMe_3), 16.5 (q d, $J_{\text{CH}}=130$ Hz, $J_{\text{CP}}=24$ Hz, $-\text{PMe}_A\text{Me}_B$),

14.3 (m, $-\text{CH}_A\text{H}_B\text{PMe}_A\text{Me}_B$), 10.7 (q d, $J_{\text{CH}}=134$ Hz, $J_{\text{CP}}=22$ Hz, $-\text{PMe}_A\text{Me}_B$).

^{31}P (^1H) NMR (#P-003, ppm, toluene, -60°C , 109.3 MHz): -20.7

(q, $J_{\text{AB}}=83$ Hz, $J_{\text{AX}}=58$ Hz, P_AMe_3), -23.7 (q, $J_{\text{BA}}=83$ Hz, $J_{\text{BX}}=26$ Hz, P_BMe_3), -53.7 (q, $J_{\text{XA}}=58$ Hz, $J_{\text{XB}}=26$ Hz, $-\text{CH}_2\text{P}_X\text{Me}_2$).

IR (#153, cm^{-1} , nujol mull, NaCl plates): 2419 (s, $\nu_{\text{C}_\alpha\text{H}_\alpha}$).

APPENDIX III

The Preparation of $\text{Me}_3\text{SiCH}=\text{Ta}(\text{CH}_2\text{SiMe}_3)_3$ Introduction

As described previously in this text a class of neopentylidene complexes, $\text{Me}_3\text{CCH}=\text{MX}_3\text{L}_n$, was prepared (see Chap. 2). As part of that research, the first nonbridging⁹⁵ trimethylsilylmethylene complex, $\text{Me}_3\text{SiCH}=\text{TaCl}_3(\text{PMe}_3)_2$, was prepared from $(\text{Me}_3\text{SiCH}_2)_2\text{TaCl}_3$. Other trimethylsilylmethyl complexes were studied to determine if additional trimethylsilylmethylene complexes exist (vide infra).

In 1971 Wilkinson reported the structure of $[\text{M}(\mu\text{-CSiMe}_3)(\text{CH}_2\text{SiMe}_3)_2]_2$ ($\text{M}=\text{Nb}, \text{Ta}$) which contained bridging trimethylsilylmethylidyne ligands.^{49a} The mechanism of formation of these complexes was not investigated, however. It seemed likely that the reactions might proceed through $\text{Me}_3\text{SiCH}=\text{M}(\text{CH}_2\text{SiMe}_3)_3$ which are the unknown silicon analogues of $\text{Me}_3\text{CCH}=\text{M}(\text{CH}_2\text{CMe}_3)_3$, the first primary alkylidene complexes.¹⁸ The greater acidity of H_α in the former complexes which is induced by the silicon atom adjacent to C_α would cause these intermediates to be unstable towards dimerization. The formation of $[\text{Ta}(\mu\text{-CSiMe}_3)(\text{CH}_2\text{SiMe}_3)_2]_2$ was studied to determine if such an intermediate existed and if so to determine how it could be isolated and converted into other mononuclear complexes with Ta-to-C multiple bonds. This appendix describes the results of that investigation.

Results and Discussion

The published preparation of $[\text{Ta}(\mu\text{-CSiMe}_3)(\text{CH}_2\text{SiMe}_3)_2]_2$, 69, which involved addition of a solution of TaCl_5 to a solution of excess $\text{Me}_3\text{SiCH}_2\text{MgCl}$, required a difficult recrystallization and gave a very low yield of product, 15%.^{49b} The oily orange residues from a typical

preparation of 69 (after as much product as possible was crystallized out) were analyzed by ^{13}C NMR. The residues (which amount to several times the mass of recoverable 69) were shown to be a mixture containing 33% $[\text{Ta}(\mu\text{-CSiMe}_3)(\text{CH}_2\text{SiMe}_3)_2]_2$, 69, with a resonance at 404 ppm for the bridging C_α and 67% of an unknown complex with a resonance at 241 ppm which might be due to a $\text{Me}_3\text{SiCH}=\text{Ta}$ moiety.

It was also observed that the unknown complex disappeared slowly with time at RT (but rapidly at higher temperatures) while the amount of 69 and TMS (tetramethylsilane) increased. Therefore, the low yield of 69 was due to the presence of a highly soluble, semi-stable intermediate in the product mixture. An improved synthesis of $[\text{Ta}(\mu\text{-CSiMe}_3)(\text{CH}_2\text{SiMe}_3)_2]_2$, 69, was developed based on this observation. The reaction of $(\text{Me}_3\text{SiCH}_2)_3\text{TaCl}_2$ ⁸⁵ with one equivalent of $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2(\text{diox})^a$ (or two equivalents of $\text{Me}_3\text{SiCH}_2\text{MgCl}$) was carried out at RT for one hour in ether. The mixture was then filtered and heated at reflux overnight. An 86% yield of 69 could be recovered after a relatively simple workup.

