SYNTHESIS AND REACTIVITY OF PHENYLIMIDO AND ALKYLIDYNE COMPLEXES OF TUNGSTEN(VI)

BY

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B.S., University of California at Los Angeles
(1978)

SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

May 18, 1983

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To my parents

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ABSTRACT

Chapter 1.

Phenylimido neopentylidene complexes of the type $W(NPh)(CHCMe_3)L_2Cl_2$ (L = PMe_3 or PEt_3) were prepared by reacting $W(NPh)(OCMe_3)_4$ with $Ta(CHCMe_3)L_2Cl_3$. $[W(NPh)(CHCMe_3)L_2R]^+$ (R = Cl or Me), $W(NPh)(CHCMe_3)(OCMe_3)_2L$, and $W(NPh)(CHCMe_3)(L)Cl_2$ were prepared straightforwardly from $W(NPh)(CHCMe_3)L_2Cl_2$. $W(NPh)Np_3Cl$ (Np = CH_2CMe_3) was prepared from $W(NPh)Cl_4$ and NpMgCl, and from it $W(NPh)(CHCMe_3)Np_2$ and $WCp(NPh)(CHCMe_3)Np$ by α-hydrogen abstraction reactions. $W(NPh)Np_3Cl$ reacts with LHCl (L = PMe_3 or py) in the presence of excess L to give $W(NPh)(CHCMe_3)L_2Cl_2$, presumably via unobservable $W(NPh)Np_2(L)Cl_2$. $W(NPh)(CH_2SiMe_3)_4$, which can be prepared from $W(NPh)(CH_2SiMe_3)_3Cl$ and $LiCH_2SiMe_3$, decomposes smoothly in a first order reaction ($\Delta H^{\ddagger}$ = 22 ±2 kcal mol^{-1}, $\Delta S^{\ddagger}$ = -8 ±4 eu) to give $W(NPh)(CHSiMe_3)(CH_2SiMe_3)_2$ while $W(NPh)(CH_2SiMe_3)_2Cl_2$ reacts with L = PMe_3 or PEt_3 to give $W(NPh)(CHSiMe_3)L_2Cl_2$. Several miscellaneous phenylimido alkyl complexes such as $W(NPh)R_3Cl$ (R = Me or Bz), $WCp(NPh)Me_3$, and $W(NPh)R_3(OCMe_3)$ (R = Me, Bz, Np) were also prepared. $W(NPh)(CCMe_3)(PMe_3)_2Cl(AlMe_2Cl)$, a tungsten neopentylidyne complex, was also synthesized by the decomposition of $[W(NPh)(CHCMe_3)(PMe_3)_2Me][AlMe_2Cl_2]$.

Chapter 2.

The reaction between $W(CCMe_3)(dimethoxyethane)Cl_3$ and excess dialkyl acetylenes yields a mixture of $[W(\eta^5\text{-}C_5R_4CMe_3)Cl_4]_2$ and $W(\eta^5\text{-}C_5R_4CMe_3)(RC{\equiv}CR)Cl_2$. Addition of one equivalent of alkyne yields monomeric tungstenacyclobutadiene complexes, $W[C(CMe_3)C(R)C(R)]Cl_3$. An X-ray structural analysis of $W[C(CMe_3)C(Me)C(Me)]Cl_3$ showed it to be a trigonal bipyramidal molecule containing axial chloride ligands and a planar WC_3 ring in which the W-C_α bondlengths are equivalent (1.861(9) and 1.864(8)Å), the C_α-C_β-C_α angle is large (118.9(8)°), and the W•••C_β bondlength (2.115(8)Å) is significantly shorter than a typical W(VI)-alkyl single bond.

A systematic investigation of the effect alkoxide ligands have on these metallacyclobutadiene complexes was undertaken by replacing the chloride ligands on $W[C(CMe_3)C(R)C(R)]Cl_3$ with t-butoxy, 2,3-dimethyl-2,3-butanediolate and 2,3,3,4-tetramethyl-2,4-pentanediolate ligands. $W[C(CMe_3)C(R)C(R)](OCMe_3)Cl_2$, $W[C(CMe_3)C(Me)C(Me)](diolate)Cl$ and $W[C(CMe_3)C(Me)C(Me)](diolate)(OCMe_3)$ were prepared and their reactivity with alkynes was investigated. $W[C(CMe_3)C(Me)C(Me)](OCMe_2CMe_2O)(OCMe_3)$ reacts with 2-butyne to give 2,3-dimethyl-2-butene and $W(\eta^5\text{-}C_5Me_4CMe_3)(O)_2(OCMe_3)$.

$W(C_3Et_3)(OCMe_2CMe_2O)(OCMe_3)$ can be isolated from an active alkyne metathesis mixture of $W(CEt)(OCMe_3)_3$ and 3-hexyne by adding pinacol. In the presence of additional 3-hexyne $W(C_3Et_3)(OCMe_2CMe_2O)(OCMe_3)$ yields 2,3-dimethyl-2-butene and $W(\eta^5\text{-}C_5Et_5)(O)_2(OCMe_3)$ quantitatively.

$W(\eta^5\text{-}C_5Et_5)(O)_2(OCMe_3)$ is also isolated from the reaction of $W(CEt)(OCMe_3)_3$ with a large excess of 3-hexyne, thereby identifying the primary decomposition pathway open to these types of alkyne metathesis catalysts.

CHAPTER 3.

Several miscellaneous tris-alkoxy tungsten(VI) alkylidyne complexes were prepared. Included are: $W(CCMe_3)(1,2\text{-dimethoxyethane})Cl_3$; $[W(CR)(OPr^i)_3]_2$ (R = Et, CMe_3); $[W(CCMe_3)(OCH_2CMe_3)_3]_2$; $[W(CCMe_3)(OR)_3(HNMe_2)]_2$ (R = Me, Ph); $[W(CCMe_3)(OR)_3]_x$ (R = Me, Et); $W(CCMe_3)(OCEt_3)_3$; and $W(CCMe_3)(OCMe_3)_2(2\text{-}(O)C_6H_4CHNMe)$. Some monodialkylamido neopentylidyne complexes were also synthesized: $[W(CCMe_3)(NR_2)Cl_3][NEt_4]$ (R = Et, Pr^i); $W(CCMe_3)(NMe_2)(PEt_3)Cl_2$; and $W(CCMe_3)(NPr^i{}_2)(OCMe_3)_2$.

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LIST OF SCHEMES

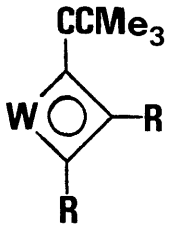
LIST OF ABBREVIATIONS USED IN TEXT

br	broad
t-butyl	tertiary butyl
Bz	benzyl
C_α	alpha carbon, directly bonded to metal
Cp	cyclopentadienyl
d	doublet
dme	1,2-dimethoxyethane
dmpe	1,2-bis(dimethylphosphine)ethane, $Me_2PCH_2CH_2PMe_2$
GC	gas chromatography
h	heptet
H_α	alpha hydrogen, directly bonded to C_α
IR	infrared
m	multiplet
Me	methyl
NMR	nuclear magnetic resonance
Np	neopentyl
Ph	phenyl
Pr	propyl
Pr^i	isopropyl
py	pyridine
q	quartet

(ABBREVIATIONS, cont'd)

R	alkyl or aryl
s	singlet
t	triplet
thf	tetrahydrofuran
tmeda	tetramethylethylenediamine

$W(CCMe_3C_2R_2)$



GENERAL INTRODUCTION

Only in the last four years has tungsten(VI) organometallic chemistry truly blossomed. Before 1979, there were few examples of such complexes and all of these, with the exception of one (and its derivatives), consisted of metal-carbon single bonds.[1] The exception was the tungsten neopentylidyne complex, $W(CCMe_3)Np_3$.[2] From this came the first tungsten(VI) alkylidene complex, $W(CCMe_3)(CHCMe_3)(CH_2CMe_3)(dmpe)$.[3] This ylenyne (yl-en-yne) provided a unique opportunity to compare metal-carbon bond distances and M-C_α-C_β angles in a neopentyl, a neopentylidene, and a neopentylidyne ligand, all bound to the same metal.[3]

The surge in syntheses of d^0 tungsten complexes containing metal-carbon multiple bonds began with the oxo alkylidene complex, $W(O)(CHCMe_3)(PEt_3)_2Cl_2$.[4] This species was prepared by a rather unusual ligand exchange reaction between a tantalum neopentylidene complex ($Ta(CHCMe_3)(PEt_3)_2Cl_3$) and a tungsten(VI) t-butoxy complex ($W(O)(OCMe_3)_4$). In this reaction all of the t-butoxy ligands on tungsten are exchanged for the neopentylidene group, two chlorides, and two phosphine ligands on tantalum. The most exciting feature of this new alkylidene complex is that it catalyzes the olefin metathesis reaction in the presence of Lewis acids.[5] The interest generated by this observation prompted us to investigate the synthesis and reactivity of isoelectronic imido alkylidene complexes (Chapter 1).

$W(CCMe_3)Np_3$, a molecule which disappeared from the "scene" for synthetic reasons (poor yields and scale-up difficulties) reappeared in 1980 when Sancho and Schrock[2] found a new, high-yield route to this complex. Soon thereafter it was discovered that the neopentyl groups in this complex could be selectively removed with HCl to give trichloroneopentylidyne

complexes.[2] These species have proved to be extremely versatile starting materials for the synthesis of a large class of new tungsten(VI) alkylidyne complexes.[2]

An important series of molecules to come from these reactions are the tris-alkoxy and tris-dialkylamido neopentylidyne complexes[2] since these species catalyze the alkyne metathesis reaction.[6] This observation suggested that the alkylidyne ligand might be the chain-carrying intermediate in such reactions.[7] Prior to this only a few reports concerned with transition metal catalyzed alkyne metathesis had appeared in the literature[8] and none of these provided any clues as to what the mechanism of this reaction might be.

Besides serving as a chain-carrying intermediate in alkyne metathesis reactions, the tungsten(VI) neopentylidyne ligand is an extremely versatile functional group in high oxidation state tungsten organometallic chemistry (Figure 1).

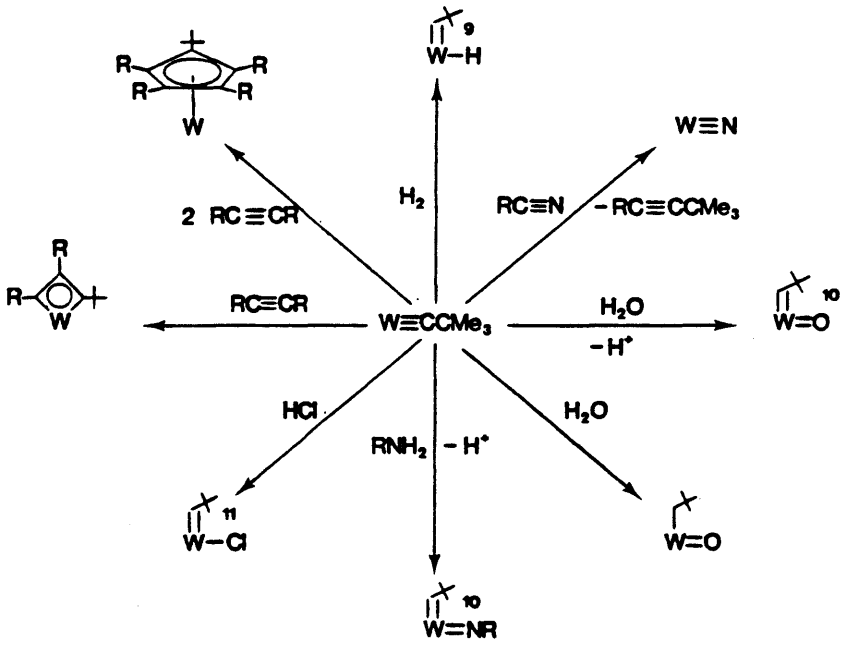


Figure 1

Chapters 2 and 3 are concerned with the chemistry of tungsten(VI) alkylidynes. In Chapter 2 I have focused on the reactivity of such species with alkynes, all the time attempting to relate our observations to the alkyne metathesis reaction. Chapter 3 deals with the preparation of a variety of tungsten(VI) alkylidyne complexes.

CHAPTER 1

Preparation of Tungsten(VI) Phenylimido Alkyl and Alkylidene Complexes

INTRODUCTION

The preparation of a large number of (primarily) neopentylidene complexes of niobium and tantalum in the past several years has depended largely on the α-hydrogen atom abstraction reaction.[12] Naturally, we have been interested in the extent to which the principles which govern Nb and Ta d^0 alkyl chemistry might extend to Group VI metal alkyl chemistry. However, testing these principles has been hampered by the fact that only a relatively small number of well-characterized Mo(VI) and W(VI) alkyls have been reported,[1] a fact which is largely the result of the unpredictable redox and disproportionation reactions which occur in the synthesis of such molecules.[13]

The first W(VI) alkylidene complex to be prepared was $W(CCMe_3)(CHCMe_3)(CH_2CMe_3)L_2$ (L = PMe_3 or 1/2 dmpe).[3] The reaction which gave it ($W(CCMe_3)(CH_2CMe_3)_3$ plus L) is a ligand induced α-hydrogen abstraction reaction (if we assume the neopentylidyne ligand plays no direct role). Later we showed that oxo alkylidene complexes ($W(O)(CHCMe_3)L_2Cl_2$; L = PR_3) could be prepared by transferring a neopentylidene ligand from tantalum to tungsten in exchange for two t-butoxide ligands.[4] The common feature of these two types of tungsten alkylidene complexes is the presence of a strong π-bonding ligand (a neopentylidyne ligand or an oxo ligand). Therefore, we considered preparing and studying tungsten alkyl complexes containing an ostensibly even better π-bonding ligand than the oxo ligand, the imido ligand.[14] In this chapter I describe the preparation of one type of phenylimido neopentylidene complex by neopentylidene ligand transfer from tantalum to tungsten, along with the preparation of several phenylimido alkyl complexes and how some of them can be converted into alkylidene

complexes by α-hydrogen abstraction reactions. The majority of this work has been published.[15]

RESULTS

Preparation of Imido Neopentylidene Complexes via Neopentylidene Ligand Transfer

The first task was to show that imido alkylidene complexes are stable species. We prepared one type by an alkylidene ligand transfer reaction (eq 1) which is entirely analogous to that used to prepare $W(O)(CHCMe_3)L_2Cl_2$

$$W(NPh)(OCMe_3)_4 + Ta(CHCMe_3)L_2Cl_3 \longrightarrow 0.5\,[Ta(OCMe_3)_4Cl]_2 + \begin{matrix} & L & \\ Cl & | & NPh \\ Cl & W & \\ & | & CHCMe_3 \\ & L & \end{matrix} \qquad (1)$$

$$L = PMe_3, PEt_3$$

complexes.[4] The required $W(NPh)(OCMe_3)_4$ complex can be prepared straightforwardly and in high yield (>90%) from $W(NPh)Cl_4(Et_2O)$. The etherate is derived from $[W(NPh)Cl_4]_n$, which in turn is prepared in large quantities from $W(O)Cl_4$ and phenylisocyanate in refluxing octane (eq 2).[16]

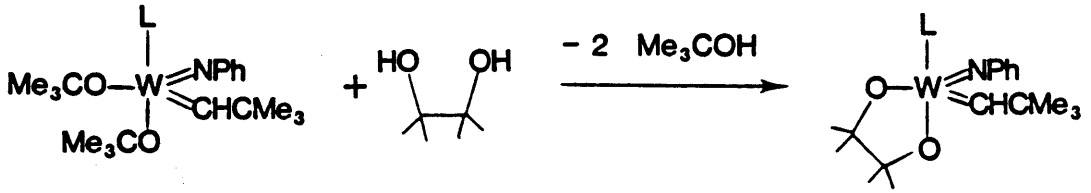
$$W(O)Cl_4 + PhNCO \xrightarrow{\text{octane}} [W(NPh)Cl_4]_n + CO_2 \qquad (2)$$

The two $W(NPh)(CHCMe_3)L_2Cl_2$ complexes appear to be entirely analogous to their oxo analogs. The imido and neopentylidene ligands are cis to one another and the phosphine ligands are trans to one another. The imido ligand should be linear[14] and the β-carbon of the neopentylidene ligand should lie in the same plane in which the imido nitrogen and the tungsten atoms lie. Therefore two isomers are possible, depending on which way the alkylidene ligand is oriented. We observe only one isomer; we assume the

one in which the t-butyl group points toward the imido ligand (cf., W(O)-$(CHCMe_3)L_2Cl_2$[17]). Pertinent ^1H and ^{13}C NMR data for these and other phenylimido alkylidene complexes we will be discussing are listed in Table I.

Several other imido neopentylidene complexes can be prepared from $W(NPh)(CHCMe_3)L_2Cl_2$ (Figure 1). In most cases the oxo analog is known. The main difference between an oxo and an imido complex is the greater stability of the latter, in general. For example, $W(NPh)(CHCMe_3)(OCMe_3)_2L$ ($L = PMe_3$, PEt_3) are stable in solution and have been shown to have labile phosphine ligands by ^1H NMR. The oxo analogs also have labile phosphine ligands; however, these complexes are unstable in solution, the major identifiable decomposition products being trialkylphosphine oxides.[4] We have seen no evidence for the corresponding trialkylphosphinimine, R_3PNPh, from any phenylimido alkylidene complex.

It is of interest to note that we prepared some chelate alkoxide derivatives from the action of $LiOCMe_2CMe_2OLi$ on $W(NPh)(CHCMe_3)(PMe_3)_2Cl_2$ or from $W(NPh)(CHCMe_3)(OCMe_3)_2L$ as shown in eq 3. The phosphine ligand in



(3)

these complexes is <u>not</u> labile, most likely the result of the lessened steric demands of the pinacol ligand relative to two t-butoxide ligands.

Another example of this enhanced stability of imido versus oxo neopentylidene complexes is found when one compares the stabilities of $[W(O)(CHCMe_3)L_2Me][AlMe_2Cl_2]$ and $[W(NPh)(CHCMe_3)L_2Me][AlMe_2Cl_2]$. The oxo

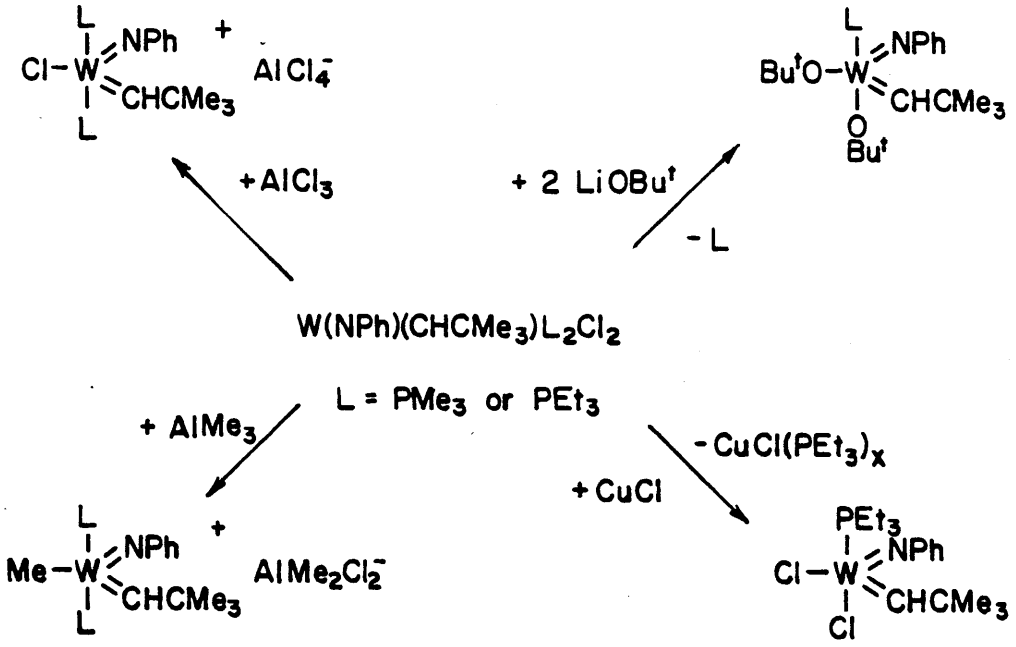


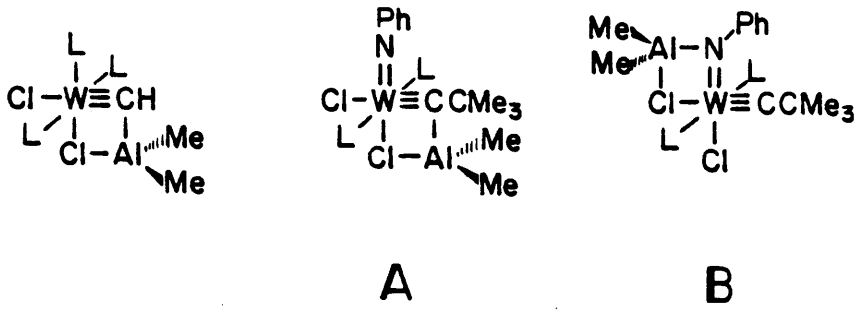
Figure 1. Preparation of some phenylimidoalkylidene complexes from $W(NPh)(CHCMe_3)L_2Cl_2$.

complex decomposes readily in solution at 25° ($t_{1/2} \approx 5$ min in $CDCl_3$) to unidentified products,[4] but the analogous phenylimido complex is stable in $CDCl_3$ at 25°.

When $[W(NPh)(CHCMe_3)(PMe_3)_2Me][AlMe_2Cl_2]$ does decompose (60° in toluene) methane evolves steadily and a single product can be isolated in high yield (eq 4). This new complex is soluble in pentane and does not conduct in dichloromethane, two facts which suggest that it is not ionic.

$$[W(NPh)(CHCMe_3)(PMe_3)_2Me][AlMe_2Cl_2] \xrightarrow[60°]{\text{toluene}} W(NPh)(CCMe_3)(PMe_3)_2Cl(AlMe_2Cl) + CH_4 \quad (4)$$

We observe signals for a pair of <u>trans</u> PMe_3 groups and two equivalent aluminum methyl groups in the ^1H NMR spectrum, and in the $^{13}C\{^1H\}$ NMR spectrum, a triplet resonance for C_α at 309.4 ppm ($^2J_{CP}$ = 12 Hz) which does not split into a doublet in the gated proton decoupled spectrum. Therefore, this product is most likely a phenylimido neopentylidyne complex. Two structures for $W(NPh)(CCMe_3)(PMe_3)_2Cl(AlMe_2Cl)$ consistent with the NMR data are shown in Figure 2. Although in one of these (A) the $AlMe_2Cl$ group is bound in a manner similar to the way it is bound in $W(CH)(PMe_3)_3Cl(AlMe_2Cl)$,[18] we favor the alternative (B) for two reasons. First, the imido ligand is not likely to be able to effectively donate its π-electron density to the metal in competition with the neopentylidyne ligand. Therefore, it should not be linear, i.e., its π-electron pair should be exposed and easily attacked by a Lewis Acid. Second, the t-butyl group should make coordination of the Lewis Acid to the neopentylidyne ligand much more difficult for steric reasons than coordination of the Lewis Acid to the methylidyne ligand.



A B

Figure 2. Structure of $W(CH)(PMe_3)_3Cl(AlMe_2Cl)$ and proposed structures for $W(NPh)(CCMe_3)(PMe_3)_2Cl(AlMe_2Cl)$.

Table I. Pertinent ^{1}H and ^{13}C NMR Data for Phenylimidoalkylidene Complexes.[a]

Compound	$^{1}H_{\alpha}$ (ppm)	$^{13}C_{\alpha}$ (ppm)	$J_{CH_{\alpha}}$ (Hz)
$W(NPh)(CHCMe_3)(PMe_3)_2Cl_2$	10.92	307	123[b]
$W(NPh)(CHCMe_3)(PEt_3)_2Cl_2$	11.92	304	119[c]
$[W(NPh)(CHCMe_3)(PMe_3)_2Cl][AlCl_4]$	10.39	303	106
$[W(NPh)(CHCMe_3)(PEt_3)_2Cl][AlCl_4]$	9.6	301	106
$W(NPh)(CHCMe_3)(PMe_3)(OCMe_3)_2$	10.17	265	114
$W(NPh)(CHCMe_3)(PEt_3)(OCMe_3)_2$	10.27	266	111[d]
$[W(NPh)(CHCMe_3)(PMe_3)_2Me][AlMe_2Cl_2]$	8.40	303	106
$[W(NPh)(CHCMe_3)(PEt_3)_2Me][AlMe_2Cl_2]$	7.84	301	105
$W(NPh)(CHCMe_3)(PEt_3)Cl_2$	10.8	301	106[e]
$W(NPh)(CHCMe_3)(CH_2CMe_3)_2$	6.61	246	106
$W(NPh)(CHSiMe_3)(CH_2SiMe_3)_2$	7.79	230	108
$W(\eta^5\text{-}C_5H_5)(NPh)(CHCMe_3)(CH_2CMe_3)$	9.81	269	117
$W(NPh)(CHSiMe_3)(PMe_3)_2Cl_2$	12.75	293	119
$W(NPh)(CHCMe_3)(py)_2Cl_2$	11.3	303	121
$W(NPh)(CHCMe_3)(PMe_3)(OCMe_2CMe_2O)$	9.66	267	112
$W(NPh)(CHCMe_3)(PEt_3)(OCMe_2CMe_2O)$	9.77	268	116

[a] Full details can be found in the Experimental Section.

[b] $J_{CH_{\alpha}}$ = 121 Hz in the analogous oxo complex.

[c] $J_{CH_{\alpha}}$ = 126 Hz in the analogous oxo complex.

[d] $J_{CH_{\alpha}}$ = 119 Hz in the analogous oxo complex.

[e] $J_{CH_{\alpha}}$ = 115 Hz in the analogous oxo complex.

Preparation of Imido Neopentyl and Neopentylidene Complexes by Direct Methods

After demonstrating that phenylimido neopentylidene complexes are stable and isolable, we wanted to demonstrate that imido neopentyl complexes can be prepared and converted into neopentylidene complexes by α-hydrogen abstraction reactions.

Yellow, sublimable $W(NPh)Np_3Cl$ ($Np = CH_2CMe_3$) is best prepared by adding three equivalents of NpMgCl to $W(NPh)Cl_4(Et_2O)$ in ether at -78°. It is a monomer in dichloromethane. Its NMR spectra are consistent with it being a trigonal bipyramid in which the three alkyl ligands occupy the equatorial positions. An analogous reaction between $W(NPh)(OCMe_3)_4$ and NpMgCl yields $W(NPh)Np_3(OCMe_3)$. Interestingly, $W(NPh)Np_3(OCMe_3)$ reacts in toluene with one equivalent of HCl gas to give $W(NPh)Np_3Cl$ quantitatively. Other derivatives can be prepared similarly (eq 5). This reaction appears to be quite general and should be applicable to the preparation of a variety of compounds with the general formula $W(NPh)R_3X$, starting from the appropriate t-butoxy complex and HX.

$$W(NPh)(CH_2CMe_3)_3(OCMe_3) + HX \longrightarrow W(NPh)(CH_2CMe_3)_3X \qquad (5)$$
$$X = Cl, Br, O_2CCF_3$$

All attempts to prepare $W(NPh)Np_2Cl_2$ were unsuccessful. However, we felt that replacing the chloride ligand(s) in this molecule with t-butoxide(s) might allow us to isolate a dineopentyl derivative. Our first attempt was the reaction of two equivalents of NpMgCl with $W(NPh)(OCMe_3)_4$ which resulted in a mixture of products. We therefore set out to prepare mixed t-butoxy/chloride complexes, hoping that the chlorides could be selectively substituted with alkyls.

$W(NPh)(OCMe_3)_2Cl_2$ may be prepared *in situ* by mixing one equivalent each of $W(NPh)Cl_4(Et_2O)$ and $W(NPh)(OCMe_3)_4$ in dichloromethane. The resultant solution begins to darken shortly after the equilibration is complete. 2-methylpropene and t-butyl chloride are the organic products found in solution. Such decomposition reactions (generally resulting in the formation of oxo-containing compounds) are not uncommon for alkoxy/halide species of early transition metals in high oxidation states.[19] This decomposition process was slowed down when the reaction was done in ether, possibly due to the coordinating ability of the ether oxygen. Subsequently, a better Lewis base was tried and when NEt_4Cl was codissolved with $W(NPh)Cl_4(Et_2O)$ and $W(NPh)(OCMe_3)_4$ in dichloromethane, a quantitative yield of yellow, crystalline $[NEt_4][W(NPh)(OCMe_3)_2Cl_3]$ is obtained (eq 6). This ionic complex appears to be stable indefinitely in dichloromethane. Brick

$$W(NPh)Cl_4(Et_2O) + W(NPh)(OCMe_3)_4 + 2\ NEt_4Cl \xrightarrow{CH_2Cl_2} 2\ [NEt_4][W(NPh)(OCMe_3)_2Cl_3] \quad (6)$$

red $[NEt_4][W(NPh)(OCMe_3)Cl_4]$ is also obtained in quantitative yield by simply rearranging the stoichiometry in eq 6 (eq 7).

$$3\ W(NPh)Cl_4(Et_2O) + W(NPh)(OCMe_3)_4 + 4\ NEt_4Cl \xrightarrow{CH_2Cl_2} 4\ [NEt_4][W(NPh)(OCMe_3)Cl_4] \quad (7)$$

$[Et_4N][W(NPh)(OCMe_3)_2Cl_3]$ reacts cleanly with $ZnNp_2$ in CH_2Cl_2 to afford $W(NPh)Np_2(OCMe_3)_2$ in high yield (eq 8). The ^1H NMR spectrum of this

$$[Et_4N][W(NPh)(OCMe_3)_2Cl_3] + ZnNp_2 \xrightarrow{CH_2Cl_2} Me_3CO\text{–}W(Ph)(Np)_2(OCMe_3) + [Et_4N][ZnCl_3] \quad (8)$$

species at -10°C is consistent with the structure shown. At higher temperatures the signals for the two t-butoxy ligands broaden due to exchange of the axial and equatorial t-butoxy groups. However, the AB patterns for the α protons in the neopentyl ligands do not change. Therefore, the intermediate in the exchange process does not contain a plane of symmetry which passes through the α-carbon atoms of the neopentyl ligands. The intermediate we favor is a cis tetragonal pyramid with the imido ligand at the apex.

An analogous reaction between $[Et_4N][W(NPh)(OCMe_3)Cl_4]$ and $ZnNp_2$ gave yellow $W(NPh)Np_2(OCMe_3)Cl$. Only one isomer is observed. We suspect the t-butoxide ligand is in an equatorial position where it would not compete as a π-electron donor with the phenylimido ligand.

An attempt to prepare $W(NPh)Np_4$ from $W(NPh)Np_3Cl$ and LiNp yields the complex shown in eq 9. $W(NPh)(CHCMe_3)Np_2$ is a red oil which can be puri-

$$W(NPh)Np_3Cl + LiNp \xrightarrow[-CMe_4]{-LiCl} W(NPh)(CHCMe_3)Np_2 \qquad (9)$$

fied by high vacuum, short path distillation. Pertinent ^1H and ^{13}C NMR data are given in Table I. A molecular weight determination confirmed that it is a monomer. It may also be prepared by reacting $W(NPh)Np_3Cl$ with $Ph_3P{=}CH_2$ in ether. $W(NPh)(CHCMe_3)Np_2$ resembles $Ta(CHCMe_3)Np_3$ in some of its reactions. For example, it reacts with one equivalent of HCl to give $W(NPh)Np_3Cl$,[20] and with an excess of dry acetone to yield 2,4,4-trimethyl-2-pentene (80%) and presumably $W(NPh)(O)Np_2$.[21]

We wanted to prepare $WCp(NPh)Np_2Cl$ ($Cp = \eta^5\text{-}C_5H_5$) in order to compare an α-hydrogen abstraction reaction in a W(VI) complex with that which is

best studied for tantalum, that is, decomposition of $TaCpNp_2Cl_2$ to give $TaCp(CHCMe_3)Cl_2$.[22] Clearly, the most convenient route to $W(NPh)CpNp_2Cl$ would be via a reaction similar to that used in tantalum (i.e., $TaNp_2Cl_3$ + $NaCp$[22]); unfortunately, the synthesis of $W(NPh)Np_2Cl_2$ has proven elusive. We therefore approached the synthesis of $WCp(NPh)Np_2Cl$ in a more circuitous manner. $W(NPh)Np_3Cl$ reacts with NaC_5H_5 as shown in equation 10. We propose that $WCp(NPh)(CHCMe_3)Np$ forms as a result of α-abstraction in

$$W(NPh)Np_3Cl + NaC_5H_5 \xrightarrow[-NaCl,-CMe_4]{THF,\ 36h} WCp(NPh)(CHCMe_3)Np \qquad (10)$$

$WCp(NPh)Np_3$ or as a result of a more complex dehydrohalogenation reaction (cf. preparation of $Ta(CHCMe_3)Np_3$[20]). $WCp(NPh)Np_2Cl$ can then be prepared as shown in eq 11. The ^1H NMR spectrum of $WCp(NPh)Np_2Cl$ consists of

$$WCp(NPh)(CHCMe_3)Np \xrightarrow[pentane]{HCl,-30^\circ} \text{Np–W(Cl)(Np)=NPh} \qquad (11)$$

a single cyclopentadienyl resonance, an AB quartet for the methylene protons of the neopentyl ligands and a singlet for the tert-butyl groups. The spectrum does not change down to -50°. The structure shown in eq 11 is consistent with these data.

We were pleased to find that $WCp(NPh)Np_2Cl$ does decompose in the dark in toluene to neopentane and presumably $WCp(NPh)(CHCMe_3)Cl$ (H_α at 10.5 ppm). Unfortunately, however, the reaction appears to be as complex as some of those in the tantalum cyclopentadienyl system[22] (the light-induced reactions especially). Therefore, this reaction is not a viable preparative route to

$WCp(NPh)(CHCMe_3)Cl$. More recently, McCullough[23] has found a convenient synthesis of this neopentylidene complex (eq 12).

$$WCp(CCMe_3)Cl_2 + PhNH_2 \xrightarrow[-HCl]{\Delta} WCp(NPh)(CHCMe_3)Cl \qquad (12)$$

The unavailability of $W(NPh)Np_2Cl_2$ prevented our examining a ligand-induced α-abstraction reaction analogous to that between MNp_2X_3 and phosphorus, nitrogen, or oxygen donor ligands (M = Nb or Ta; X = Cl or Br[24]). As we might now expect,[20,24] ligand-induced α-abstraction is slow if two t-butoxide ligands are present. An excess of PMe_3 (4 equiv) does not react with $W(NPh)Np_2(OCMe_3)_2$ in benzene upon heating the mixture to 60° for 3.5 days. A noticeable change occurs when a benzene solution of $W(NPh)Np_2(OCMe_3)_2$ containing PEt_3 is irradiated with 360-nm high intensity light from a medium-pressure Hg lamp, but the reaction is obviously complex and was not investigated further.

$W(NPh)(OCMe_3)Np_2Cl$ reacts slowly with excess PMe_3 to give after 30 h in CH_2Cl_2 a small amount of a new alkylidene complex, presumably $W(NPh)(CHCMe_3)(OCMe_3)(PMe_3)_2Cl$. The predominant species in solution is a phosphine adduct of the starting bis-neopentyl complex.

We overcame the problem of the unavailability of $W(NPh)Np_2Cl_2$ and finally accomplished a direct synthesis of $W(NPh)(CHCMe_3)L_2Cl_2$ through the reaction shown in eq 13. We have not examined this reaction in great detail but have made some observations which allow us to suggest a

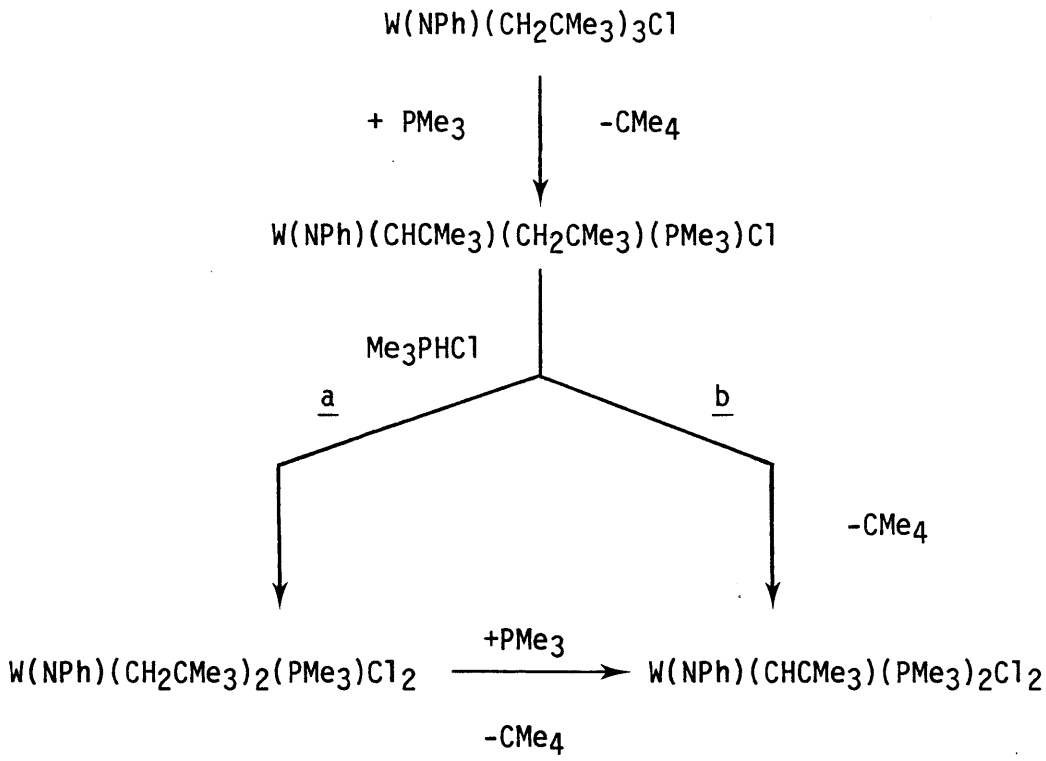
$$W(NPh)Np_3Cl + LHCl + L\ (\text{excess}) \xrightarrow[CHCl_3,\ 24h]{60\text{-}80^\circ} W(NPh)(CHCMe_3)L_2Cl_2 + 2\ CMe_4 \qquad (13)$$

(e.g., L = PMe_3, pyridine)

mechanism. First, in an attempt to prepare $W(NPh)(CHCMe_3)(L)Cl_2$ from $W(NPh)Np_3Cl$ and Et_3PHCl (no excess PEt_3 present) we observed no reaction in $CHCl_3$ after two days at 70°. Apparently, a free Lewis base is necessary to "activate" the tungsten complex. Indeed, PMe_3 alone reacts with $W(NPh)Np_3Cl$ at 70° in C_6D_6 to give neopentane and 2,2,5,5-tetramethyl-3-hexene, the usual product of bimolecular decomposition of a neopentylidene complex.[12] Therefore, we believe that PMe_3 promotes an α-hydrogen abstraction reaction to form $W(NPh)(CHCMe_3)Np(PMe_3)Cl$, which subsequently decomposes under these conditions. In the presence of Me_3PHCl, however, $W(NPh)(CHCMe_3)Np(PMe_3)Cl$ reacts rapidly in one of the two ways shown in Scheme I. In one (a) the alkylidene ligand is protonated to give the bis-neopentyl complex, which should decompose and/or react rapidly with more PMe_3 to give the observed product. In the other (b) the neopentyl ligand itself is protonated. Since we have observed protonation of the neopentylidene ligand in $WCp(NPh)(CHCMe_3)(CH_2CMe_3)$ in preference to the neopentyl ligand (see above), we believe path a is the more likely.

Preparation of Imido Trimethylsilylmethyl and Trimethylsilylmethylidene Complexes

In tantalum chemistry trimethylsilylmethyl complexes almost always can be prepared more simply and in higher yield than neopentyl complexes,[1] perhaps in part because the trimethylsilylmethyl ligand is less susceptible to α-abstraction reactions.[12] Therefore, we hoped to be able to prepare trimethylsilylmethyl analogs of two of the neopentyl species we could not prepare, $W(NPh)Np_2Cl_2$, and the supposed precursor to $W(NPh)(CHCMe_3)Np_2$, $W(NPh)(CH_2CMe_3)_4$.



Scheme I. Possible pathways to $W(NPh)(CHCMe_3)(PMe_3)_2Cl_2$ from $W(NPh)(CH_2CMe_3)_3Cl$, PMe_3(xs), and PMe_3HCl.

Trigonal bipyramidal $W(NPh)(CH_2SiMe_3)_3Cl$ can be prepared from $W(NPh)Cl_4(Et_2O)$ and 1.5 equivalents of $Zn(CH_2SiMe_3)_2$. Addition of $LiCH_2SiMe_3$ to $W(NPh)(CH_2SiMe_3)_3Cl$ in pentane yields yellow, crystalline $W(NPh)(CH_2SiMe_3)_4$. A 250 MHz ^1H NMR spectrum of $W(NPh)(CH_2SiMe_3)_4$ at -85° shows signals for two types of CH_2SiMe_3 groups in a ratio of 3:1, indicative of a trigonal bipyramidal geometry with the NPh group occupying an axial position. At -40° the trimethylsilylmethyl groups begin to equilibrate on the ^1H NMR time scale. Similar fluxional behavior has been observed for $Ta(CH_2CMe_3)_4X$ (X = Cl[20] or $OCMe_3$[25]).

When $W(NPh)(CH_2SiMe_3)_4$ is heated to 60° in toluene one equivalent of tetramethylsilane evolves and $W(NPh)(CHSiMe_3)(CH_2SiMe_3)_2$ can be isolated in high yield as a dark red oil. (NMR data are listed in Table I). The conversion of $W(NPh)(CH_2SiMe_3)_4$ to $W(NPh)(CHSiMe_3)(CH_2SiMe_3)_2$ can be followed by ^1H NMR at 250 MHz. The rate was found to be first order and concentration independent, consistent with an intramolecular α-hydrogen abstraction reaction. Rate constants and activation parameters are given in Table II.

$W(NPh)(CH_2SiMe_3)_2Cl_2$ may be synthesized as shown in eq 14. An excess of $[Et_4N][W(NPh)Cl_5]$ is required to avoid forming a large amount of

$$[Et_4N][W(NPh)Cl_5] + Zn(CH_2SiMe_3)_2 \xrightarrow{CH_2Cl_2} W(NPh)(CH_2SiMe_3)_2Cl_2 + [Et_4N][ZnCl_3] \quad (14)$$

$W(NPh)(CH_2SiMe_3)_3Cl$. An AB pattern for the methylene protons in the ^1H NMR spectrum of $W(NPh)(CH_2SiMe_3)_2Cl_2$ suggests that the molecule is a trigonal bipyramid with the phenylimido group occupying an axial position, but we cannot rule out a square pyramidal structure on the basis of these NMR data alone.