A synthesis of the intermediate which is believed to be $\text{Me}_3\text{SiCH}=\text{Ta}(\text{CH}_2\text{SiMe}_3)_3$,^b 70, was also developed. The reaction $(\text{Me}_3\text{SiCH}_2)_3\text{TaCl}_2$ and one equivalent of $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2(\text{diox})$ was carried out at -30°C for 20 mins. and at RT for 5 mins. The product was recovered from the reaction mixture by a cold workup and recrystallized at -30°C from pentane.

^aThis was prepared by adding 1.5 equivalents of dioxane to 1.0 equivalents of $\text{Me}_3\text{SiCH}_2\text{MgCl}$. (The use of $\text{LiCH}_2\text{SiMe}_3$ leads to intractable materials in the preparation of 69.)

^bA dimeric structure for 70 has not been ruled out but seems unlikely for steric reasons.

The ^1H NMR spectrum of $\underline{70}$ is entirely consistent with its formulation. The spectrum contains a small singlet at 4.30 τ for H_α as well as singlets for the equivalent methylene protons and the two kinds of $-\text{SiMe}_3$ groups. In this respect the spectrum is similar to that of $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3$, $\underline{1}$. The ^{13}C (^1H) NMR spectrum of $\underline{70}$ is also consistent with the proposed structure. The C_α resonance of the $=\text{CHSiMe}_3$ group appears at 240.9 ppm while the C_α resonance of the three equivalent $-\text{CH}_2\text{SiMe}_3$ groups occurs at 85.8 ppm. There are two other resonances as expected; one each for the two different $-\text{SiMe}_3$ groups.

This complex, $\text{Me}_3\text{SiCH}=\text{Ta}(\text{CH}_2\text{SiMe}_3)_3$, $\underline{70}$, is stable indefinitely in the solid state at -30°C . In solution at RT, however, $\underline{70}$ is slowly (but quantitatively) converted into $[\text{Ta}(\mu\text{-CSiMe}_3)(\text{CH}_2\text{SiMe}_3)_2]_2$, $\underline{69}$, by a mechanism which evolves one equivalent of TMS per Ta. This decomposition can be carried out as cleanly but faster at higher temperatures.

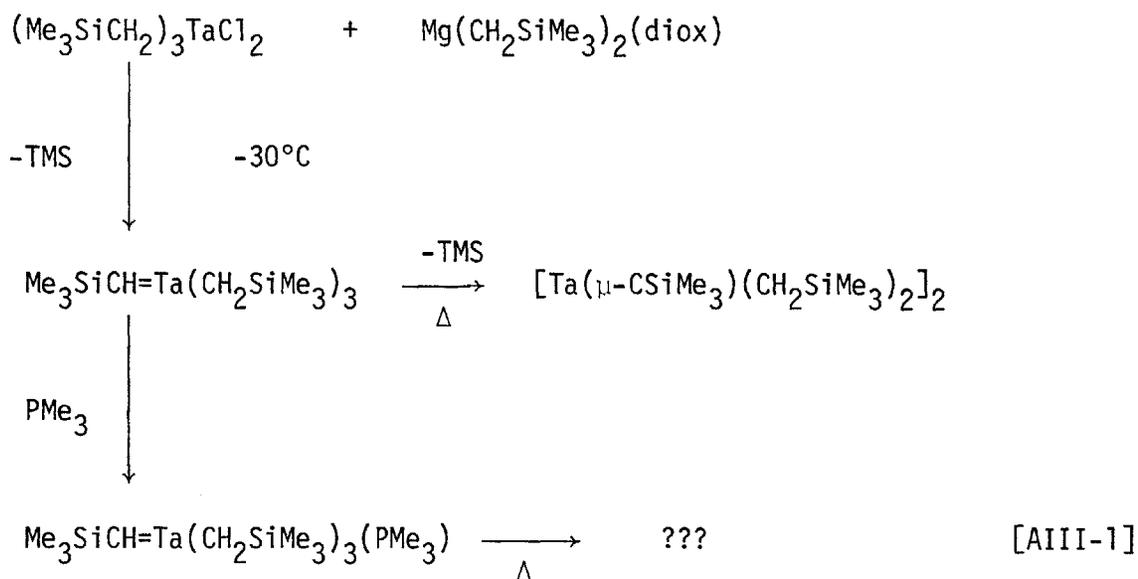
$[\text{Ta}(\mu\text{-CSiMe}_3)(\text{CH}_2\text{SiMe}_3)_2]_2$, $\underline{69}$, does not react to cleave the bridge (either when heated or when photolysed) in the presence of ligands such as PMe_3 .^{49b} In fact, $\underline{69}$ is stable in solution for days at 100°C and only starts to decompose with the evolution of TMS at a reasonable rate at 140°C . PMe_3 does not trap any of the thermal decomposition products. When irradiated with ultraviolet light, $\underline{69}$ decomposes slowly with evolution of TMS, but again PMe_3 does not trap the decomposition products.