Table II. Kinetic and Activation Parameters for Decomposition of $W(NPh)(CH_2SiMe_3)_4$ in toluene-d_8

T, K	k x 10^3, min^{-1}	$t_{1/2}$
347	74 ± 3	9 ± 0.3
341	45 ± 1	15 ± 0.4
335	25 ± 1	28 ± 1
330	12 ± 0.5	57 ± 2
322	5.7 ± 0.3	122 ± 6
$\Delta H^{\ddagger}$ = 22 kcal ±2 mol^{-1}	$\Delta S^{\ddagger}$ = -8 ±4 eu	

[a] Data were obtained by ^1H NMR integration of the methylene resonances in starting material vs. product vs. time. The rate constant was determined by a linear least-squares fit of the data; correlation coefficients were always > 0.98. Errors in k were determined by a standard statistical method based on standard deviations. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were determined by a least-squares fit of ln (k/T) vs. 1/T. The errors were determined by a standard statistical method based on standard deviations.

We are now in a position to test whether $W(NPh)R_2Cl_2$ complexes can be induced to lose RH on addition of donor ligands, a reaction which we could only infer for R = CH_2CMe_3. $W(NPh)(CH_2SiMe_3)_2Cl_2$ reacts with two equivalents of PMe_3 or PEt_3 in methylene chloride to give $W(NPh)(CHSiMe_3)(PR_3)_2Cl_2$ and Me_4Si. Addition of one equivalent yields a mixture of $W(NPh)(CHSiMe_3)(PEt_3)_2Cl_2$ and $W(NPh)(CH_2SiMe_3)_2Cl_2$ which remains unchanged after heating for two days at 60°. The reason, we propose, is first, that α-abstraction occurs in seven-coordinate $W(NPh)(CH_2SiMe_3)_2(PEt_3)_2Cl_2$, and second, that PEt_3 in $W(NPh)(CHSiMe_3)(PEt_3)_2Cl_2$ is not labile. These results contrast sharply with those found for related tantalum species. For example, a mixture of $Ta(CHCMe_3)(PMe_3)_2Cl_3$ and $Ta(CH_2CMe_3)_2Cl_3$ soon yields $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ quantitatively.[24] The PMe_3 ligands in $Ta(CHCMe_3)(PMe_3)_2Cl_3$ are observed to be quite labile.

Preparation of Some Imido Methyl and Benzyl Complexes

In this section we report the preparation of several methyl and benzyl complexes, a task which we pursued for the sake of completeness. However, as it turns out, some unique methods were needed to synthesize such species and from these endeavors came some very useful synthetic techniques which have now found application in many other systems (e.g., $W(OMe)_3Np_3$[26] and $W(MeC{\equiv}CMe)(CH_2SiMe_3)_3Cl$[27]).

$W(NPh)Cl_4(Et_2O)$ reacts with $ZnMe_2$ to give predominantly an insoluble, uncharacterized precipitate. We speculated that $ZnCl_2$ was the cause of a secondary reaction and therefore devised a method of removing it from the reaction as quickly as possible (eq 15). The tetraethylammonium salt of $ZnCl_3^-$ forms rapidly and is relatively insoluble in dichloromethane.

$$[Et_4N][W(NPh)Cl_5] + 1.5\ ZnMe_2 + 0.5\ NEt_4Cl \xrightarrow[-30°]{CH_2Cl_2} W(NPh)Me_3Cl + 1.5\ [NEt_4][ZnCl_3] \quad (15)$$

Similarly, $W(NPh)Me_3(OCMe_3)$, a yellow oil, can be prepared best by reacting $[Et_4N][W(NPh)(OCMe_3)Cl_4]$ with $ZnMe_2$ in dichloromethane. Although there may be a problem associated with a secondary reaction involving $ZnCl_2$ in this case also, the main problem is that $W(NPh)(OCMe_3)Cl_3$ is not stable enough to use as a starting material. Both $W(NPh)Me_3Cl$ and $W(NPh)Me_3(OCMe_3)$ appear to be trigonal bipyramidal molecules analogous to the neopentyl and trimethylsilylmethyl complexes.

$W(NPh)Me_3Cl$ reacts readily with LiMe in ether to give LiCl and an unstable yellow product. We propose that the product is $W(NPh)Me_4$ but it could not be isolated without extensive decomposition. $W(NPh)Me_3Cl$ also reacts with NaC_5H_5 to give yellow crystalline $WCp(NPh)Me_3$. The fact that two types of methyl ligands are observed by NMR at 25° suggests that $WCp(NPh)Me_3$ is a tetragonal pyramid.

The only facile route into benzyl chemistry which we have found is via $W(NPh)Bz_3(OCMe_3)$, prepared from $[Et_4N][W(NPh)(OCMe_3)Cl_4]$ and BzMgCl in THF at 0°. $W(NPh)Bz_3Cl$ can then be prepared by treating $W(NPh)Bz_3(OCMe_3)$ with HCl gas.

DISCUSSION

In this chapter I have described the synthesis of a variety of phenylimido alkylidene complexes. Complimenting this class of reactions, Rocklage and Schrock have more recently found a different route to complexes of the type $W(NR)(CHCMe_3)L_2Cl_2$ (L = PMe_3, PEt_3) starting with an amido neopentylidyne complex (eq 16).[10] The beauty of this reaction lies

$$W(CCMe_3)(NHR)L_2Cl_2 \xrightarrow{\Delta} W(CHCMe_3)(NR)L_2Cl_2 \qquad (16)$$

in the ability to prepare a large variety of alkyl and arylimido neopentylidene complexes (e.g., R = H,[10] Ph,[10] n-Pr[28]).

We have already cited a couple of examples that indicate the greater stability of phenylimido versus oxo alkylidene complexes. Indeed, the oxo group is not always a simple ancillary ligand and in one example is transformed from a π-donor ligand to a neutral two-electron donor (eq 17).[1g]

$$W(O)(CHCMe_3)(PEt_3)_2Cl_2 + C_2Cl_6 \xrightarrow[-Cl_2C=CCl_2]{THF} W(CCMe_3)(OPEt_3)Cl_3 + Et_3PHCl \qquad (17)$$

A similar reaction involving $W(NPh)(CHCMe_3)(PEt_3)_2Cl_2$ does not occur. This contrast in reactivity between the oxo and imido complexes may simply be a result of the thermodynamics of this reaction. The driving force for the reaction outlined in eq 17 is most certainly derived from formation of the tungsten alkylidyne unit and the P=O bond. Phosphorus-oxygen double bonds are quite strong (~130 kcal/mol)[29] and provide the driving force for many transformations (e.g., Wittig reactions). The phosphorus-nitrogen double bonds in phosphinimines are comparatively weaker.[30]

Although structural studies have indicated that M≡O bond lengths are generally shorter than those for M≡NR (taking into account the smaller bonding radius of multiply bonded oxygen),[14] the chemical reactivity of these ligands, as demonstrated above and in other cases, does not always adhere to this ordering. Wentworth and Maata have shown that an oxo group can be selectively removed from a Mo(VI) complex containing a phenylimido moiety (eq 18).[31] The fact that the reactivity of this Mo(VI) system can be changed simply by placing an electron-withdrawing nitro group on the

$$Mo(NPh)(O)(S_2CNEt_2)_2 + HCl(ex) \xrightarrow[-H_2O]{CH_2Cl_2} Mo(NPh)Cl_2(S_2CNEt_2)_2 \qquad (18)$$

para position of the phenyl ring is interesting. A protonation reaction similar to that in eq 18 now results in the selective cleavage of the $NPhNO_2$ group (as H_2NPhNO_2), leaving $Mo(O)Cl_2(S_2CNEt_2)_2$. This observation suggests that electronic factors are more important in determining the potential reactivity of oxo versus phenylimido ligands than other considerations such as steric constraints imposed by the phenyl ring.

Encouraged by the general stability of tungsten alkylidene complexes containing a phenylimido ligand, we pursued the preparation of these molecules in a more direct fashion than the alkylidene transfer reaction (eq 1), namely, via α-abstraction. This required that we find synthetically viable routes to the appropriate alkyl complexes, a task with which we have had a good deal of success. It is interesting that the routes to the most generally occurring molecules in this work, i.e. $W(NPh)R_3X$, all differed. Unlike in tantalum(V) chemistry where dialkyl zinc reagents are used to prepare the majority of complexes of the type

$TaR_{3-x}Cl_{2+x}$ (x = 0,1,2; R = CH_3, CH_2Ph, CH_2SiMe_3 and CH_2CMe_3), we have only had success with $ZnMe_2$ and $Zn(CH_2SiMe_3)_2$ when starting with $W(NPh)Cl_4X$ (X = Cl^- and Et_2O, respectively). $Zn(CH_2CMe_3)_2$ reactions gave only intractable materials and the most common organic by-products from several different reactions (using trap to trap methods and GC analysis) were neopentane and 2,2,5,5-tetramethylhexane. Both of these products are indicative of neopentyl radicals and suggest that complexes of the formula $W(NPh)(CH_2CMe_3)_{2-x}Cl_{2+x}$ (x = 0,1) may be inherently unstable.

Several anionic tungsten complexes were found to be useful starting materials for the preparation of a variety of phenylimido alkyl derivatives. For example, several attempts at preparing $W(NPh)(CH_3)_3Cl$ starting from $W(NPh)Cl_4(Et_2O)$ and $ZnMe_2$ (solvent, temperature and addition procedures were varied) gave large amounts of colored precipitates (more than theory for $ZnCl_2$) and consequently, low yields of product. We believe that these insolubles arise from complexation of zinc salts to the metal center. Some recent work by Osborn and coworkers supports this contention.[1c] They have found that a variety of Lewis acids, including $ZnCl_2$, will bind to oxo and methylimido units in W(VI) alkyl and alkylidene complexes. We found that the reaction of $ZnCl_2$ with NEt_4Cl not only serves to deactivate the Lewis acid nature of this molecule by formation of $[ZnCl_3][NEt_4]$, but also aids in the separation of products (a good deal of the $[ZnCl_3][NEt_4]$ precipitates from solution as the reaction proceeds). Therefore, in alkylation reactions starting with $[W(NPh)Cl_5][NEt_4]$, the main role of the additional chloride ion is to stop complexation between $ZnCl_2$ and the phenylimido ligand. We have also found that the chloride ion was useful in the preparation of two t-butoxy/chloride complexes. It

seems likely that in these cases formation of the anionic tungsten species stops bimolecular decomposition reactions.[19b]

Although the syntheses of several of the aforementioned phenylimido alkyl complexes differ from those found in Ta(V) chemistry, the resulting molecules appear to have a reaction chemistry that is very similar to their tantalum analogs (e.g., comparing $W(NPh)R_3Cl$ with TaR_3Cl_2). Since many of the tantalum systems have been previously reported on in detail we feel there is no need to discuss the reactions leading to many of the alkylidene complexes reported in this work.

Although we have not performed any experiments which conclusively show that the reaction of $W(NPh)Np_3Cl$ with $LiCH_2CMe_3$ to give $W(NPh)(CHCMe_3)Np_2$ proceeds via α-hydrogen abstraction through $W(NPh)(CH_2CMe_3)_4$ it seems highly probable, in light of our results with the isolable trimethylsilylmethyl analog of this intermediate. We believe that the concentration independence and first order nature of the thermal decomposition of $W(NPh)(CH_2SiMe_3)_4$ are consistent with an intramolecular α-abstraction mechanism.

The low values for J_{CH_α} (105-115 Hz) listed in Table I are indicative of some distortion of the neopentylidene ligand toward a large $W{=}C_\alpha{-}C_\beta$ angle.[12] Although no imido alkylidene complex has been studied by single crystal x-ray diffraction, we can propose that the correlation of $\angle W{=}C_\alpha{-}C_\beta$ with J_{CH_α} in the imido alkylidene complex is similar to what it is in $W(O)(CHCMe_3)(PMe_3)_2Cl_2$ where J_{CH_α} = 121 Hz and $\angle W{=}C_\alpha{-}C_\beta$ = 140°.[17] The fact that the values for J_{CH_α} in several oxo complexes are, in three out of the four cases noted in Table I, slightly higher than the values for J_{CH_α} in the analogous imido complexes, could be taken as evidence that the neopentylidene ligand is slightly more distorted in the imido complexes than in

the oxo complexes. Unfortunately, it is not yet known how significant relatively small differences in the degree of distortion of the alkylidene ligand might correlate with rates and/or selectivities of reactions of alkylidene complexes, e.g., in the olefin metathesis reaction.

EXPERIMENTAL SECTION

All experiments were done under nitrogen either by standard Schlenk techniques or in a Vacuum Atmospheres HE 43-2 drybox. Solvents were rigorously purified and dried under N_2 by standard techniques and transferred into the drybox without exposure to air. $WOCl_4$ was prepared either by the reaction of WO_3 with S_2Cl_2[4] or by the method described below. $Ta(CHCMe_3)L_2Cl_3$ (L = PMe_3, PEt_3[24]), PMe_3,[32] $LiCH_2CMe_3$,[20] $ZnMe_2$[33] and $Zn(CH_2CMe_3)_2$[20] were prepared by published methods. $Zn(CH_2SiMe_3)_2$ and $LiCH_2SiMe_3$ were prepared in a manner analogous to that described for $Zn(CH_2CMe_3)_2$ and $LiCH_2CMe_3$, respectively. Tetraethylammonium chloride was purchased from standard sources and dried in vacuo (50 μ) at 90 to 100° for at least 24h.

^{13}C NMR spectra are reported in the proton gated decoupled mode (unless otherwise noted). If coupling to phosphorus and/or tungsten can be observed in the proton broad band decoupled spectrum, then it is reported as part of the data for the ^1H-gated decoupled spectrum even though in this mode long-range C-H coupling usually obscures small C-P couplings. All ^{31}P NMR spectra were observed at ~30° and 36.2 MHz. All chemical shifts are reported in ppm downfield from TMS (^1H or ^{13}C) or 30% H_3PO_4 (^{31}P).

Preparation of $WOCl_4$

Finely ground WCl_6 (54.5 g, 0.14 mol) was suspended in dichloromethane (350 ml) and the mixture was stirred vigorously while a dichloromethane solution (40 ml) of Me_3SiOMe (14.3 g, 0.14 mol) was added dropwise over a 4 h period. The mixture was filtered and the orange precipitate was washed with pentane and dried in vacuo. The dichloromethane was removed from the filtrate in vacuo leaving a red-orange solid. This material along

with the above orange precipitate were combined and sublimed at 80° (<0.1μ) to give 42.7 g (91%) of pure, crystalline $WOCl_4$. This preparation is the scaled-up version of an observation made by Handy et al.[19a]

Preparation of $W(NPh)Cl_4(Et_2O)$

Freshly distilled phenyl isocyanate (7.0 g, 58.8 mmol) was added to an octane suspension (250 ml) of finely ground $WOCl_4$ (20.0 g, 58.5 mmol). The mixture was heated to reflux while stirring until CO_2 evolution had ceased. A green powder was filtered off, washed with pentane (50 ml), and dried in vacuo to give 23.2 g of crude $[W(NPh)Cl_4]_x$. This material was dissolved in ether (200 ml) and the solution was filtered off and concentrated in vacuo to give green crystals (25.9 g; 90%): ^1H NMR ($CDCl_3$, 60 MHz) δ 7.95-7.38 (m, 5, NPh), 5.28 (q, 4, $J_{HH} \approx 7$ Hz, $O(\underline{CH_2}CH_3)_2$), 1.55 (t, 6, $J_{HH} \approx 7$ Hz, $O(CH_2\underline{CH_3})_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 22.5 MHz) δ 149.6 (NPh ipso), 134.6, 131.4, and 127.2 (NPh), 66.2 ($\underline{CH_2}CH_3$), 13.2 ($CH_2\underline{CH_3}$).

Pure $[W(NPh)Cl_4]_x$ can be prepared by removing the ether from $W(NPh)Cl_4(Et_2O)$ in vacuo (0.1 μ, 25°, 24h).

Preparation of $W(NPh)(OCMe_3)_4$

An ether solution (200 ml) of $W(NPh)Cl_4(Et_2O)$ (12.68 g, 25.8 mmol) was cooled to 0° and $LiOCMe_3$ (8.27 g, 103.3 mmol) in 120 ml of ether was added rapidly (2 m). The reaction was stirred for 12 h and filtered through Celite. The salts were washed with 100 ml of pentane. The solvent was removed in vacuo leaving yellow crystals which were recrystallized from pentane (total 13.67 g, 93%): ^1H NMR ($CDCl_3$, 250 MHz) δ 7.37-6.93 (m, 5, NPh), 8.40 (s, 36, $OCMe_3$); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 154.6 (br s, NPh

ipso), 127.9, 126.3 and 125.2 (NPh), 81.4 (br s, $O\underline{C}Me_3$), 31.4 (q, J_{CH} = 126 Hz, $OC\underline{Me}_3$); mass spectrum parent ion at 567; mol wt (CH_2Cl_2, differential vapor pressure) calcd 567, found 546. The product may be sublimed (125°, <1 μ), but yields are typically 20% lower.

Preparation of $[Et_4N][W(NPh)Cl_5]$

Et_4NCl (2.04 g, 12.3 mmol) was added to a well-stirred solution of $W(NPh)Cl_4(Et_2O)$ (6.0 g, 12.2 mmol) in 40 ml of dichloromethane. Some product crystallized out immediately. After 5 min the solution was cooled to -30°C. Two crops of lime green flakes were collected by filtration, washed with pentane and dried *in vacuo* (7.10 g; 100%).

Preparation of $[Et_4N][W(NPh)(OCMe_3)_2Cl_3]$ and $[Et_4N][W(NPh)(OCMe_3)Cl_4]$

$W(NPh)Cl_4(Et_2O)$ (2.0 g, 4.1 mmol) and Et_4NCl (1.35 g, 8.2 mmol) were codissolved in 40 ml of dichloromethane and after a few minutes $W(NPh)(OCMe_3)_4$ (2.31 g, 4.1 mmol) was added. After 8 h the orange solution was filtered and concentrated *in vacuo*. Addition of pentane and cooling to -30° afforded four crops of yellow microcrystals of $[Et_4N][W(NPh)(OCMe_3)_2Cl_3]$ (5.1 g, 95%): ^1H NMR ($CDCl_3$, 60 MHz) δ 7.5-7.1 (m, 5, NPh), 3.3 (br m, 8, $N(C\underline{H}_2CH_3)_4$), 1.5 (s, 18, $OC\underline{Me}_3$), 1.3 (br m, 12, $N(CH_2C\underline{H}_3)_4$).

A similar procedure employing 0.63 g (3.8 mmol) of Et_4NCl, 1.4 g (2.9 mmol) of $W(NPh)Cl_4(Et_2O)$, and 0.54 g (0.95 mmol) of $W(NPh)(OCMe_3)_4$ in 40 ml of dichloromethane gave 2.35 g (100%) of brick red $[Et_4N][W(NPh)(OCMe_3)Cl_4]$ upon removing the solvent from the reaction mixture *in vacuo*: ^1H NMR ($CDCl_3$, 60 MHz) δ 7.7-6.8 (m, 5, NPh), 3.2 (br, 8, $N(C\underline{H}_2CH_3)_4$), 1.6 (s, 9, $OC\underline{Me}_3$), 1.2 (br, 12, $N(CH_2C\underline{H}_3)_4$). $[Et_4N][W(NPh)(OCMe_3)Cl_4]$ can be recrystallized at -30° from a saturated CH_2Cl_2 solution.

Preparation of $W(NPh)(CHCMe_3)(PMe_3)_2Cl_2$

$W(NPh)(OCMe_3)_4$ (9.4 g, 16.6 mmol) and $Ta(CHCMe_3)(PMe_3)_2Cl_3$ (8.4 g, 16.6 mmol) were dissolved in 75 ml of ether. After 12 h pale orange crystals were collected by filtration, washed with pentane and dried in vacuo (5.5 g). Addition of the washings to the mother liquor precipitated another 1.92 g of product which may be recrystallized from minimal toluene by adding pentane and cooling to -30°C (total 7.42 g, 79%): ^1H NMR ($CDCl_3$, 250 MHz) δ 10.92 (t, 1, $^3J_{HP}$ = 4.4 Hz, $CHCMe_3$), 7.51-7.12 (m, 5, NPh), 1.68 (t, 18, $^2J_{HP}$ = 4.6 Hz, PMe_3), 1.30 (s, 9, $CHCMe_3$); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 307.0 (d, J_{CH} = 123 Hz, $^2J_{CP}$ = 11 Hz, $CHCMe_3$), 154.8 (s, NPh ipso), 128.2, 127.2 and 126.4 (NPh), 46.4 (s, $CHCMe_3$), 34.3 (q, J_{CH} = 125 Hz, $CHCMe_3$), 16.2 (q t, J_{CH} = 130 Hz, J_{CP} = 15 Hz, PMe_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ -8.1 (s, J_{PW} = 288 Hz). Anal. Calcd for $WC_{17}H_{33}Cl_2NP_2$: C, 35.94; H, 5.85. Found: C, 36.25; H, 5.95.

The solvent from the above mother liquors was removed in vacuo leaving a sticky orange solid. Sublimation of this material (80°, 1μ) gave 5 g (60%) of pale yellow, crystalline $[Ta(OCMe_3)_4Cl]_2$.[24]

Preparation of $W(NPh)(CHCMe_3)(PEt_3)_2Cl_2$

The procedure is the same as that for $W(NPh)(CHCMe_3)(PMe_3)_2Cl_2$ starting with $Ta(CHCMe_3)(PEt_3)_2Cl_3$. This derivative does not crystallize from the reaction mixture until the solution is concentrated and cooled to -30°: ^1H NMR (C_6D_6, 90 MHz) δ 11.92 (t, 1, $^3J_{HP}$ = 3.9 Hz, $CHCMe_3$), 7.90-6.91 (m, 5, NPh), 1.99 (m, 12, $P(CH_2CH_3)_3$), 1.35 (s, 9, $CHCMe_3$), 0.93 (m, 18, $P(CH_2CH_3)_3$); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 303.8 (d, J_{CH} = 119 Hz, $^2J_{CP}$ = 11 Hz, $CHCMe_3$), 155.3 (s, NPh ipso), 128.3, 126.2 and 125.6 (NPh), 46.2 (s,

$CHCMe_3$), 34.7 (q, J_{CH} = 126 Hz, $CHCMe_3$), 17.4 (tt, J_{CH} = 127 Hz, J_{CP} = 13 Hz, $P(CH_2CH_3)_3$), 7.9 (q, J_{CH} = 127 Hz, $P(CH_2CH_3)_3$); $^{31}P\{^1H\}$NMR ($CDCl_3$) δ 15.7 (s, J_{PW} = 273 Hz). Anal. Calcd for $WC_{23}H_{45}Cl_2NP_2$: C, 42.35; H, 6.95. Found: C, 41.97; H, 7.08.

Preparation of $[W(NPh)(CHCMe_3)(PMe_3)_2Cl][AlCl_4]$

$W(NPh)(CHCMe_3)(PMe_3)_2Cl_2$ (1.0 g, 1.8 mmol) was dissolved in 15 ml of dichloromethane and $AlCl_3$ (0.24 g, 1.8 mmol) was added. The mixture was stirred for 0.5 h and filtered through Celite. Decreasing the volume *in vacuo* and cooling to -30° gave 1.18 g (95%) of bright yellow crystals: ^1H NMR ($CDCl_3$, 250 MHz) δ 10.39 (br s, 1, $CHCMe_3$), 7.46-7.34 (m, 5, NPh), 1.72 (t, 18, $^2J_{HP}$ = 4.8 Hz, PMe_3), 1.32 (s, 9, $CHCMe_3$); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 303.4 (d, J_{CH} = 106 Hz, $^2J_{CP}$ = 8 Hz, $CHCMe_3$), 153.3 (s, NPh ipso), 129.7, 129.5 and 126.8 (NPh), 48.6 (s, $CHCMe_3$), 31.4 (q, J_{CH} = 127 Hz, $CHCMe_3$), 14.9 (qt, J_{CH} = 132 Hz, J_{CP} = 15 Hz, PMe_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 6.5 (s, J_{PW} = 273 Hz); conductivity (CH_2Cl_2, 1.13×10^{-3} M) 48 cm^{-1} M^{-1} Ω^{-1}. Anal. Calcd for $WC_{17}H_{33}AlCl_5NP_2$: C, 29.11; H, 4.74. Found: C, 28.99; H, 5.05.

Preparation of $[W(NPh)(CHCMe_3)(PEt_3)_2Cl][AlCl_4]$

This product was prepared from $W(NPh)(CHCMe_3)(PEt_3)_2Cl_2$ by a procedure similar to that described above: ^1H NMR ($CDCl_3$, 60 MHz) δ 9.6 (s, 1, $CHCMe_3$), 7.2 (br s, 5, NPh), 2.0 (m, 12, $P(CH_2CH_3)_3$), 1.4 (s, 9, $CHCMe_3$), 1.1 (m, 18, $P(CH_2CH_3)_3$); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 300.5 (d, J_{CH} = 106 Hz, $^2J_{CP}$ = 8 Hz, $CHCMe_3$), 153.8 (s, NPh ipso), 129.3, 128.4 and 126.9 (NPh), 48.6 (s, $CHCMe_3$), 31.8 (q, J_{CH} = 126 Hz, $CHCMe_3$), 16.4 (tt, J_{CH} =

127 Hz, J_{CP} = 13 Hz, P($\underline{C}H_2CH_3)_3$), 8.0 (q, J_{CH} = 125 Hz, P($CH_2\underline{C}H_3)_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 37.2 s, J_{PW} = 264 Hz).

Preparation of [W(NPh)($CHCMe_3$)($PMe_3)_2$Me][$AlMe_2Cl_2$]

$AlMe_3$ (640 μl, 6.7 mmol) was added to a stirred toluene/pentane solution (30 ml/5 ml) of W(NPh)($CHCMe_3$)($PMe_3)_2Cl_2$ (3.48 g, 6.1 mmol). An orange solid precipitated immediately and the mixture was cooled to 30°C. Pale orange crystals were isolated by filtration and washed with toluene (20 ml) and pentane (3.66 g, 93%): ^1H NMR ($CDCl_3$, 250 MHz) δ 8.40 (br s, 1, $C\underline{H}CMe_3$), 7.36-7.16 (m, 5, NPh), 1.68 (t, 18, $^2J_{HP}$ = 4.0 Hz, PMe_3), 1.28 (s, 9, $CHC\underline{Me}_3$), 0.85 (t, 3, $^3J_{HP}$ = 16.5 Hz, WMe), -0.68 (s, 6, $AlMe_2Cl_2$); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 302.8 (d, J_{CH} = 106 Hz, J_{CP} = 9 Hz, $\underline{C}HCMe_3$), 154.3 (s, NPh ipso), 129.2, 127.9 and 126.2 (NPh), 47.7 (s, $CH\underline{C}Me_3$), 38.0 (qt, J_{CH} = 119 Hz, $^2J_{CP}$ = 9 Hz, WMe), 31.1 (q, J_{CH} = 125 Hz, $CHC\underline{Me}_3$), 15.0 (qt, J_{CH} = 132 Hz, J_{CP} = 15 Hz, PMe_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ -8.3 (s, J_{PW} = 286 Hz); conductivity (CH_2Cl_2, 8.93×10^{-4} M) 45 cm^{-1} M^{-1} Ω^{-1}. Anal. Calcd for $WC_{20}H_{42}AlCl_2NP_2$: C, 37.52; H, 6.61. Found: C, 37.06; H, 6.74.

Preparation of [W(NPh)($CHCMe_3$)($PEt_3)_2$Me][$AlMe_2Cl_2$]

A toluene solution (15 ml) of W(NPh)($CHCMe_3$)($PEt_3)_2Cl_2$ (2.0 g, 3.1 mmol) was treated with $AlMe_3$ (295 μl, 3.1 mmol). An orange oil formed immediately. Pentane was added (6 ml) and the solution was shaken until the oil crystallized. The solution was cooled to -30° and the pale orange crystals were filtered off, washed with pentane and dried in vacuo (2.12 g, 95%): ^1H NMR ($CDCl_3$, 250 MHz) δ 7.84 (s, 1, $C\underline{H}CMe_3$), 7.38-7.22 (m, 5, NPh), 1.99 (m, 12, P($C\underline{H}_2CH_3)_3$), 1.31 (s, 9, $CHC\underline{Me}_3$), 1.13 (m, 18,

$P(CH_2\underline{C}H_3)_3$), 0.76 (t, 3, $^3J_{HP}$ = 15.0 Hz, WMe), -0.65 (s, 6, $AlMe_2Cl_2$); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 300.8 (d, J_{CH} = 105 Hz, $^2J_{CP}$ = 8 Hz, $\underline{C}HCMe_3$), 154.9 (s, NPh ipso), 129.0, 128.1 and 126.9 (NPh), 48.3 (s, $CH\underline{C}Me_3$), 35.5 (qt, J_{CH} = 119 Hz, $^2J_{CP}$ = 9 Hz, WMe), 31.7 (q, J_{CH} = 125 Hz, $CHC\underline{Me}_3$), 16.9 (tt, J_{CH} = 130 Hz, J_{CP} = 14 Hz, $P(\underline{C}H_2CH_3)_3$), 8.1 (q, J_{CH} = 125 Hz, $P(CH_2\underline{C}H_3)_3$), -5.7 (br, $AlMe_2Cl_2$); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 32.4 (s, J_{PW} = 254 Hz).

Preparation of $W(NPh)(CHCMe_3)(PMe_3)(OCMe_3)_2$

$LiOCMe_3$ (0.35 g, 4.4 mmol) was added to a stirred solution of $W(NPh)(CHCMe_3)(PMe_3)_2Cl_2$ (1.25 g, 2.2 mmol) in 10 ml of THF. After 24 h the THF was removed in vacuo leaving a yellow solid which was extracted with pentane (40 ml). The mixture was filtered and the pentane was removed in vacuo. The yellow solid was dissolved in ether and the solution was concentrated in vacuo until crystallization began. At this point the sample was stored at -30° for 12 h to give 0.9 g of product. The mother liquor was further concentrated to give another 0.1 g (total 1.0 g, 79%): ^1H NMR (toluene-d_8, 250 MHz, 0°) δ 10.17 (d, 1, $^3J_{HP}$ = 3.4 Hz, $C\underline{H}CMe_3$), 7.08-6.77 (m, 5, NPh), 1.64 (s, 9, $OCMe_3$), 1.47 (s, 9, $OCMe_3$), 1.31 (s, 9, $CHC\underline{Me}_3$), 0.51 (d, 9, $^2J_{HP}$ = 8.3 Hz, PMe_3); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 265.3 (d, J_{CH} = 114 Hz, $\underline{C}HCMe_3$), 156.9 (s, NPh ipso), 128.2, 125.6 and 122.6 (NPh), 76 (br s, $O\underline{C}Me_3$), 43.8 (s, $CH\underline{C}Me_3$), 34.0 (q, J_{CH} = 125 Hz, $CHC\underline{Me}_3$), 32.5 (q, J_{CH} = 125 Hz, $OC\underline{Me}_3$), 16.2 (qd, J_{CH} = 130 Hz, J_{CP} = 24 Hz, PMe_3); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 1.2 (s, J_{PW} = 269 Hz). Anal. Calcd for $WC_{22}H_{42}NO_2P$: C, 46.57; H, 7.46. Found: C, 46.67; H, 7.48.

Preparation of $W(NPh)(CHCMe_3)(PEt_3)(OCMe_3)_2$

$W(NPh)(CHCMe_3)(PEt_3)_2Cl_2$ (1.58 g, 2.4 mmol) was dissolved in ether and the solution was cooled to -30°. $LiOCMe_3$ (0.39 g, 4.8 mmol) was added in one portion and the temperature allowed to rise to ambient. After 16 h the reaction mixture was filtered and the ether was removed in vacuo. The resulting sticky solid was extracted with pentane. The mixture was filtered, concentrated, and cooled to -30° to give orange crystals (1.20 g, 81%): ^1H NMR (toluene-d_8, 250 MHz, -30°) δ 10.27 (br s, 1, $CHCMe_3$), 7.25-6.78 (m, 5, NPh), 1.69 (s, 9, $OCMe_3$), 1.53 (s, 9, $OCMe_3$), 1.47-1.36 (m under singlet at 1.43, 15, $P(CH_2CH_3)_3$ and $CHCMe_3$), 0.81 (m, 9, $P(CH_2CH_3)_3$); ^{13}C NMR (toluene-d_8, 62.83 MHz) δ 265.87 (d, $J_{CH} \approx 111$ Hz, $CHCMe_3$), 157.72 (br s, NPh ipso), 130.1-123.3 (overlapping resonances of NPh and toluene-d_8), 76.85 (s, $OCMe_3$), 76.11 (s, $OCMe_3$), 43.55 (s, $CHCMe_3$), 34.71 (q, J_{CH} = 119.2 Hz, $CHCMe_3$), 32.91 (q, J_{CH} = 122.1 Hz, $OCMe_3$), 17.20 (td, J_{CH} = 127.9 Hz, J_{CP} = 20.3 Hz, $P(CH_2CH_3)_3$), 8.72 (q, J_{CH} = 127.9 Hz, $P(CH_2CH_3)_3$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 32.1 (s, J_{PW} = 261 Hz).

Preparation of $W(NPh)(CHCMe_3)(PEt_3)Cl_2$

CuCl (80 mg, 0.8 mmol) was added to a vigorously stirred solution of $W(NPh)(CHCMe_3)(PEt_3)_2Cl_2$ (0.50 g, 0.77 mmol) in 10 ml of toluene. After 6 h the solvent was removed in vacuo until a large fraction of white $CuCl(PEt_3)_x$ precipitated. The $CuCl(PEt_3)_x$ was then filtered off and pentane was added to the filtrate just short of cloudiness. Cooling to -30° yielded 0.35 g (85%) of orange crystals: ^1H NMR (C_6D_6, 60 MHz) δ 10.8 (d, 1, $^3J_{HP}$ = 3 Hz, $CHCMe_3$), 7.2 (br, 5, NPh), 2.1 (m, 6, $P(CH_2CH_3)_3$), 1.3 (s, 9, $CHCMe_3$), 1.1 (m, 9, $P(CH_2CH_3)_3$); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 300.5

(d, J_{CH} = 106 Hz, $^2J_{CP}$ = 8 Hz, $CHCMe_3$), 153.7 (s, NPh ipso), 129.3, 128.4 and 126.9 (NPh), 48.6 (s, $CHCMe_3$), 31.8 (q, J_{CH} = 127 Hz, $CHCMe_3$), 16.4 (td, J_{CH} = 127 Hz, J_{CP} = 14 Hz, $P(CH_2CH_3)_3$), 8.0 (q, J_{CH} = 125 Hz, $P(CH_2CH_3)_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 37.2 (s, J_{PW} = 264 Hz).

Preparation of $W(NPh)(CHCMe_3)(PMe_3)(OCMe_2CMe_2O)$

(a) From $W(NPh)(CHCMe_3)(PMe_3)_2Cl_2$ and $LiOCMe_2CMe_2OLi$ (V-73).

$LiOCMe_2CMe_2OLi$ (0.23 g, 1.8 mmol) was added to a THF solution (30 ml) of $W(NPh)(CHCMe_3)(PMe_3)_2Cl_2$ (1.0 g, 1.8 mmol). After stirring for 24 h the volatiles were removed in vacuo, leaving a gummy oil. This was extracted exhaustively with pentane and the extracts were filtered through Celite and the pentane was removed in vacuo. The resulting foam was dissolved in a minimum of pentane and cooled to -30°C. Yellow crystals were isolated by filtration and dried in vacuo (0.62 g, 66%).

(b) From $W(NPh)(CHCMe_3)(OCMe_3)_2(PMe_3)$ and pinacol (VIII-24).

Pinacol (90 mg, 0,74 mmol) was added to a toluene solution (8 ml) of $W(NPh)(CHCMe_3)(OCMe_3)_2(PMe_3)$ (0.42 g, 0.74 mmol). After 10 minutes the volatiles were removed in vacuo. The yellow solid was extracted with a minimum of pentane, filtered and cooled to -30°C. Yellow crystals were isolated by filtration and dried in vacuo (0.28 g, 70%).

(V-73) ^1H NMR (C_6D_6, 250 MHz) δ 9.66 (d, 1, $^3J_{HP}$ = 3.4 Hz, $CHCMe_3$), 7.21-7.09 (m, 5, NPh), 1.52, 1.47, 1.44 and 1.32 (s, 12, $OCMe_2CMe_2O$), 1.27 (s, 9, $CHCMe_3$), 1.10 (d, 9, $^2J_{HP}$ = 9.8 Hz, PMe_3). (V-73) ^{13}C NMR (C_6D_6, 22.5 MHz) δ 266.5 (d, J_{CH} = 112.1 Hz, $^2J_{CP}$ = 11 Hz, $CHCMe_3$), 157.7 (s, NPh ipso), 128.6, 125.3 and 123.5 (NPh), 90.8 (s, $^3J_{CP}$ = 6.6 Hz, $OCMe_2CMe_2O$), 84.0 (s, $OCMe_2CMe_2O$), 44.2 (s, $CHCMe_3$), 33.8, 28.7, 28.4 and 26.1 (q, J_{CH}

~125 Hz, $OCMe_2\underline{C}Me_2O$ and $CHCMe_3$, not respectively), 15.5 (dt, J_{CH} = 132 Hz, J_{CP} = 31 Hz, PMe_3). (V-73) $^{31}P\{^1H\}$ NMR (C_6D_6) δ 8.6 (s, J_{PW} = 347 Hz).

Preparation of $W(NPh)(CHCMe_3)(PEt_3)(OCMe_2CMe_2O)$ (XV-22)

This was prepared in a manner similar to the PMe_3 derivative starting with $W(NPh)(CHCMe_3)(OCMe_3)_2(PEt_3)$ and pinacol.

(XV-22) ^1H NMR (C_6D_6, 250 MHz) δ 9.77 (d, 1, $^3J_{HP}$ = 3.5 Hz, $^2J_{HW}$ = 13 Hz, $C\underline{H}CMe_3$), 7.34 (d, 2, $^3J_{HoHm}$ = 8.1 Hz, NPh ortho), 7.10 (t, 2, J_H = 7.9 Hz, NPh meta), 6.84 (t, 1, $^3J_{HpHm}$ = 7.3 Hz, NPh para), 1.53, 1.49, 1.44 and 1.33 (s, 12, $OCMe_2CMe_2O$), 1.51 (m, 6, $P(C\underline{H}_2CH_3)_3$), 1.34 (s, 9, $CHC\underline{Me}_3$), 0.79 (m, 9, $P(CH_2C\underline{H}_3)_3$). (XV-22) ^{13}C NMR (C_6D_6, 67.9 MHz) δ 268.2 (d, J_{CH} = 116 Hz, $^2J_{CP}$ = 11.6 Hz, J_{CW} = 160 Hz, $\underline{C}HCMe_3$), 158.1 (s, NPh ipso), 128.6, 125.4 and 123.6 (NPh), 90.8 (s, $^3J_{CP}$ = 8.8 Hz, $O\underline{C}Me_2\underline{C}Me_2O$), 83.8 (s, $O\underline{C}Me_2\underline{C}Me_2O$), 44.5 (s, $CH\underline{C}Me_3$),34.1, 28.6, 28.4 and 26.1 (q, J_{CH} ~125 Hz, $OC\underline{Me}_2C\underline{Me}_2O$ and $CHC\underline{Me}3$, not respectively), 17.7 (dt, J_{CH} = 128 Hz, J_{CP} = 26.5 Hz, $P(\underline{C}H_2CH_3)_3$), 8.09 (q, J_{CH} = 128 Hz, $P(CH_2\underline{C}H_3)_3$). (XV-22) $^{31}P\{^1H\}$ NMR (C_6D_6) δ 38.1 (s, J_{PW} = 327 Hz).

Preparation of $W(NPh)(CCMe_3)(AlMe_2Cl)(PMe_3)_2Cl$

$[W(NPh)(CHCMe_3)(PMe_3)_2Me][AlMe_2Cl_2]$ (3.62 g, 5.65 mmol) was suspended in toluene (40 ml) and the mixture was heated to 50°. Gas evolved steadily. After 14 h at 50° the now homogeneous, dark orange solution was filtered and the toluene filtrate was concentrated in vacuo until crystallization began. Cooling to -30° gave 2.1 g of orange crystals. The mother liquor was further concentrated. Pentane was added and the solution was cooled to -30° to give another 1.1 g of product (total 91%): ^1H NMR (C_6D_6, 250 MHz)

δ 7.26-6.86 (m, 5, NPh), 1.42 (t, 18, $^2J_{HP}$ = 4.4 Hz, PMe_3), 0.83 (s, 9, $CCMe_3$), -0.27 (s, 6, $AlMe_2$); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 309.4 (s, $^2J_{CP}$ = 12 Hz, $\underline{C}CMe_3$), 163.7 (s, NPh ipso), 127.4, 123.2 and 120.6 (NPh), 50.9 (s, $C\underline{C}Me_3$), 31.6 (q, J_{CH} = 125 Hz, $CC\underline{Me}_3$), 16.5 (qt, J_{CH} = 132 Hz, J_{CP} = 15 Hz, PMe_3), -6.9 (q, J_{CH} = 116 Hz, $AlMe_2$); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ -14.1 (s, J_{PW} = 298 Hz). Anal. Calcd for $WC_{19}H_{38}AlCl_2NP_2$: C, 36.56; H, 6.14. Found: C, 36.68; H, 6.06.

Preparation of $W(NPh)(CH_2CMe_3)_3Cl$

A solution of $W(NPh)Cl_4(Et_2O)$ (8.95 g, 18.2 mmol) in 200 ml of ether was cooled to -78° and stirred vigorously while three equivalents of NpMgCl (1.34 M in ether) were added rapidly. The reaction was warmed to room temperature slowly. After 24 h at room temperature the mixture was filtered through Celite and the magnesium salts were washed thoroughly with ether. The solvent was removed from the filtrate in vacuo. The resulting dark oily solid was dissolved in pentane and the solution treated with activated charcoal. Filtration and removal of the pentane in vacuo left a dark solid that was sublimed at 80-90°C (1μ) to give 4.32 g (45%) of pale yellow crystals: ^1H NMR (C_6D_6, 250 MHz) δ 7.56-6.88 (m, 5, NPh), 2.42 (s, 6, $^2J_{HW}$ = 9.6 Hz, $C\underline{H}_2CMe_3$), 1.13 (s, 27, $CH_2C\underline{Me}_3$); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 153.7 (s, NPh ipso), 128.8, 128.0 and 127.5 (NPh), 92.9 (t, J_{CH} = 121 Hz, J_{CW} = 79.1 Hz, $\underline{C}H_2CMe_3$), 36.2 (s, $CH_2\underline{C}Me_3$), 34.3 (q, J_{CH} = 125.2 Hz, $CH_2C\underline{Me}_3$); Mol. wt. (CH_2Cl_2, differential vapor pressure) Calcd 524, found 522. Anal. Calcd for $WC_{21}H_{38}ClN$: C, 48.15; H, 7.31. Found: C, 48.37; H, 7.20.