Therefore, if monomeric Ta carbyne or biscarbene complexes with $-\text{CH}_2\text{SiMe}_3$ groups are to be prepared, it must be through a monomeric species such as $\underline{70}$ since the bridging carbyne complex, $\underline{69}$, cannot be cleaved. Consequently, the reaction of $\text{Me}_3\text{SiCH}=\text{Ta}(\text{CH}_2\text{SiMe}_3)_3$ with PMe_3 was studied.

The preparation of $\text{Me}_3\text{SiCH}=\text{Ta}(\text{CH}_2\text{SiMe}_3)_3$, 70, in the presence of excess PMe_3 leads to a stable complex on warming to RT. This complex has been identified as $\text{Me}_3\text{SiCH}=\text{Ta}(\text{CH}_2\text{SiMe}_3)_3(\text{PMe}_3)$, 71, by ^1H and ^{13}C NMR. The ^1H NMR spectrum of 71 contains a small singlet at 3.86 τ for H_α and a doublet at 9.00 τ for PMe_3 ($J_{\text{HP}}=5.0$ Hz) as well as the other expected resonances. The ^{13}C NMR spectrum of 71 contains a doublet at 251.8 ppm ($J_{\text{C}_\alpha\text{H}_\alpha}=96$ Hz) for C_α of the carbene ligand and a triplet at 77.3 ppm ($J_{\text{CH}}=106$ Hz) for the C_α of the $-\text{CH}_2\text{SiMe}_3$ ligands. Also present are a quartet of doublets for the PMe_3 ligand at 16.5 ppm ($J_{\text{CH}}=130$ Hz, $J_{\text{CP}}=12$ Hz) as well as two quartets for the two types of $-\text{SiMe}_3$ groups at 3.8 and 3.2 ppm ($J_{\text{CH}}=118$ Hz for both).

The unexpected isolation of $\text{Me}_3\text{SiCH}=\text{Ta}(\text{CH}_2\text{SiMe}_3)_3(\text{PMe}_3)$, 71, which is an extremely crowded molecule is even more remarkable because it is stable for days in solution at RT. The carbon analogue, " $\text{Me}_3\text{CCH}=\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{PMe}_3)$ " cannot even be observed and has been postulated only as a transient intermediate in the formation of bisneopentylidene complexes (see Chap. 1). This seems to be another example of the "reluctance" of $-\text{CH}_2\text{SiMe}_3$ groups (compared to $-\text{CH}_2\text{CMe}_3$ groups) to undergo ligand induced α -hydrogen abstraction (see Chap. 2). The decomposition of $\text{Me}_3\text{SiCH}=\text{Ta}(\text{CH}_2\text{SiMe}_3)_3(\text{PMe}_3)$, 71, under more rigorous conditions, which has not yet been investigated, could lead to monomeric carbyne or biscarbene complexes through loss of TMS but loss of PMe_3 could also occur in which case $[\text{Ta}(\mu\text{-CSiMe}_3)(\text{CH}_2\text{SiMe}_3)_2]_2$ would be the expected product. These results are summarized in Eq. AIII-1. (None

of the analogous reactions for niobium have been investigated as yet.)



Experimental

1. Preparation of $[\text{Ta}(\mu\text{-CSiMe}_3)(\text{CH}_2\text{SiMe}_3)_2]_2$ (69).

a. from $(\text{Me}_3\text{SiCH}_2)_3\text{TaCl}_2$ [VII-39].