Preparation of $W(NPh)(CH_2CMe_3)_3Br$

A solution of $W(NPh)(CH_2CMe_3)_3(OCMe_3)$ (1.0 g, 1.8 mmol; see later preparation) in toluene (20 ml) was cooled to 0°. HBr gas (50 ml, 2.2 mmol) was added above it in a closed system. After stirring the reaction for 0.5 h the toluene was removed in vacuo. The resulting orange oil was extracted with pentane. Activated charcoal was added and the mixture was filtered. Pure $W(NPh)(CH_2CMe_3)_3Br$ (0.95 g, 94%) was obtained as a tan solid after filtration and removal of the pentane in vacuo. $W(NPh)(CH_2CMe_3)_3Br$ may be recrystallized from ether by adding acetonitrile and cooling to -30°. ^1H NMR (C_6D_6, 250 MHz) δ 7.53 (d, 2, $^3J_{HoHm}$ = 8.8 Hz, NPh ortho), 7.03 (t, 2, $J_{H_{observed}}$ = 7.8 Hz, NPh meta), 6.88 (t, 1, $^3J_{HpHm}$ = 7.3 Hz, NPh para), 2.51 (s, 6, $^2J_{HW}$ = 9.8 Hz, $C\underline{H}_2CMe_3$), 1.13 (s, 27, $CH_2C\underline{Me}_3$); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 153.2 (s, NPh ipso), 128.8, 128.4 and 127.9 (NPh), 95.8 (t, J_{CH} = 125.2 Hz, J_{CW} = 79.1 Hz, $\underline{C}H_2CMe_3$), 36.6 (s, $CH_2\underline{C}Me_3$), 34.5 (q, J_{CH} = 125.2 Hz, $CH_2C\underline{Me}_3$).

Preparation of $W(NPh)(CH_2CMe_3)_3(O_2CCF_3)$

$W(NPh)(CH_2CMe_3)_3(O_2CCF_3)$ is prepared by a procedure analogous to that used to prepare $W(NPh)(CH_2CMe_3)_3Br$ above, using neat CF_3CO_2H: ^1H NMR (C_6D_6, 60 MHz) δ 7.5-6.9 (m, 5, NPh), 2.34 (s, 6, $^2J_{HW} \approx 9$ Hz, $C\underline{H}_2CMe_3$), 1.18 (s, 27, $CH_2C\underline{Me}_3$); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 160.4 (q, J_{CF} = 40 Hz, O_2CCF_3), 154.5 (s, NPh ipso), 129.0-127.0 (NPh), 95.9 (t, J_{CH} = 122 Hz, J_{CW} = 81.3 Hz, $\underline{C}H_2CMe_3$), 36.8 (s, $CH_2\underline{C}Me_3$), 33.7 (q, J_{CH} = 125 Hz, $CH_2C\underline{Me}_3$).

Preparation of $W(NPh)(CH_2CMe_3)_3(OCMe_3)$

A 1.19 M solution of Me_3CCH_2MgCl (19 ml) was added dropwise to a stirred solution of $W(NPh)(OCMe_3)_4$ (4.18 g, 7.4 mmol) in 150 ml of ether at 0°. After 12 h the reaction was filtered and the salts were washed with pentane until the washings were colorless. The solvent was removed from the filtrate in vacuo and the tan-colored residue was sublimed at 85°C and ~0.1μ to give 3.0 g (73%) of yellow crystals in two crops: ^1H NMR (C_6D_6, 250 MHz) δ 7.60 (d, 2, $^3J_{HoHm}$ = 8.6 Hz, NPh ortho), 7.24 (t, 2, $J_{H_{observed}}$ = 7.3 Hz, NPh meta), 6.90 (t, 1, $^3J_{HpHm}$ = 7.3 Hz, NPh para), 1.94 (s, 6, $^2J_{HW}$ = 9.9 Hz, CH_2CMe_3), 1.58 (s, 9, $OCMe_3$), 1.17 (s, 27, CH_2CMe_3); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 157.3 (s, NPh ipso), 128.0, 127.2 and 123.7 (NPh), 80.9 (s, $OCMe_3$), 78.0 (t, J_{CH} = 124 Hz, J_{CW} = 85.0 Hz, CH_2CMe_3), 34.8 (s, CH_2CMe_3), 34.3 (q, J_{CH} = 124 Hz, CH_2CMe_3), 31.4 (q, J_{CH} = 125 Hz, $OCMe_3$). Anal. Calcd for $WC_{25}H_{47}NO$: C, 53.48; H, 8.44. Found: C, 53.41; H, 8.55.

Preparation of $W(NPh)(CH_2CMe_3)_2(OCMe_3)_2$

A solution of $[Et_4N][W(NPh)(OCMe_3)_2Cl_3]$ (2.0 g, 3.0 mmol) in dichloromethane (40 ml) was cooled to -30° and a pentane solution (8 ml) of $ZnNp_2$ (0.63 g, 3.0 mmol) was added dropwise with stirring. The reaction mixture was warmed to room temperature, stirred for 2 h, and filtered. The solvent was removed in vacuo. The residue was extracted with pentane, the mixture was filtered, and the pentane removed in vacuo to give pure (by ^1H NMR) $W(NPh)(CH_2CMe_3)_2(OCMe_3)_2$ as a waxy yellow solid (1.48 g, 86%): ^1H NMR (toluene-d_8, 250 MHz, 0°C) δ 7.43-6.82 (m, 5, NPh), 2.33 (d, 2, $^2J_{H_AH_B}$ = 8.8 Hz, $CH_AH_BCMe_3$), 2.02 (d, 2, $^2J_{H_AH_B}$ = 8.8 Hz, $CH_AH_BCMe_3$), 1.64 (s, 9,

$OCMe_3$), 1.33 (s, 9, $OCMe_3$), 1.19 (s, 18, $CH_2\underline{C}Me_3$); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 156.5 (s, NPh ipso), 128.4, 128.0 and 124.8 (NPh), 84.1 (t, J_{CH} = 127.5 Hz, J_{CW} = 90.1 Hz, $\underline{C}H_2CMe_3$), 82.9 (br s, $O\underline{C}Me_3$), 35.8 (s, $CH_2\underline{C}Me_3$), 35.1 (q, J_{CH} = 125 Hz, $CH_2C\underline{H}_3$), 32.1 (q, J_{CH} = 125 Hz, $OC\underline{H}_3$). An analytical sample was obtained by recrystallization from ether by adding acetonitrile and cooling to -30°. Anal. Calcd for $WC_{24}H_{45}NO_2$: C, 51.16; H, 8.05. Found: C, 50.92; H, 7.78.

Preparation of $W(NPh)(CH_2CMe_3)_2(OCMe_3)Cl$

A solution of $[NEt_4][W(NPh)(OCMe_3)Cl_4]$ (1.0 g, 1.6 mmol) in 40 ml of dichloromethane was cooled to -30° and $Zn(CH_2CMe_3)_2$ (0.32 g, 1.5 mmol) in pentane (5 ml) was added dropwise. After warming the reaction mixture to room temperature and stirring for 4 h, pentane (10 ml) was added and the mixture was filtered. The volatiles were then removed in vacuo. The oily residue was dissolved in pentane (10 ml) and this solution treated with activated charcoal and filtered. The pentane was removed from the filtrate in vacuo leaving a sticky yellow solid after drying in vacuo for several hours (0.61 g, 72%, pure by ^1H and ^{13}C NMR): ^1H NMR (C_6D_6, 270 MHz) δ 7.30 (d, 2, $^3J_{HoHm}$ = 8.8 Hz, NPh ortho), 7.09 (t, 2, $J_{H_{observed}}$ = 7.8 Hz, NPh meta), 6.86 (t, 1, $^3J_{HpHm}$ = 7.3 Hz, NPh para), 3.23 (d, 2, $^2J_{H_AH_B}$ = 9.8 Hz, $^2J_{HW}$ = 10.3 Hz, $C\underline{H}_A\underline{H}_BCMe_3$) 2.27 (d, 2, $^2J_{H_AH_B}$ = 9.8 Hz, $^2J_{HW}$ = 9.5 Hz, $CH_A\underline{H}_BCMe_3$), 1.27 (s, 9, $OCMe_3$), 1.15 (s, 18, $CH_2C\underline{H}_3$); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 153.7 (s, NPh ipso), 129.0, 128.3 and 128.0 (NPh), 92.5 (t, J_{CH} = 124 Hz, J_{CW} = 81.1 Hz, $\underline{C}H_2CMe_3$), 88.4 (s, $O\underline{C}Me_3$), 37.1 (s, $CH_2\underline{C}Me_3$), 34.9 (q, J_{CH} = 125 Hz, $CH_2C\underline{H}_3$), 31.3 (q, J_{CH} = 127 Hz, $OC\underline{H}_3$).

Preparation of $W(NPh)(CHCMe_3)(CH_2CMe_3)_2$

(a) From $W(NPh)Np_3Cl$ and Ph_3PCH_2

A solution of $W(NPh)(CH_2CMe_3)_3Cl$ (1.94 g, 3.7 mmol) in ether (40 ml) was cooled to -30°. Ph_3PCH_2 (1.07 g, 3.89 mmol) dissolved in 25 ml of ether was added dropwise to the stirred solution. After addition was complete the reaction mixture was warmed to room temperature and stirred for 24 h. The mixture was filtered and the $Ph_3PCH_3^+Cl^-$ was washed with pentane and dried in vacuo; yield 1.1 g (95%). The solvent was removed from the filtrate in vacuo leaving a dark oil which was distilled at 100-110°C (0.1μ) in a short path apparatus to give 1.1 g (61%) of pure product as an orange-red oil: ^1H NMR (toluene-d_8, 250 MHz) δ 7.35-6.87 (m, 5, NPh), 6.61 (br s, 1, $^2J_{HW}$ = 9.3 Hz, $CHCMe_3$), 1.33 (br s, 4, $^2J_{HW}$ = 9.3 Hz, CH_2CMe_3), 1.21 (s, 9, $CHCMe_3$), 1.14 (s, 18, CH_2CMe_3); the ^1H NMR spectrum was identical at -20°; ^{13}C NMR (toluene-d_8, 62.83 MHz) δ 246.1 (d, J_{CH} = 106 Hz, J_{CW} = 163 Hz, $CHCMe_3$), 157.5 (t, $^2J_{CH_{ortho}}$ = 9.0 Hz, $^2J_{CW}$ = 45 Hz, NPh ipso), 129.3-124.9 (overlapping resonances of NPh and toluene-d_8), 88.5 (t, J_{CH} = 112 Hz, J_{CW} = 95 Hz, CH_2CMe_3), 46.2 (s, $CHCMe_3$), 36.1 (s, CH_2CMe_3), 35.1 (q, J_{CH} = 124 Hz, CH_2CMe_3), 33.4 (q, J_{CH} ≈ 126 Hz, $CHCMe_3$); Molecular weight (differential vapor pressure, ether, 0°C): Calcd. 487, found 413 at 4.6×10^{-2} M.

(b) From $W(NPh)Np_3Cl$ and LiNp

A pentane solution (30 ml) of $W(NPh)(CH_2CMe_3)_3Cl$ (1.52 g, 2.9 mmol) was cooled to -30°C and $LiCH_2CMe_3$ (0.23 g, 2.9 mmol) was added in solid portions while stirring the mixture. The solution turned orange and LiCl precipitated. The reaction was warmed to room temperature. After stirring for 8 h, the mixture was filtered and the pentane was removed in vacuo leaving a red oil which was 95% pure $W(NPh)(CHCMe_3)(CH_2CMe_3)_2$ by ^1H NMR.

Preparation of $W(\eta^5\text{-}C_5H_5)(NPh)(CHCMe_3)(CH_2CMe_3)$

A solution of $W(NPh)(CH_2CMe_3)_3Cl$ (3.0 g, 5.7 mmol) in THF (40 ml) was cooled to -30°. NaC_5H_5 (0.56 g, 6.3 mmol) was added as a solid and the solution was warmed to room temperature. After stirring for 36 h the reaction mixture was filtered and the THF removed from the filtrate in vacuo. The resulting dark oil was extracted with pentane and activated charcoal was added. The mixture was filtered and the orange filtrate was concentrated and cooled to -30° to give 2.2 g of yellow crystals (80%): ^1H NMR (C_6D_6, 250 MHz) δ 9.81 (s, 1, $CHCMe_3$), 7.12-6.85 (m, 5, NPh), 5.37 (s, 5, C_5H_5), 2.21 (d, 1, $^2J_{H_AH_B}$ = 13.6 Hz, $^2J_{HW}$ = 9.6 Hz, $CH_AH_BCMe_3$), 2.03 (d, 1, $^2J_{H_BH_A}$ = 13.6 Hz, $^2J_{HW}$ = 9.6 Hz, $CH_AH_BCMe_3$), 1.36 (s, 9, CMe_3), 1.19 (s, 9, CMe_3); ^{13}C NMR (C_6D_6, 62.83 MHz) δ 268.7 (d, J_{CH} = 117.4 Hz, $CHCMe_3$), 157.9 (s, NPh ipso), 128.6, 125.5 and 124.5 (NPh), 101.8 (d, J_{CH} = 178.4 Hz, C_5H_5), 46.5 (s, $CHCMe_3$), 36.7 (s, CH_2CMe_3), 34.3 (q, J_{CH} = 124.4 Hz, CMe_3), 33.8 (q, J_{CH} = 124.4 Hz, CMe_3); the CH_2CMe_3 resonance, which was never observed in the 13C NMR spectra, is believed to lie under the CMe_3 resonances. Anal. Calcd for $WC_{21}H_{31}N$: C, 52.40; H, 6.49. Found: C, 52.67; H, 6.74.

Preparation of $W(\eta^5\text{-}C_5H_5)(NPh)(CH_2CMe_3)_2Cl$

A pentane solution (40 ml) of $W(\eta^5\text{-}C_5H_5)(NPh)(CHCMe_3)(CH_2CMe_3)$ (0.74 g, 1.5 mmol) was cooled to -30° and HCl gas (34 ml, 15 mmol) was added by syringe. A yellow powder precipitated immediately. After 15 minutes the yellow powder was filtered off and dissolved in 10 ml of toluene. Addition of pentane followed by cooling to -30° gave orange, flaky crystals (0.64 g, 80%): ^1H NMR ($CDCl_3$, 250 MHz, -40°) δ 7.35-7.11

(m, 5, NPh), 6.16 (s, 5, C_5H_5), 2.95 (d, 2, $^2J_{H_AH_B}$ = 12.9 Hz, $CH_AH_BCMe_3$), 2.19 (d, 2, $^2J_{H_BH_A}$ = 12.9 Hz, $^2J_{HW}$ = 10.3 Hz, $CH_AH_BCMe_3$), 1.26 (s, 18, CH_2CMe_3); $^{13}C\{^1H\}$ NMR (toluene-d_8, 22.5 Hz, -10°) δ 158.2 (NPh ipso), 130-124 (NPh), 106.1 (C_5H_5), 67.9 (CH_2CMe_3), 38.8 (CH_2CMe_3), 35.7 (CH_2CMe_3). Anal. Calcd for $WC_{21}H_{33}NCl$: C, 48.71; H, 6.42. Found: C, 46.56; H, 5.51. The analysis value is presumably low because the product is not stable at room temperature. It should be stored at ca. -30°.

Preparation of $W(NPh)(CHCMe_3)(PMe_3)_2Cl_2$ from $W(NPh)(CH_2CMe_3)_3Cl$ and Me_3PHCl

Me_3PHCl (0.11 g, 0.95 mmol) and PMe_3 (0.27 ml, 2.8 mmol) were added to a chloroform solution (8 ml) of $W(NPh)(CH_2CMe_3)_3Cl$ (0.50 g, 0.95 mmol). The mixture was stirred and heated to 60°C in a glass bomb for 24 h. Filtration, followed by removing the solvent *in vacuo* left an orange solid which was recrystallized from toluene at -30° (0.35 g, 65%).

Preparation of $W(NPh)(CHCMe_3)(py)_2Cl_2$

A solution containing $W(NPh)(CH_2CMe_3)_3Cl$ (0.50 g, 0.95 mmol), pyridine•HCl (0.11 g, 0.95 mmol), and pyridine (0.54 ml, 6.7 mmol) in chloroform (6 ml) was heated at 60°C for 48 h. The volatiles were then removed *in vacuo*. The red residue was extracted with a 1:1 mixture of toluene and dichloromethane and the extract was filtered and concentrated *in vacuo*. Pentane was added and the mixture was cooled to -30° to give 0.40 g of yellow crystals (73%): ^1H NMR ($CDCl_3$, 60 MHz) δ 11.3 (s, 1, $CHCMe_3$), 9.1 (br, 10, py), 7.1 (br, 5, NPh), 1.0 (s, 9, $CHCMe_3$). ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 303.2 (d, J_{CH} = 121 Hz, $CHCMe_3$), 154.8, 152.2 and 138.5 (py), 128.0, 126.4 and 124.3 (NPh), 45.8 ($CHCMe_3$), 33.3 (q, J_{CH} = 125 Hz, $CHCMe_3$).

Preparation of $W(NPh)(CH_2SiMe_3)_3Cl$

$Zn(CH_2SiMe_3)_2$ (3.67 g, 15.3 mmol) in 10 ml of pentane was added dropwise to a vigorously stirred suspension of $W(NPh)Cl_4(Et_2O)$ (5.0 g, 10.2 mmol) in pentane. After 1 h the mixture was filtered and the zinc salts were washed with pentane (20 ml). The combined filtrates were concentrated in vacuo until crystallization began. The solution was cooled to -30° for 12 h and beige, powdery $W(NPh)(CH_2SiMe_3)_3Cl$ was collected by filtration and dried in vacuo (4.03 g). The mother liquor was concentrated further and cooled to -30° again. Two more crops were obtained for a total of 4.93 g (85%): ^1H NMR (C_6D_6, 250 MHz) δ 7.48-7.04 (m, 5, NPh), 2.18 (s, 6, $^2J_{HW}$ = 8.1 Hz, $C\underline{H}_2SiMe_3$), 0.25 (s, 27, $CH_2Si\underline{Me}_3$); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 153.0 (s, NPh ipso), 129.0, 128.8 and 127.4 (NPh), 72.4 (t, J_{CH} = 118.8 Hz, J_{CW} = 74.7 Hz, $\underline{C}H_2SiMe_3$), 2.9 (q, J_{CH} = 118.7 Hz, $CH_2Si\underline{Me}_3$). Anal. Calcd for $WC_{18}H_{38}ClNSi_3$: C, 37.79; H, 6.70. Found: C, 38.11; H, 6.63.

Preparation of $W(NPh)(CH_2SiMe_3)_2Cl_2$

$[Et_4N][W(NPh)Cl_5]$ (2.50 g, 4.29 mmol) was suspended in 75 ml of dichloromethane and $Zn(CH_2SiMe_3)_2$ (0.71 g, 2.96 mmol) in 5 ml of dichloromethane was added dropwise to the well-stirred solution over a 0.5 h period. After 2 h pentane (20 ml) was added to aid in precipitation of the Zn salts and the mixture was filtered. The insolubles were washed with ether and the solvent was removed in vacuo from the combined filtrates. The residue was extracted with pentane (20 ml). The mixture was filtered and the filtrate was concentrated in vacuo. Cooling to -30° gave orange crystals which were isolated by filtration and dried in vacuo (0.92 g, 60%

based on $Zn(CH_2SiMe_3)_2$): ^1H NMR (C_6D_6, 250 MHz) δ 7.31-7.02 (m, 5, NPh), 2.96 (d, 2, $^2J_{H_AH_B}$ = 6.25 Hz, $^2J_{HW}$ ≈ 10 Hz, $CH_AH_BSiMe_3$), 2.82 (d, 2, $^2J_{H_BH_A}$ = 6.25 Hz, $^2J_{HW}$ ≈ 10 Hz, $CH_AH_BSiMe_3$), 0.16 (s, 18, $CH_2Si\underline{Me}_3$); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 151.0 (s, NPh ipso), 129-127 (NPh), 86.9 (t, JCH = 125.2 Hz, J_{CW} ≈ 78 Hz, $\underline{C}H_2SiMe_3$), 2.1 (q, J_{CH} = 118.6 Hz, $CH_2Si\underline{Me}_3$); Molecular weight (cyclohexane, cryoscopic) calcd 520, found 468.

Preparation of $W(NPh)(CH_2SiMe_3)_4$

(a) From $W(NPh)(CH_2SiMe_3)_3Cl$ and $LiCH_2SiMe_3$

$LiCH_2SiMe_3$ (0.12 g, 1.3 mmol) was added in one portion to a stirred solution of $W(NPh)(CH_2SiMe_3)_3Cl$ (0.75 g, 1.3 mmol) in pentane (40 ml) which had been cooled to -30°. The solution became orange and LiCl precipitated as the reaction warmed to room temperature. After 4 h the reaction mixture was filtered and the pentane was removed from the filtrate in vacuo leaving red-orange crystals. These were dissolved in a minimum of ether. One volume of acetonitrile was added. Yellow crystals (0.38 g) were collected after 24 h at -30°, washed with CH_3CN, and dried in vacuo. The mother liquor was further concentrated and cooled to -30° to give another 0.24 g of product (total 0.62 g, 76%): ^1H NMR (toluene-d_8, 0.1M, -85°, 250 MHz) δ 7.4-6.8 (m, 5, NPh), 1.92 (br s, 6, equatorial $\underline{C}H_2SiMe_3$), 1.11 (br s, 2, axial $\underline{C}H_2SiMe_3$), 0.58 (br s, 9, axial $CH_2Si\underline{Me}_3$), 0.23 (br s, 27, equatorial $CH_2Si\underline{Me}_3$); ^1H NMR (25°) δ 7.4-6.8 (m, 5, NPh), 1.57 (s, 8, $^2J_{HW}$ = 7.6 Hz, $\underline{C}H_2SiMe_3$), 0.23 (s, 36, $CH_2Si\underline{Me}_3$); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 154.0 (s, NPh ipso), 128.6, 127.5 and 126.6 (NPh), 79.9 (t, J_{CH} = 115 Hz, J_{CW} = 61.5 Hz, $\underline{C}H_2SiMe_3$), 3.0 (q, J_{CH} = 119 Hz, $CH_2Si\underline{Me}_3$). Anal. Calcd for $WC_{22}H_{49}NSi_4$: C, 42.36; H, 7.92. Found: C, 39.98; H, 7.27. (The values

found compare quite favorably with those calculated for loss of one Me_4Si: C, 40.29; H, 6.95.) This product decomposes noticeably in the solid state at room temperture in ~1 day, and therefore should be stored at ca. -30°.

(b) From $W(NPh)Cl_4(Et_2O)$ and Me_3SiCH_2MgCl

A solution of $W(NPh)Cl_4(Et_2O)$ (2.0 g, 4.1 mmol) in 50 ml of ether was added dropwise to Me_3SiCH_2MgCl in ether (80 ml, 16.5 mmol) which was kept at -78°C. After the addition was complete the mixture was allowed to warm to room temperature and was stirred for 16 h. The magnesium salts were filtered off and washed with ether. The solvent was removed from the combined filtrates in vacuo leaving a solid which was isolated and purified as above (1.02 g, 40%).

Preparation of $W(NPh)(CHSiMe_3)(CH_2SiMe_3)_2$

A solution of $W(NPh)(CH_2SiMe_3)_4$ (1.0 g, 1.6 mmol) in toluene (30 ml) was heated at 60° for 5 h. Removing all volatiles in vacuo left a dark red oil which was pure by ^1H and ^{13}C NMR.

^1H NMR (toluene-d_8, 250 MHz, 25°) δ 7.79 (s, 1, $CHSiMe_3$), 7.29-6.98 (m, 5, NPh), 0.63 (s, 4, $^2J_{HW}$ = 9.8 Hz, CH_2SiMe_3), 0.22 (s, 9, $CHSiMe_3$), 0.14 (s, 18, CH_2SiMe_3); ^1H NMR (70°) δ 7.89 (s, 1, $^2J_{HW}$ = 8.8 Hz, $CHSiMe_3$), 7.29-6.98 (m, 5, NPh), 0.70 (d, 2, $^2J_{H_AH_B}$ = 10.7 Hz, $CH_AH_BSiMe_3$), 0.62 (d, 2, $^2J_{H_BH_A}$ = 10.7 Hz, $CH_AH_BSiMe_3$), 0.21 (s, 9, $CHSiMe_3$), 0.13 (s, 18, CH_2SiMe_3). We believe that the equivalence of the trimethylsilylmethyl α-protons in the 25° ^1H NMR spectrum is accidental. ^{13}C NMR (C_6D_6, 22.5 MHz): 230.4 (d, J_{CH} = 108 Hz, J_{CW} = 127 Hz, $CHSiMe_3$), 157.4 (s, NPh ipso), 128.8, 125.0 and 124.7 (NPh), 60.8 (t, J_{CH} = 110 Hz, J_{CW} = 83.5 Hz, CH_2SiMe_3), 2.6 (q, J_{CH} = 119 Hz, $CHSiMe_3$ and CH_2SiMe_3).

Preparation of $W(NPh)(CHSiMe_3)(PMe_3)_2Cl_2$

PMe_3 (0.12 ml, 2.1 mmol) was added to 12 ml of dichloromethane containing 0.45 g (0.86 mmol) of $W(NPh)(CH_2SiMe_3)_2Cl_2$. After 18 h the dichloromethane was removed in vacuo. The residue was extracted with toluene (20 ml). The extract was filtered and concentrated in vacuo to ~10 ml. Pentane was added and the solution was cooled to -30° to give orange crystals (0.44 g, 88%): ^1H NMR ($CDCl_3$, 270 MHz) δ 12.75 (t, 1, $^3J_{HP}$ = 4.6 Hz, C<u>H</u>SiMe$_3$), 7.45 (d, 2, $^2J_{HoHm}$ = 7.3 Hz, NPh ortho), 7.28 (t, 2, $J_{H_{observed}}$ = 7.4 Hz, NPh meta), 7.12 (t, 1, $^3J_{HpHm}$ = 7.3 Hz, NPh para), 1.60 (t, 18, $^2J_{HP}$ = 4.7 Hz, PMe_3), 0.17 (s, 9, CHSi<u>Me</u>$_3$); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 293.1 (d, J_{CH} = 119 Hz, $^2J_{CP}$ = 9 Hz, <u>C</u>HCMe$_3$), 154.7 (s, NPh ipso), 128.4 and 126.9 (NPh), 16.1 (qt, J_{CH} = 132 Hz, J_{CP} = 15 Hz, PMe_3), 3.0 (q, J_{CH} = 119 Hz, CHSi<u>Me</u>$_3$; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ -7.0 (s, J_{PW} = 288 Hz).

Preparation of $W(NPh)(CH_3)_3Cl$

$[Et_4N][W(NPh)Cl_5$ (6.6 g, 11.2 mmol) was suspended in 150 ml of dichloromethane along with Et_4NCl (0.93 g, 5.6 mmol). After cooling the mixture to 0° $ZnMe_2$ (1.2 ml, 16.9 mmol) in 10 ml of pentane was added rapidly (1 min) while stirring the suspension. After 17 h the reaction mixture was filtered and the solids washed with toluene. The solvent was removed from the filtrate in vacuo leaving a tan solid which was extracted with ether (75 ml). The extract was filtered and concentrated in vacuo until crystallization began. Cooling to -30° gave 2.41 g of a tan powder. Concentrating the mother liquor further gave another 0.65 g of product (total 3.06 g, 77%). The product may be recrystallized at -30° from

dilute ether solutions to give golden needles: ^{1}H NMR (C_6D_6, 250 MHz) δ 7.06-6.89 (m, 5, NPh), 1.28 (s, 9, $^2J_{HW}$ = 8.1 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 151.8 (s, NPh ipso), 128.6, 128.0 and 127.2 (NPh), 53.8 (q, J_{CH} = 128 Hz, J_{CW} = 75.2 Hz, CH_3). Anal. Calcd for $WC_9H_{14}ClN$: C, 30.41; H, 3.97. Found: C, 30.70; H, 4.05.

Preparation of $W(NPh)(CH_3)_3(OCMe_3)$

$[Et_4N][W(NPh)(OCMe_3)Cl_4]$ (2.17 g, 3.50 mmol) was dissolved in 60 ml of dichloromethane and the solution was cooled to -30°. A pentane solution (5 ml) of $ZnMe_2$ (360 μl) was added dropwise to the stirred solution. The reaction became bright yellow and a white precipitate formed. After 1 h pentane (20 ml) was added to aid precipitation of the zinc salts and the salts were filtered off. The volatiles were removed from the filtrate *in vacuo* leaving an oily orange solid. Extraction of this material with pentane followed by filtration and removal of the pentane *in vacuo* gave a yellow-orange oil that is pure $W(NPh)(CH_3)_3(OCMe_3)$ by ^{1}H NMR (0.96 g, 70%). ^{1}H NMR (C_6D_6, 60 MHz) δ 7.3-6.8 (m, s, NPh), 1.4 (s, 9, $OCMe_3$), 1.0 (s, 9, $^2J_{HW} \approx 9$ Hz, CH_3); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 156.3 (br s, NPh, ipso), 128.5, 126.9 and 124.7 (NPh), 79.8 (br s, $O\underline{C}Me_3$), 40.8 (q, J_{CH} = 127.4 Hz, J_{CW} = 81.3 Hz, CH_3), 31.76 (q, J_{CH} = 125 Hz, $OC\underline{Me}_3$).

Preparation of $W(\eta^5\text{-}C_5H_5)(NPh)(CH_3)_3$

NaC_5H_5 (0.12 g, 1.4 mmol) was added to a THF solution (15 ml) of $W(NPh)(CH_3)_3Cl$ (0.41 g, 1.2 mmol) which had been cooled to -30°. The reaction mixture was warmed to room temperature and stirred for 8 h. The THF was removed *in vacuo* and the residue was extracted with pentane. The

pentane extract was filtered and the filtrate was concentrated in vacuo and cooled to -30° to give yellow crystals (0.41 g, 92%): ^{1}H NMR (C_6D_6, 270 MHz) δ 7.04-6.83 (m,5, NPh), 5.09 (s, 5, C_5H_5), 1.28 (s, 6, $^2J_{HW} \approx 6$ Hz, CH_3), 0.92 (s, 3, $^2J_{HW} \approx 6$ Hz, CH_3); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 158.0 (s, NPh ipso), 128.4-122.3 (NPh), 103.3 (d, J_{CH} = 178 Hz, C_5H_5), 23.6 (q, J_{CH} = 127 Hz, $J_{CW} \approx 62$ Hz, CH_3 trans to NPh), 17.6 (q, J_{CH} = 129 Hz, $J_{CW} \approx 51$ Hz, CH_3 cis to NPh).

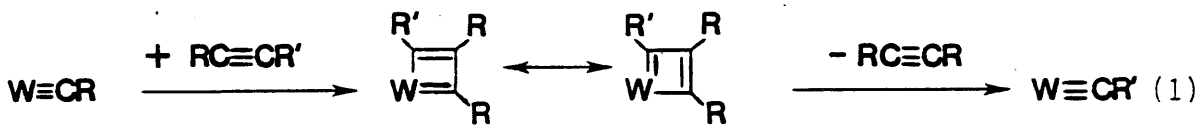
Preparation of $W(NPh)(CH_2Ph)_3Cl$

$[Et_4N][W(NPh)(OCMe_3)Cl_4]$ (2.41 g, 3.9 mmol) was suspended in THF which was kept at 0° while $PhCH_2MgCl$ (11 ml, 0.94M in ether) was added dropwise. After stirring for 24 h at 25° the solvent was removed from the reaction mixture in vacuo. Extraction of the dark residue with ether followed by filtration and removal of the ether in vacuo gave a dark orange oil which was dissolved in toluene (50 ml). After cooling this solution to 0°, HCl gas (96 ml, 4.3 mmol) was added by syringe. After 0.5 h all volatiles were removed in vacuo. The residue was extracted with ether, the extract was filtered, and the filtrate was concentrated in vacuo until crystallization began. Cooling the solution to -30° gave a total of 1.2 g (3 crops) of yellow crystals (53%): ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.53-7.24 (m, 20, CH_2Ph and NPh), 3.24 (s, 6, $^2J_{HW}$ = 9.8 Hz, CH_2Ph); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 151.9 (br s, NPh ipso), 135.4-126.9 (CH_2Ph and NPh), 66.4 (t, J_{CH} = 142 Hz, J_{CW} = 77.7 Hz, CH_2Ph). Anal. Calcd for $WC_{27}H_{26}NCl$: C, 55.55; H, 4.49. Found: C, 55.99; H, 4.71.

CHAPTER 2

INTRODUCTION

In 1975 Katz and McGinnis[7] proposed that transition metal carbyne complexes might catalyze alkyne metathesis via metallacyclobutadiene intermediates (eq 1). This proposal was the logical extension of another



(1)

hypothesis these authors presented concerning the olefin metathesis reaction, namely, that metal carbene complexes and metallacyclobutanes were viable intermediates. This latter suggestion is now well documented[34]. However, not until recently had an alkylidyne complex (e.g., $W(CCMe_3)(OCMe_3)_3$[6]) been shown to catalyze alkyne metathesis.

Evidence supporting the intermediate nature of tungsten(VI) alkylidynes in alkyne metathesis was provided by the stoichiometric metathesis reaction outlined in eq 2.[6] However, the existence of metallacyclobuta-

$$W(CCMe_3)(OCMe_3)_3 \xrightarrow[-\ PhC{\equiv}CCMe_3]{+\ PhC{\equiv}CPh} W(CPh)(OCMe_3)_3 \qquad (2)$$

diene intermediates was still hypothetical since such species had not been isolated nor observed spectroscopically.

Although complexes of the type $W(CR)(OCMe_3)_3$ are phenomenal catalysts for the homogeneous metathesis of dialkyl and diaryl alkynes, Sancho has noted that at high concentrations of alkynes the catalyst is deactivated.[35] This observation sparked our curiosity and led us to undertake studies

aimed at elucidating the deactivation pathway(s). We naturally also became interested in more general questions such as: what other reactions, besides metathesis, can occur between tungsten(VI) alkylidyne complexes and alkynes?

In this chapter I report on the results we have obtained from studies directed at learning more about the reactivity of tungsten(VI) alkylidynes with alkynes. The order in which I have chosen to report these details is, for the most part, chronologically the way this chemistry developed. Hopefully, this will convey to the reader some of the excitement which I experienced while working in this area of chemistry. Furthermore, it is intended to demonstrate that our group's approach to studying transition metal catalysis (e.g., synthesis of potential intermediates and exploration of their reaction chemistry) can be very adventuresome and rewarding.

RESULTS

Preparation of $W(\eta^5\text{-}C_5R_4CMe_3)(RC{\equiv}CR)Cl_2$ and $[W(\eta^5\text{-}C_5R_4CMe_3)Cl_4]_2$ (R = Me, Et)

Jose Sancho noted that $[W(CCMe_3)Cl_4][NEt_4]$ reacts with dialkyl alkynes, but no metathesis products are observed[35]. Looking into this reaction in more detail I found that when $[W(CCMe_3)Cl_4][NEt_4]$ reacts with excess 3-hexyne (ca 10 equivalents in dichloromethane), bright red, pentane-soluble crystals are isolated in yields that consistently accounted for approximately 40-50% (by weight) of the original tungsten used in the reaction. From analytical data (C, H, and Cl) we were able to determine that this compound had the empirical formula, $W(CCMe_3)(EtC{\equiv}CEt)_3Cl_2$. A molecular weight measurement in dichloromethane showed that the species was a monomer.

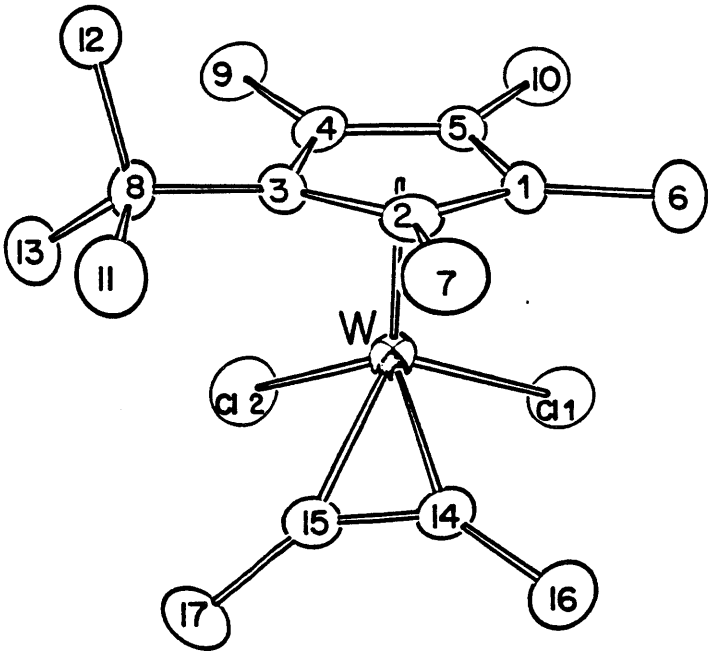
A similar reaction with 2-butyne proceeds more quickly and again gives bright red crystals (ether soluble), now with the empirical formula $W(CCMe_3)(MeC{\equiv}CMe)_3Cl_2$. Both complexes exhibit broad ^1H NMR spectra which do not improve significantly upon heating or cooling the solutions. Furthermore, we observed an EPR signal (g_{AV} = 1.91) for $W(CCMe_3)(EtC{\equiv}CEt)_3Cl_2$. In the infrared spectrum of $W(CCMe_3)(2\text{-butyne})_3Cl_2$ there is a band at 1676 cm^{-1} (1665 cm^{-1} for the 3-hexyne derivative).

Both of these compounds can be obtained more straightforwardly by reacting an excess of the alkyne with $W(CCMe_3)(dme)Cl_3$. In this reaction a less soluble, paramagnetic, orange complex with the empirical formula $W(CCMe_3)(alkyne)_2Cl_4$ also forms in ~50% yield by weight. A molecular weight study of "$W(CCMe_3)(EtC{\equiv}CEt)_2Cl_4$" in dichloromethane at 0°C (by differential vapour pressure measurement) showed it to be a dimer.

An x-ray structural study of "$W(CCMe_3)(2\text{-butyne})_3Cl_2$", performed by Churchill and Wasserman,[36] shows it to be $W(\eta^5\text{-}C_5Me_4CMe_3)(2\text{-butyne})Cl_2$ (Figure 1), a species which is closely related to the diamagnetic Ta(III) derivatives, $Ta(\eta^5\text{-}C_5Me_5)(alkyne)Cl_2$.[37] As in $Ta(\eta^5\text{-}C_5Me_5)(PhC{\equiv}CPh)Cl_2$,[37] the axis of the acetylene ligand in $W(\eta^5\text{-}C_5Me_4CMe_3)(MeC{\equiv}CMe)Cl_2$ lies parallel to the plane of the cyclopentadienyl ligand, and the acetylene carbon-carbon bond length is lengthened considerably as a result of its strong bond to the metal.

Based on the above results, it makes sense that $[W(CCMe_3)(alkyne)_2Cl_4]_2$ are also substituted cyclopentadienyl complexes; i.e., $[W(\eta^5\text{-}C_5R_4CMe_3)Cl_4]_2$. This was confirmed by preparing $[W(CCMe_3)(alkyne)_2Cl_4]_2$ in high yields from $W(\eta^5\text{-}C_5R_4CMe_3)(alkyne)Cl_2$ and excess chlorine.

Figure 1. X-Ray Crystal Structure of $W(\eta^5\text{-}C_5Me_4CMe_3)(MeC{\equiv}CMe)Cl_2$


12
9
10
4
5
8
3
1
6
2
13
11
7
W
Cl 2
Cl 1
15
14
17
16

Preparation and Reactivity of $W[C(CMe_3)C(R)C(R)]Cl_3$ (R = Me, Et)

Upon examining the previously mentioned reactions more carefully, we found that addition of one equivalent of 2-butyne or 3-hexyne to $W(CCMe_3)(dme)Cl_3$ yields violet, diamagnetic crystals. ^1H NMR spectra indicated that the 1,2-dimethoxyethane ligand was gone and only one alkyne ligand had been incorporated into the new complexes. Furthermore, the two alkyl groups of the alkyne unit were inequivalent. ^{13}C NMR studies demonstrated that there were three lowfield resonances (Table I), two of which had very similar chemical shifts; the third was located ~110 ppm upfield. This combined information suggested that these new compounds were tungstenacyclobutadiene complexes consisting of metallacycle rings that are the average of the two resonance structures shown in Figure 2.

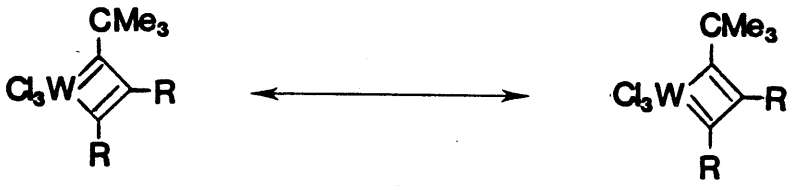


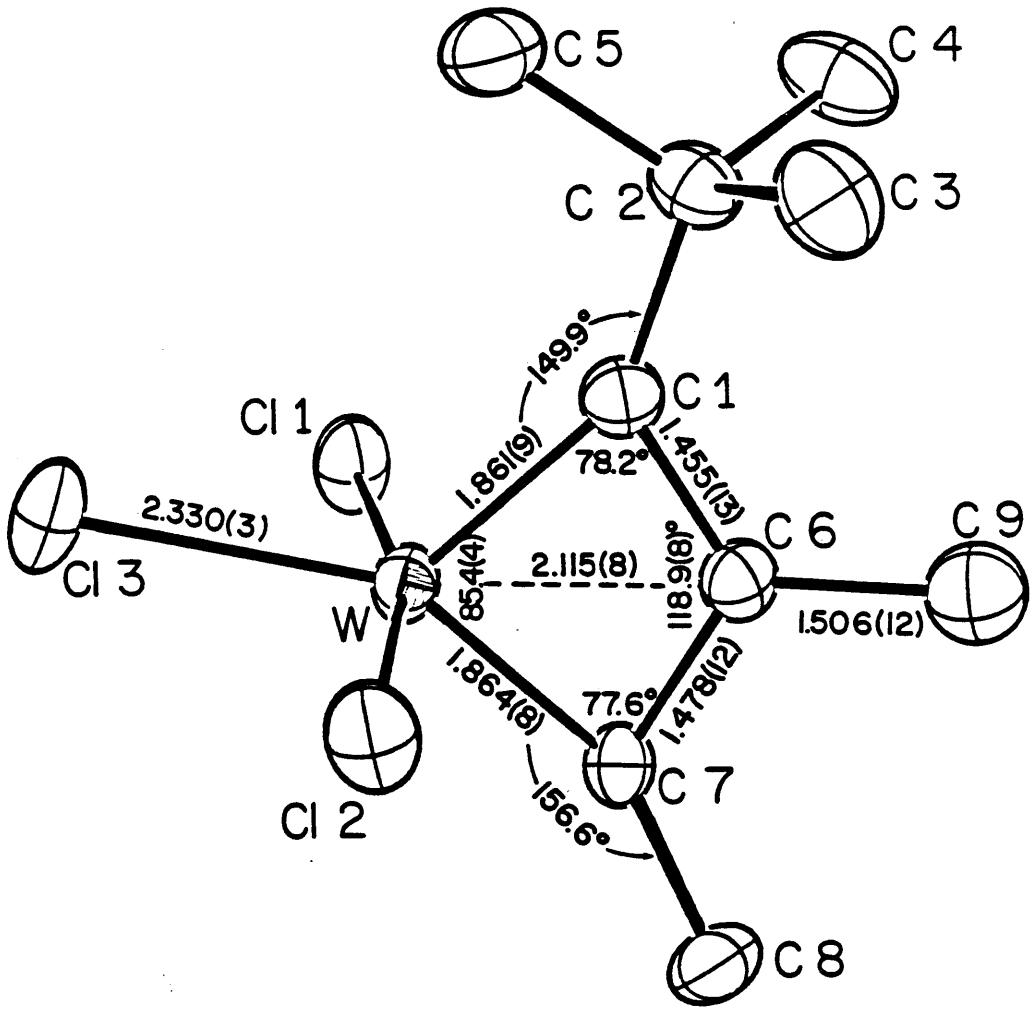
Figure 2.