$\text{Mg}(\text{CH}_2\text{SiMe}_3)_2(\text{diox})$ (1.44 g, 5 mmol) in 10 mL of ether was added dropwise with stirring to $(\text{Me}_3\text{SiCH}_2)_3\text{TaCl}_2$ (2.57 g, 5 mmol) in 20 mL of ether at RT. The yellow solution became orange as the MgCl_2 salts precipitated. After one hr. the reaction was filtered and the orange filtrate was heated at reflux overnight. The orange solution was filtered again and the solvent volume was reduced in vacuo. The product was recovered by cooling the concentrated ether solution to -30°C . The crude product was then recrystallized from pentane at -30°C to give orange crystals of 69. The yield was 1.90 g (86%). NOTE: Without heating the yield is 1.06 g (48%).

b. from $\text{Me}_3\text{SiCH}=\text{Ta}(\text{CH}_2\text{SiMe}_3)_3$ [VIII-53].

$\text{Me}_3\text{SiCH}=\text{Ta}(\text{CH}_2\text{SiMe}_3)_3$ (0.53 g, 1 mmol) was dissolved in 5 mL of pentane and heated to 35°C in a closed flask for 12 hrs. The orange solution was filtered and the solvent was removed from the filtrate in vacuo to give orange crystals of 69. The yield was 0.43 g (98%).

^1H NMR (τ , C_6D_6 , 35°C, 90 MHz): 9.00 (s, 8, $-\text{CH}_2\text{SiMe}_3$), 9.45 (s, 36, $-\text{CH}_2\text{SiMe}_3$), 9.79 (s, 18, $\equiv\text{CSiMe}_3$).

^{13}C NMR (τ , ppm, C_6D_6 , 28°C, 15 MHz, ^1H gated decoupled): 404.7 (s, $\equiv\text{CSiMe}_3$), 79.2 (t, $J_{\text{CH}}=105$ Hz, $-\text{CH}_2\text{SiMe}_3$), 5.1 (q, $J_{\text{CH}}=119$ Hz, $\equiv\text{CSiMe}_3$), 3.9 (q, $J_{\text{CH}}=119$ Hz, $-\text{CH}_2\text{SiMe}_3$).

2. Preparation of $\text{Me}_3\text{SiCH}=\text{Ta}(\text{CH}_2\text{SiMe}_3)_3$ (70) [VIII-53].

$\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$ (diox) (1.44 g, 5 mmol) in 20 mL of cold ether was added dropwise with stirring to $(\text{Me}_3\text{SiCH}_2)_3\text{TaCl}_2$ (2.57 g, 5 mmol) in 50 mL of ether at -30°C. The reaction was stirred for 20 mins. at -30°C. The yellow solution became orange as the MgCl_2 salts precipitated. The mixture was allowed to warm to RT for 5 mins. and was then cooled to -30°C again. The cold solution was filtered. The solvent was removed from the filtrate in vacuo to give orange crystals of 70. The yield was 2.46 g (93%). The product can be recrystallized from pentane at -30°C if desired. The product was stored at -30°C.

^1H NMR (τ , C_6D_6 , 35°C, 60 MHz): 4.30 (s, 1, $=\text{CHSiMe}_3$), 9.21 (s, 6, $-\text{CH}_2\text{SiMe}_3$), 9.65 (s, 9, $=\text{CHSiMe}_3$), 9.83 (s, 27, $-\text{CH}_2\text{SiMe}_3$).

^{13}C (^1H) NMR (τ , ppm, C_6D_6 , 28°C, 15 MHz): 240.9 (s, $=\text{CHSiMe}_3$), 85.8 (s, $-\text{CH}_2\text{SiMe}_3$), 5.2 (s, $=\text{CHSiMe}_3$), 3.8 (s, $-\text{CH}_2\text{SiMe}_3$).

3. Preparation of $\text{Me}_3\text{SiCH}=\text{Ta}(\text{CH}_2\text{SiMe}_3)_3(\text{PMe}_3)$ (71) [VIII-41].

$(\text{Me}_3\text{SiCH}_2)_3\text{TaCl}_2$ (1.54 g, 3 mmol) and PMe_3 (0.69 g, 9 mmol, 2 fold excess) were dissolved in 20 mL of ether and cooled to -30°C . Then $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2(\text{diox})$ (0.86 g, 3 mmol) in 20 mL of cold ether was added dropwise with stirring to the yellow solution. The solution became orange as MgCl_2 salts precipitated and was allowed to warm to RT. The solution was filtered. The solvent was removed from the filtrate in vacuo to give 71 as an orange microcrystalline solid. The yield was 1.74 g (96%). The product can be recrystallized from pentane at -30°C if desired.