An x-ray structural study of $W(CCMe_3)(MeC{\equiv}CMe)Cl_3$ confirmed this proposal (Figure 3).[39] The molecule is nearly a trigonal bipyramid with axial chloride ligands ($\angle$ Cl(1)-W-Cl(2) = 166.12(9)°) and an essentially planar WC_3 ring lying in the equatorial plane. The substituent carbon atoms (C(2), C(8), C(9)) and Cl(3) also lie in the equatorial plane. The W-C_α bond-lengths are equal and slightly shorter than the W=C_α double bond distance of 1.942(9)Å found in $W(CCMe_3)(CHCMe_3)(CH_2CMe_3)(dmpe)$[3] or of 1.882(14)Å found in $W(O)(CHCMe_3)(PEt_3)Cl_2$.[5] Carbon-carbon distances within the four-membered

Table I. ^{13}C NMR Data for Tungstenacyclobutadiene Complexes

Compound	C_α (ppm)	C_β (ppm)	$^{J}C_\alpha W$ (Hz)
$W(CCMe_3C_2Me_2)Cl_3$	267.5, 263.4	150.7	
$W(CCMe_3C_2Et_2)Cl_3$	267.6, 266.7	150.3	
$W[C_\alpha(CMe_3)C(Me)C_\alpha(CMe_3)]Cl_3$	273.0	148.1	102
$W(CCMe_3C_2Me_2)(OCMe_3)Cl_2$	265.6, 259.1	134.2	93, 116
$W(CCMe_3C_2Et_2)(OCMe_3)Cl_2$	266.4, 265.7	137.4	93, 110
$W(CCMe_3C_2Me_2)(OCH(Me)CH_2Cl)Cl_2$	267.9, 260.2	140.5	
$W(CCMe_3C_2Me_2)(OCMe_2CMe_2O)Cl$	250.1, 241.3	143.0	
$W(CCMe_3C_2Et_2)(OCMe_2CMe_2O)Cl$	248.8, 248.7	145.8	
$W(CCMe_3C_2Me_2)(OCMe_2CMe_2CMe_2O)Cl$	251.5, 238.9	139.0	
$W(CCMe_3C_2Me_2)(OCMe_2CMe_2O)(OCMe_3)$	232.1, 225.2	128.9	122, 134
$W(CCMe_3C_2Me_2)(OCMe_2CMe_2CMe_2O)(OCMe_3)$	238.6, 221.4	124.5	113, 145
$W(C_3Et_3)(OCMe_2CMe_2O)(OCMe_3)$	226.5	132.9	
$W(C_3Et_3)(OCH(CF_3)_2)_3$[11]	242.9	147.3	127

Figure 3. X-Ray Crystal Structure of $W[C(CMe_3)C(Me)C(Me)]Cl_3$.


C 5
C 4
C 2
C 3
149.9°
C 1
Cl 1
1.861(9)
78.2°
1.455(13)
2.330(3)
Cl 3
W
85.4(4)
2.115(8)
118.9(8)°
C 6
C 9
1.506(12)
1.864(8)
77.6°
1.478(12)
Cl 2
C 7
156.6°
C 8

ring are intermediate between those expected for purely double and single bonds, but are slightly closer to the latter. The three most surprising features are the large C_α-C_β-C_α angle (118.9(8)°), the short W-C_β distance (far shorter than the W-C_α single bond length of 2.258(8)Å in $W(CCMe_3)(CHCMe_3)(CH_2CMe_3)(dmpe)$[3]), and the large W-C(1)-C(2) and W-C(7)-C(8) angles (149.9(7)° and 156.6(7)°, respectively). These results contrast sharply with those for $Rh(C_3Ph_3)Cl_2(PMe_2Ph)_2$[39] and $[Ir(C_3Ph_3)(CO)(Cl)(PMe_3)_2]^+$ [40] in which little, if any, multiple metal-carbon bond character is present, and the metallacyclic unit is compressed along the C_α-$C_{\alpha'}$ direction. (The Cα-Cα' distance in $W[C(CMe_3)C(Me)C(Me)]Cl_3$ is 2.525(12)Å but in $Rh(C_3Ph_3)Cl_2(PMe_2Ph)_2$[39] it is only 2.156(6)Å.)

As expected, these metallacycles react further with alkyne to give the mixture of cyclopentadienyl compounds discussed in the previous section. The most likely pathway by which these complexes arise is disproportionation of some intermediate tungsten(IV) species, possibly "$W(\eta^5\text{-}C_5R_4CMe_3)Cl_3$", as shown in eqs 3 and 4.

$$W(CCMe_3)(dme)Cl_3 + 2\ RC{\equiv}CR \longrightarrow \text{"}W(\eta^5\text{-}C_5R_4CMe_3)Cl_3\text{"} \qquad (3)$$

$$\text{"}W(\eta^5\text{-}C_5R_4CMe_3)Cl_3\text{"} \xrightarrow{0.5\ RC{\equiv}CR} 0.5\ W(\eta^5\text{-}C_5R_4CMe_3)(RC{\equiv}CR)Cl_2 + 0.25\ [W(\eta^5\text{-}C_5R_4CMe_3)Cl_4]_2 \qquad (4)$$

Unfortunately, we have never isolated or observed "$W(\eta^5\text{-}C_5R_4CMe_3)Cl_3$". If one equivalent of alkyne is added to the appropriate metallacyclobutadiene complex, only the mixture of cyclopentadienyl products along with starting material are isolated. We have also attempted to trap this proposed d^2 intermediate by oxidizing it to $W(\eta^5\text{-}C_5R_4CMe_3)(O)Cl_3$.[41] For

example, many reduced metal complexes are known to deoxygenate epoxides to give metal oxo complexes and an olefin.[42] Therefore, we treated an ether solution containing $W(CCMe_3)(dme)Cl_3$ and excess propylene oxide ($W(CCMe_3)(dme)Cl_3$ does not react with propylene oxide) with five equivalents of 2-butyne. After a short period of time the solution became a clear cherry red color and no $[W(\eta^5\text{-}C_5R_4CMe_3)Cl_4]_2$ precipitated. At first this was an encouraging observation. However, a ^1H NMR spectrum of the reaction mixture indicated that there were two compounds present (apparently isomers), each of which contained one alkyne and one "propylene oxide" unit. ^{13}C NMR showed that they were new metallacyclobutadiene complexes. Not surprisingly, $W(CCMe_3C_2Me_2)Cl_3$ reacts with propylene oxide to give the same mixture of compounds. The reaction that is occurring is the stoichiometric ring opening of an epoxide by a Lewis acid to give a mixture of chlorohydrin substituted metallacyclobutadiene complexes (eq 5). An independent synthesis of one of these isomers was accomplished by reacting $W(CCMe_3C_2Me_2)Cl_3$ with 3-chloro-2-propanol.

$$2\ W(CCMe_3C_2Me_2)Cl_3 + 2\ \text{(epoxide)} \longrightarrow W(CCMe_3C_2Me_2)(OCH(Me)CH_2Cl)Cl_2 + W(CCMe_3C_2Me_2)(OCH_2CH(Me)Cl)Cl_2 \qquad (5)$$

We have also attempted to synthesize "$W(\eta^5\text{-}C_5R_4CMe_3)Cl_3$" by reducing $W(\eta^5\text{-}C_5R_4CMe_3)Cl_4$. However, with one equivalent of Na/Hg, a new product is obtained (diamagnetic) in ~50% yield along with unreacted starting material. A good yield of this new compound is realized when two equivalents of Na/Hg are used (eq 6). The structure of this species is not known at this time but a reasonable guess is that n=2 and a tungsten-tungsten triple bond is present.

$$0.5\ [W(\eta^5\text{-}C_5Me_4CMe_3)Cl_4]_2 + 2\ Na/Hg \longrightarrow {}^1/_n\ [W(\eta^5\text{-}C_5Me_4CMe_3)Cl_2]_n \quad (6)$$

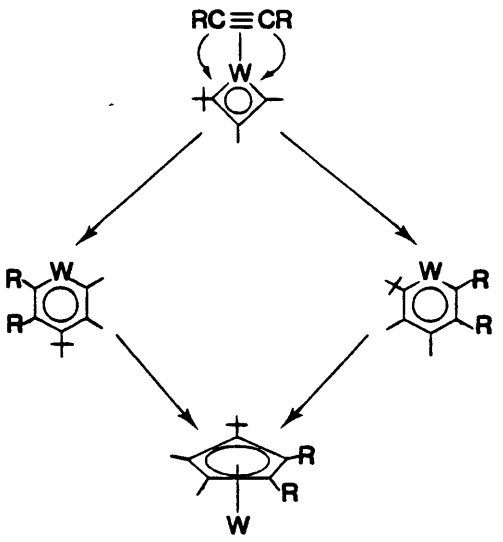
It is conceivable that $[W(\eta^5\text{-}C_5R_4CMe_3)Cl_2]_n$ might be an intermediate in the reaction leading to our mixture of d^1 and d^3 cyclopentadienyl complexes (eqs 3 and 4) as shown in eq 7. However, this can be ruled out since $[W(\eta^5\text{-}C_5Me_4CMe_3)Cl_2]_n$ does <u>not</u> react with 2-butyne under the conditions normally employed in these reactions.

$$2\ \text{"}W(\eta^5\text{-}C_5Me_4CMe_3)Cl_3\text{"} \longrightarrow 0.5\ [W(\eta^5\text{-}C_5Me_4CMe_3)Cl_4]_2 + {}^1/_n\ [W(\eta^5\text{-}C_5Me_4CMe_3)Cl_2]_n \quad (7)$$

$$\xrightarrow{\not\equiv\ MeC\equiv CMe} W(\eta^5\text{-}C_5Me_4CMe_3)(MeC\equiv CMe)Cl_2$$

<u>Mechanistic Details of Cyclopentadienyl Ring Formation From Tungstenacyclobutadiene Complexes and Alkynes</u>

In the previous section we proposed a mechanism for the formation of cyclopentadienyl complexes from tungsten(VI) neopentylidyne complexes and alkynes. However, we did not consider any of the details associated with formation of the cyclopentadienyl ring. The simplest mechanism we envisioned for this reaction involves coordination of alkyne to the metallacyclobutadiene complex followed by insertion into one of the metal-carbon bonds (Scheme I). As shown, this would produce two different metallacyclohexatriene rings.[44] However, only <u>one</u> type of cyclopentadienyl ring is produced if ring formation occurs via coupling of the two alpha carbons of the metallacycle (Scheme I).



Scheme I.

If the metallacycle is reacted with the same type of alkyne used to make the metallacycle, no mechanistic information can be obtained since only one type of cyclopentadienyl ring can be formed (assuming no metathesis reaction occurs). When a different, symmetric alkyne (RC≡CR) is used, there are, in theory (disregarding any particular mechanism), four possible isomers one can obtain (Figure 4). Only one of these (A) should be formed if the mechanism proposed in Scheme I is operating.

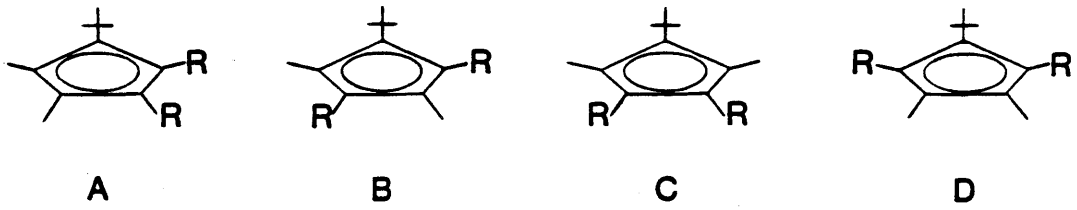


Figure 4

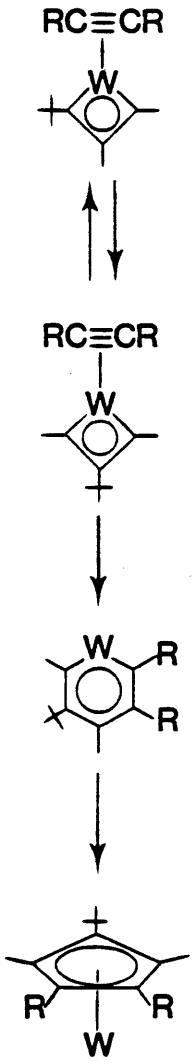
We reacted $W(CCMe_3C_2Me_2)Cl_3$ with excess 3-hexyne and isolated the $[W(\eta^5\text{-}C_5Me_2Et_2CMe_3)Cl_4]_2$ that precipitates from the reaction. The fact that both types of cyclopentadienyl products obtained from this reaction are paramagnetic makes analysis difficult. We got around this problem by

preparing the d^0 neopentylidyne complex, $W(\eta^5\text{-}C_5Me_2Et_2CMe_3)(CCMe_3)Cl_2$, from $W(\eta^5\text{-}C_5Me_2Et_2CMe_3)Cl_4$ and $ZnNp_2$.[27] A ^1H NMR spectrum of the crude pentane extracts from this reaction was very clean and showed that two isomers of this neopentylidyne complex are present. One of these isomers contains a cyclopentadienyl ring whose spectrum is consistent with the ring geometry expected if our original mechanism is correct (Scheme I). Unfortunately, it is not possible to distinguish (by ^1H NMR) between isomer A and isomer B (Figure 4), although we assume isomer A is correct.

The other isomer in this mixture contains a more symmetric cyclopentadienyl ring in that the methyl groups in this ring are equivalent. We believe this compound has the cyclopentadienyl ring configuration of isomer C in Figure 4 (but we cannot rule out the possibility that it is isomer D).

It is important to emphasize that we always use excess alkyne in these reactions, yet we <u>never</u> observe the formation of pentamethyl- or pentaethylcyclopentadienyl rings. These products are expected if the metallacycle ring breaks up under these conditions to give a mixture of alkylidyne complexes.

The fact that we observe two types of cyclopentadienyl rings in the above reaction argues against the mechanism we proposed in Scheme I. However, if we incorporate into this mechanism another step that allows for the reversible rearrangement of the metallacycle ring upon coordination of alkyne we can see how the other cyclopentadienyl ring isomer might form (Scheme II). So far we have not been able to isolate or observe a rearrangement product of this type. We hoped that by adding a bulky alkyne such as di-t-butyl acetylene to a solution of the metallacycle, cyclopentadienyl ring formation would be slowed down or stopped yet some rearranged



Scheme II. Revised Mechanism for Cyclopentadienyl Ring Formation.

arranged metallacycle might be isolated. However, all we observed was starting material, possibly a result of the alkyne being too bulky and therefore not being able to bind (even weakly) to the metal complex.

We have obtained some indirect evidence for a process which is capable of equilibrating the methyl groups of $W(CCMe_3C_2Me_2)Cl_3$. When this metallacycle is reacted with two equivalents of pyridine a mixture of isomeric bis-pyridine complexes is obtained. The same mixture may also be obtained by reacting $W(CCMe_3)(py)_2Cl_3$ with 2-butyne. The most interesting feature of these species is that the methyl groups of the metallacycles are equivalent by ^1H NMR. When tetramethylethylenediamine (TMEDA) is used only one isomer is obtained and again the methyl groups of the metallacycle are equivalent by ^1H NMR at room temperature. Upon cooling a dichloromethane solution of this complex, the metallacycle methyl resonance broadens and finally splits into two broad singlets at -70°C. Interestingly, this TMEDA complex cannot be prepared from $W(CCMe_3)(TMEDA)Cl_3$ and 2-butyne (cf. pyridine complex). This rules out the possibility that $W(CCMe_3C_2Me_2)(TMEDA)Cl_3$ might be a simple alkyne adduct of $W(CCMe_3)(TMEDA)Cl_3$.

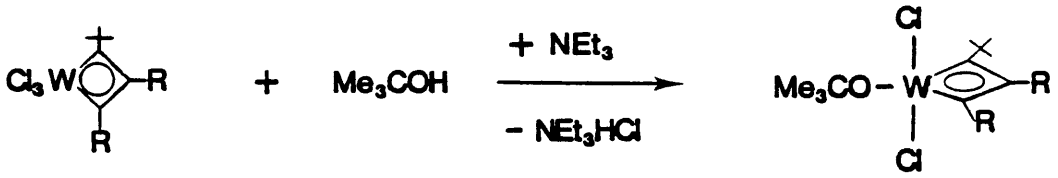
At this time it is hard to speculate about the structural details of these molecules. It is not clear whether the equilibration of the methyl groups is due to some fluxional process associated with the nitrogen ligands or the metallacycle ring. Furthermore, we do not know whether these species are six-coordinate cations or neutral, seven-coordinate compounds. However, regardless of the structure of these complexes, they exemplify a process by which the alkyl groups of metallacyclobutadiene rings can be rearranged by addition of a Lewis base (at least on the NMR time scale).

Neither of these metallacycle complexes react further with alkyne, presumably because the nitrogen ligands are blocking potential coordination sites on the metal. This supports the first step of our overall mechanism (Schemes I and II) leading to cyclopentadienyl ring formation which entailed alkyne coordination before reaction with the metallacycle ring.

Preparation and Reactivity of $W(CCMe_3C_2R_2)(OCMe_3)Cl_2$ (R = Me, Et)

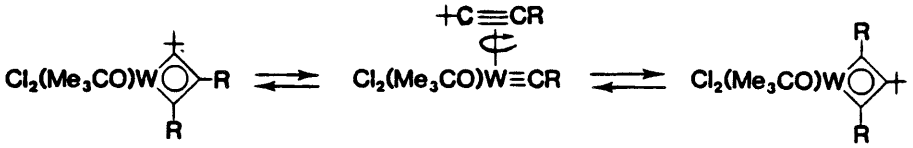
With isolable metallacyclobutadiene complexes now in hand, it was of interest to investigate the role (if any) these species play in alkyne metathesis. We approached this topic by undertaking a systematic investigation of the effect alkoxide ligands have on the stability of these metallacycles with the question in mind: what makes $W(CR)(OCMe_3)_3$ such good alkyne metathesis catalysts? It seemed obvious that if metallacyclobutadiene complexes are intermediates in alkyne metathesis, then under the appropriate conditions (i.e. right combination of ligands) we should see metathetical cleavage of the metallacycle ring to give a mixture of alkylidyne complexes, or at least an equilibrium between an alkylidyne complex and a metallacyclobutadiene (e.g., eq 1). Therefore, we started these studies by stepwise replacement of the chloride ligands on $W(CCMe_3C_2R_2)Cl_3$ with alkoxide ligands.

The first reaction we tried along these lines is outlined in eq 8. The ^1H NMR spectrum of $W(CCMe_3C_2Et_2)(OCMe_3)Cl_2$ exhibits two quartets for the methylene protons of the ethyl groups which suggests that the t-butoxide ligand is located in the same plane as the $W(CCMe_3C_2Et_2)$ core as shown in eq 8. If the t-butoxide were in an axial position, there would be no plane of symmetry in the complex and each set of methylene protons would be diastereotopic, giving rise to a more complex set of resonances.



(8)

These mono-t-butoxy metallacycle complexes do not exhibit any characteristic reactivity with alkynes that might suggest their intermediacy in alkyne metathesis. For example, these species do not metathesize 3-heptyne to an equilibrium mixture of 3-hexyne and 4-octyne. Furthermore, if these complexes were in equilibrium with an alkylidyne/alkyne complex, we might expect to observe partial rearrangement of the metallacycle to the more symmetric structure shown in eq 9. We have seen no evidence for this type



(9)

of reaction, even under conditions where an external alkyne might promote this reaction (vide supra). For example, $W(CCMe_3C_2Et_2)(OCMe_3)Cl_2$ does not react to any significant extent with three equivalents of 3-hexyne after 2 h (by ^1H NMR). After one day, the ^1H NMR spectrum of this reaction was significantly broadened, probably the result of forming paramagnetic cyclopentadienyl complexes (cf. $W(CCMe_3C_2R_2)Cl_3$ + alkyne). A similar reaction between $W(CCMe_3C_2Me_2)(OCMe_3)Cl_2$ and five equivalents of 2-butyne (in ether), after 2 h, showed predominantly starting material. $W(CCMe_3C_2Me_2)(OCMe_3)Cl_2$ was also reacted with 3-hexyne (one equivalent) to see if any $W(CCMe_3C_2Et_2)(OCMe_3)Cl_2$ forms; however, after 40 minutes there was no detectable

reaction. These experiments demonstrate that replacing a chloride ligand with a t-butoxide ligand in these metallacycle complexes serves only to slow down, relative to $W(CCMe_3C_2R_2)Cl_3$, any reaction with alkyne. Identification of any products from the above reactions was not pursued.