^1H NMR (#404, τ , C_6D_6 , 35°C , 60 MHz); 3.86 (s, 1, $=\text{CHSiMe}_3$), 9.00 (d, 9, $^2J_{\text{HP}}=5.0$ Hz, PMe_3), 9.80 (s, 9, $=\text{CHSiMe}_3$), 9.80 (s, 27, $-\text{CH}_2\text{SiMe}_3$), 9.84 (s, 6, $-\text{CH}_2\text{SiMe}_3$).

^{13}C NMR (#142, ppm, C_6D_6 , 28°C , 15 MHz, ^1H gated decoupled): 251.8 (d, $J_{\text{CH}}=96$ Hz, $=\text{CHSiMe}_3$), 77.3 (t, $J_{\text{CH}}=106$ Hz, $-\text{CH}_2\text{SiMe}_3$), 16.5 (q, $J_{\text{CH}}=130$ Hz, $J_{\text{CP}}=12$ Hz, PMe_3), 4.2 (q, $J_{\text{CH}}=118$ Hz, $=\text{CHSiMe}_3$), 3.6 (q, $J_{\text{CH}}=118$ Hz, $-\text{CH}_2\text{SiMe}_3$).

4. Reaction of $[\text{Ta}(\mu\text{-CSiMe}_3)(\text{CH}_2\text{SiMe}_3)_2]_2$ with PMe_3 .

a. thermally [VIII-36].

$[\text{Ta}(\mu\text{-CSiMe}_3)(\text{CH}_2\text{SiMe}_3)_2]_2$ (0.044 g, 0.05 mmol) and PMe_3 (0.038 g, 0.5 mmol, 5 equivalents per Ta) were dissolved in 0.5 mL of benzene in a NMR tube. The reaction was monitored by ^1H NMR (#401). The sample was allowed to stand for one day each at RT, 80°C , and 100°C . After each day the ^1H NMR spectrum showed that no reaction had occurred. The sample was heated to 130°C for one day and the orange solution began to darken

in color. The ^1H NMR spectrum showed that a trace of TMS was present. The sample was heated to 140°C for six days as some solid material formed. After each day the ^1H NMR spectrum showed that the amount of starting material decreased as the amount of TMS increased. No other peaks appeared. At the end only PMe_3 and TMS were present in the dark brown solution.

b. photolytically [VIII-40].

$[\text{Ta}(\mu\text{-CSiMe}_3)(\text{CH}_2\text{SiMe}_3)_2]_2$ (0.044 g, 0.05 mmol) and PMe_3 (0.038 g, 0.5 mmol, 5 equivalents per Ta) were dissolved in 0.5 mL of pentane in a NMR tube. The reaction was monitored by ^1H NMR (#408). The ^1H NMR spectrum prior to irradiation with a Hg vapor lamp showed no reaction as expected. The sample was irradiated for 2.5 hrs. The solution had become dark brown. The ^1H NMR spectrum showed only starting materials. The sample was irradiated for another 6.5 hrs. The solution was very dark. The ^1H NMR spectrum showed that some TMS was present while the amount of starting material had decreased. The sample was irradiated for an additional 11 hrs. The ^1H NMR spectrum showed that more TMS was present while the amount of starting material had continued to decrease. No new peaks appeared.

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BIOGRAPHICAL NOTE

Gregory A. Rupprecht was born October 31, 1953 in Trenton, NJ and is the son of Robert A. Rupprecht (son of Mr. and Mrs. John B. Rupprecht) and Kathleen J. Rupprecht (daughter of Mr. and Mrs. Joseph L. Mooney). He attended grammar school in Levittown, PA and Cherry Hill, NJ. In June, 1971 he graduated second in his class from Christian Brothers Academy in Syracuse, NY.

He enrolled at the University of Notre Dame, College of Science, in September, 1971. During this time he majored in chemistry and performed research under Professor W. Robert Scheidt on the stereochemistry of metalloporphyrins and their derivatives. He was elected to Phi Beta Kappa and received his B.S. degree, summa cum laude, in chemistry in May, 1975.

In September, 1975 he enrolled at the Massachusetts Institute of Technology in the Graduate School in the Department of Chemistry. There he investigated the organometallic chemistry of niobium and tantalum under Professor Richard R. Schrock. He explored new methods for the catalytic oligomerization and metathesis of olefins. He was elected to Sigma Xi and graduated with a Ph. D. degree in inorganic chemistry in August, 1979.

On June 11, 1977 he married Kathleen D. McFadden in Springfield, PA. He is interested in photography and enjoys soccer and tennis. His next position will be as a postdoctoral research associate under Professor Walter G. Klemperer at Columbia University, where he will study the interaction of polymolybdates and polytungstates with organometallic species.