Since one t-butoxide ligand did not drastically change the reactivity of the metallacyclobutadiene unit (with respect to alkyne metathesis) we focused on placing a second t-butoxide ligand on the metal. Our first attempt involved adding one equivalent of t-butanol (in the presence of NEt_3) to $W(CCMe_3C_2Me_2)(OCMe_3)Cl_2$. After allowing the reaction to proceed 1.5 h in ether, a ^1H NMR spectrum of the crude residue showed that the predominant species present was starting material. Although there were several other resonances, none looked encouraging for $W(CCMe_3C_2Me_2)$-$(OCMe_3)_2Cl$. Some of the extra resonances belonged to $W(CHCMe_3)(OCMe_3)_2Cl_2$ (H_α at 10.67 ppm) which was confirmed by comparison (^1H and ^{13}C NMR) with an authentic sample (see Appendix II). Another resonance at 9.31 ppm (with tungsten satellites) may belong to H_α of $W(CHCMe_3)(OCMe_3)Cl_3$, but this is speculative. Mechanistic details concerning how these neopentylidene complexes are formed were not pursued.

Our next attempt at preparing $W(CCMe_3C_2R_2)(OCMe_3)_2Cl$ is shown in eq 10. Only a mixture of alkylidyne complexes and starting metallacycle was

$$W(CCMe_3C_2Me_2)(OCMe_3)Cl_2 + LiOCMe_3 \xrightarrow{\text{-alkynes}} \underset{\sim 50\%}{W(CR)(OCMe_3)_3} \qquad (10)$$

$$(R = Me, CMe_3)$$

obtained. It appears that $W(CCMe_3C_2R_2)(OCMe_3)_2Cl$ is either synthetically difficult to prepare, or is inherently unstable. One possible mechanism by

which the mixture of alkylidyne complexes is obtained may involve a kinetic phenomenon ($k_2 >> k_1$) On the other hand, steric considerations alone would render this hypothesis relatively unattractive. A second possibility is

$$W(CCMe_3C_2Me_2)(OCMe_3)Cl_2 + 0.5\ LiOCMe_3 \xrightarrow{k_1} 0.5\ W(CCMe_3C_2Me_2)(OCMe_3)_2Cl$$

$$W(CCMe_3C_2Me_2)(OCMe_3)_2Cl + LiOCMe_3 \xrightarrow{k_2} \text{"}W(CCMe_3C_2Me_2)(OCMe_3)_3\text{"}$$

$$\text{"}W(CCMe_3C_2Me_2)(OCMe_3)_3\text{"} \longrightarrow W(CR)(OCMe_3)_3 + \text{alkynes}$$

Scheme III

one that involves disproportionation of the bis-alkoxide metallacycle intermediate (Scheme IV). Such reactions are quite common in alkoxide/halide complexes of tungsten(VI) (see Chapter 1 and references 26 and 45). We prefer the second of the two proposed mechanisms.

$$W(CCMe_3C_2Me_2)(OCMe_3)Cl_2 + LiOCMe_3 \longrightarrow W(CCMe_3C_2Me_2)(OCMe_3)_2Cl$$

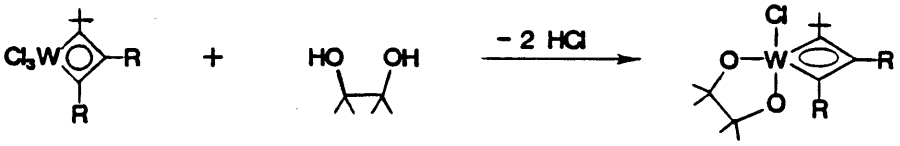
$$W(CCMe_3C_2Me_2)(OCMe_3)_2Cl \longrightarrow 0.5\ W(CCMe_3C_2Me_2)(OCMe_3)Cl_2 + 0.5\ \text{"}W(CCMe_3C_2Me_2)(OCMe_3)_3\text{"}$$

$$\text{"}W(CCMe_3C_2Me_2)(OCMe_3)_3\text{"} \longrightarrow W(CR)(OCMe_3)_3 + \text{alkynes}$$

Scheme IV

Preparation and Reactivity of Bis and Tris-Alkoxy Tungstenacyclobutadiene Complexes

We reasoned that if the disproportionation reaction outlined in Scheme IV occurs when attempting to prepare $W(CCMe_3C_2R_2)(OCMe_3)_2Cl$, then a chelating alkoxide ligand might prevent this reaction (by virtue of the enhanced stability supplied by the chelate effect). Our first choice was the pinacolate ligand (2,3-dimethyl-2,3-butanediol), and its reaction with $W(CCMe_3C_2R_2)Cl_3$ is shown in eq 11. NMR data are consistent with a trigonal

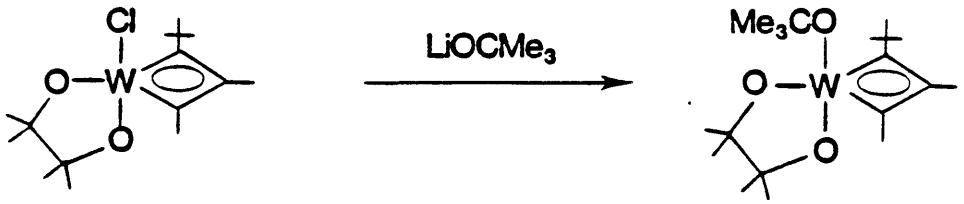


(11)

bipyramidal structure (eq 11) and indicate that the metallacycle ring is still intact. Much like $W(CCMe_3C_2R_2)(OCMe_3)Cl_2$, these pinacolato complexes are quite stable. For example, $W(CCMe_3C_2Me_2)(OCMe_2CMe_2O)Cl$ shows no signs of rearrangement at 60°C in benzene. Furthermore, this complex shows absolutely no reactivity with 3-hexyne at 60°C for 1.4 h (by ^1H NMR). Similarly, an ether solution of this material does not react with a five-fold excess of 2-butyne after 2.5 h at room temperature.

When a benzene solution of $W(CCMe_3C_2Me_2)(OCMe_2CMe_2O)Cl$ is treated with two equivalents of pyridine, some of the resonances in the ^1H NMR spectrum change, suggesting that the pyridine is coordinating to the metal center. However, the pyridine is not bound strongly and may be removed in vacuo.

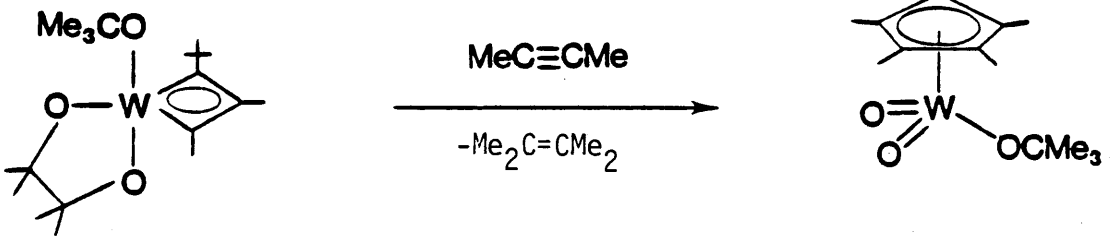
Since these bis-alkoxy metallacycles are stable and have no features which might be deemed characteristic of an alkyne metathesis intermediate, we continued with our substitution chemistry and reacted $W(CCMe_3C_2Me_2)$-$(OCMe_2CMe_2O)Cl$ with $LiOCMe_3$ (eq 12). A ^{13}C NMR spectrum of the orange/red,



(12)

sublimable solid isolated from this reaction demonstrates that it is in fact a tris-alkoxy tungstenacyclobutadiene complex.

A toluene solution of this material may be heated at 70°C with no evidence of decomposition. Unlike its chloride precursor, a solution of $W(CCMe_3C_2Me_2)(OCMe_2CMe_2O)(OCMe_3)$ does not interact with pyridine (by ^1H NMR), but it does react with alkynes. Metathesis does not occur (checked with 3-heptyne), but instead we once again observe the quantitative formation of a complex containing a cyclopentadienyl ligand (eq 13). Similar to $W(CCMe_3C_2Me_2)Cl_3$, $W(CCMe_3C_2Me_2)(OCMe_2CMe_2O)(OCMe_3)$ reacts with excess 3-hexyne to give a mixture of cyclopentadienyl complexes (eq 14). It is



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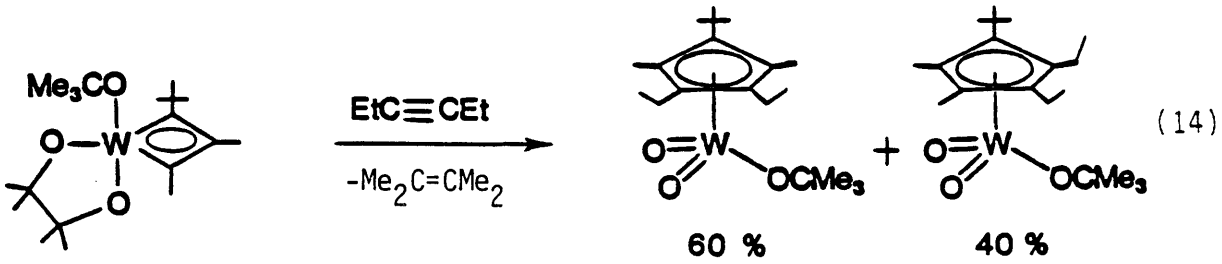
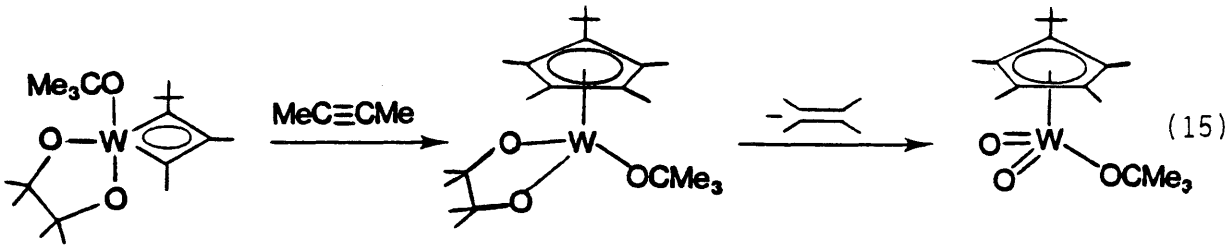


(14)

noteworthy that these metallacycle complexes do not react with bulky alkynes. For example, no reaction was observed (by ^1H NMR) with $Me_3SiC{\equiv}CSiMe_3$ (even at 55°C for 68 h in a sealed tube) or $Me_3CC{\equiv}CMe$ (five equivalents for 70 h at 25°C).

The most logical pathway by which these tungsten(VI) dioxo complexes form is shown in eq 15. Such a mechanism is similar to that proposed by Sharpless and co-workers, who found that reduced tungsten halides react with

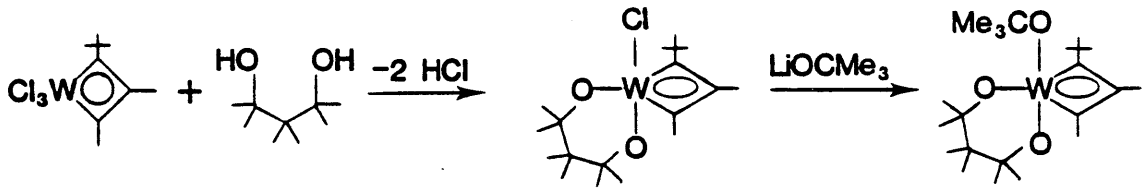


(15)

1,2-diols in the presence of base (MeLi or a pyridine) to give olefins and presumably tungsten oxo complexes.[46] As in the trichloride system, we attempted to trap this proposed d^2 intermediate using propylene oxide (e.g., to give $CpW(O)(OCMe_3)(OCMe_2CMe_2O)$. However, only the final cyclopentadienyl product shown in eq 15 was obtained.

The fact that we had now prepared a stable, isolable tris-alkoxy metallacyclobutadiene complex was rather puzzling. However, a pinacol ligand does not take the place of two t-butoxide ligands either electronically or sterically (see Discussion section). Therefore, we prepared a more "flexible" six-membered ring complex, hoping that this would come closer to mimicking two t-butoxide ligands (Scheme V). Apparently this analogy was still not good enough since a stable, tris-alkoxy metallacycle complex was again isolated, as shown in Scheme V. This new metallacyclobutadiene complex does not react as cleanly with alkyne as $W(CCMe_3C_2Me_2)(OCMe_2CMe_2O)(OCMe_3)$, presumably because the pathway to a dioxocyclopentadienyl complex is not as straightforward as in the pinacol system.

The above results pertaining to tris-alkoxy metallacyclobutadiene complexes do not rule out the possibility that such species may be intermediates in alkyne metathesis. They simply suggest that the equilibrium



Scheme V.

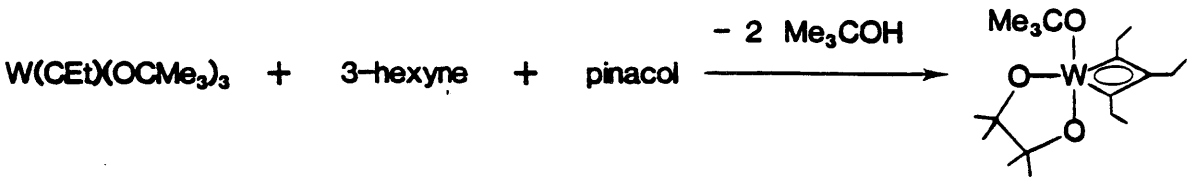
between an alkylidyne complex and its corresponding metallacyclobutadiene complex (eq 1) has been shifted completely to the side of the metallacycle, presumably due to some inherent instability of the alkylidyne intermediate (i.e., $W(CR)(OCMe_2CMe_2O)(OCMe_3)$). To test this hypothesis, we attempted to prepare such an alkylidyne complex via many different pathways (e.g., starting with $W(CCMe_3)Cl_4^-$, $W(CCMe_3)(dme)Cl_3$, $W(CCMe_3)(NPr^i_2)_3$, $W(CCMe_3)Np_3$) but were never successful. In several cases, the only products isolated or observed were alkylidene complexes (see Appendix II). For example, when $W(CCMe_3)(OCMe_3)_3$ is reacted with pinacol, the neopentylidene complex shown in eq 16 is obtained quantitatively.

$$W(CCMe_3)(OCMe_3)_3 + \text{pinacol} \xrightarrow{-Me_3COH} W(CHCMe_3)(OCMe_2CMe_2O)(OCMe_3)_2 \qquad (16)$$

Isolation of a Tungstenacyclobutadiene Complex from an Active Metathesis Mixture. Preparation of $W(C_3Et_3)(OCMe_2CMe_2O)(OCMe_3)$

Since a pinacolate ligand is capable of stabilizing a metallacyclobutadiene complex, we reasoned that perhaps a metallacycle intermediate could be "trapped" from an active catalyst system by introducing pinacol. Indeed, when a cold (-20°C) toluene solution containing $W(CEt)(OCMe_3)_3$ and 3-hexyne is treated with pinacol an essentially instantaneous reaction occurs and one

isolates a red, distillable, low-melting solid (eq 17). NMR data confirm the presence of the metallacyclobutadiene ring in this species. In the



(17)

^{1}H NMR spectrum the pinacolate ligand appears as a broad resonance at room temperature. This resonance sharpens to a singlet upon heating (70°C), and upon cooling (to -40°C) splits into two singlets that each account for two methyl groups. The alpha and beta ethyl groups of the metallacycle do not equilibrate in this temperature range. The low-temperature spectrum is consistent with the trigonal bipyramidal structure shown in eq 17. A reasonable mechanism that accounts for the equilibration of all four pinacol methyl resonances in the high temperature spectrum is outlined in Figure 5. An interesting possibility associated with this process is that the

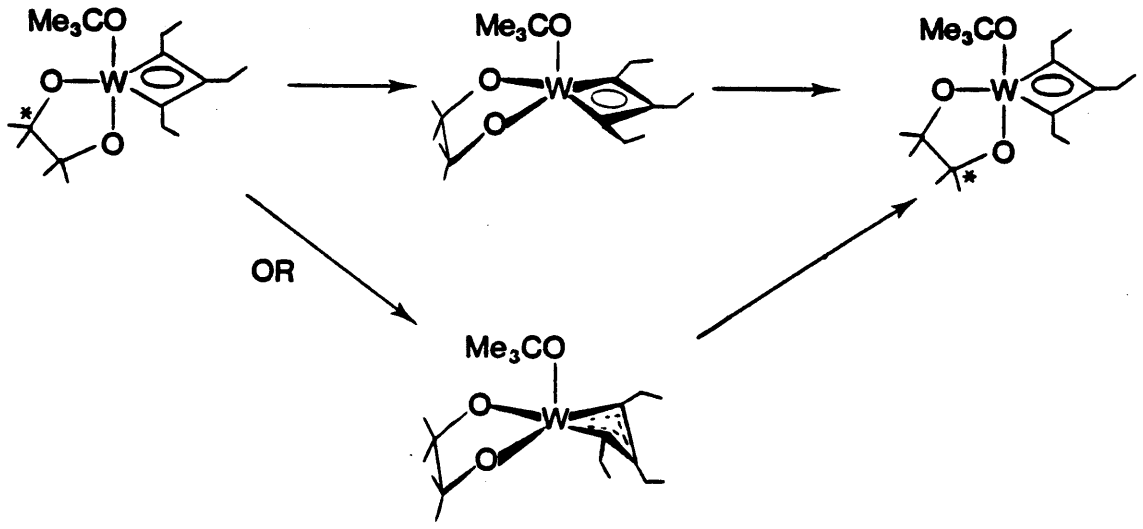


Figure 5.

metallacycle ring may become distorted (e.g., non-planar) as it passes through the square pyramidal intermediate (Figure 5). A distorted metallacyclobutadiene complex has recently been prepared by McCullough and characterized by x-ray diffraction techniques[47] (Figure 6).

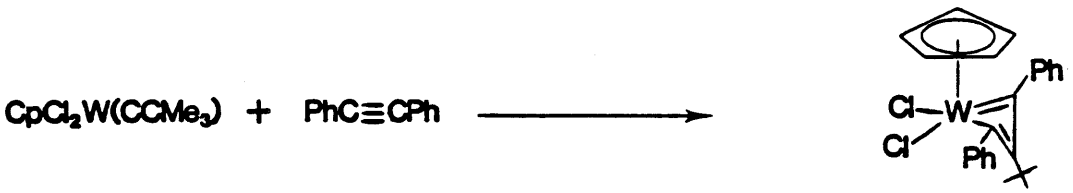
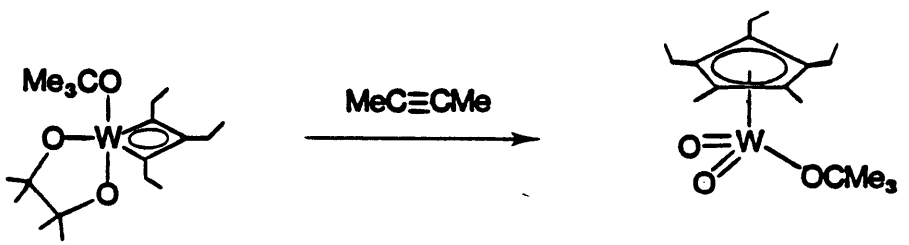


Figure 6.

$W(C_3Et_3)(OCMe_2CMe_2O)(OCMe_3)$ reacts with 3-hexyne to give a tungsten(VI) dioxo complex that contains a pentaethylcyclopentadienyl ring (eq 18). The

$$W(C_3Et_3)(OCMe_2CMe_2O)(OCMe_3) + \text{3-hexyne} \longrightarrow W(\eta^5\text{-}C_5Et_5)(O)_2(OCMe_3) \quad (18)$$

fact that all of the steps leading to this cyclopentadienyl complex proceed in high yield has allowed the chemistry of such species to be explored in more detail.[41] $W(C_3Et_3)(OCMe_2CMe_2O)(OCMe_3)$ also reacts with excess 2-butyne to give one product which we believe has the structure shown in eq 19.



(19)

Deactivation of Alkyne Metathesis Catalysts

Sancho noted that high concentrations of alkynes in our active alkyne metathesis systems causes catalyst deactivation.[35] For obvious reasons, it was of interest to investigate this reaction in greater detail. We were immediately able to rule out a bimolecular reaction (eq 20), similar to that observed in some olefin metathesis systems[48] since it was shown that the reverse of this reaction actually occurs.[49]

$$2\ W(CR)(OCMe_3)_3 \xrightarrow{-RC\equiv CR} (Me_3CO)_3W\equiv W(OCMe_3)_3 \qquad (20)$$

To simplify our experiments we chose to examine degenerate metathesis systems. Therefore, we reacted $W(CEt)(OCMe_3)_3$ with neat 3-hexyne (~20 equivalents). After approximately one hour the volatiles were removed in vacuo and a ^1H NMR of the residue showed predominantly starting material. However, several other resonances were also present. If the same reaction is allowed to proceed for three days, all of the $W(CEt)(OCMe_3)_3$ disappears and an orange/red oily solid is isolated. The ^1H NMR spectrum of this material is quite "clean" and consists of two products. One of these was isolated by selective crystallization and was shown to be $W(\eta^5\text{-}C_5Et_5)(O)_2(OCMe_3)$ by analysis (C and H), mass spectroscopy (molecular ion at 494) and comparison with an authentic sample (prepared as shown in eq 18). The ^1H NMR spectrum of the second compound consists of four quartets (for the methylene reaonances of the ethyl groups) centered at 4.30, 3.55, 2.60 and 2.27 ppm in a ratio of 1:2:1:1, respectively. Along with the methyl resonances of the ethyl groups there are also two t-butoxide peaks in a ratio of 1:2. A ^{13}C NMR spectrum of the mixture of compounds (unfortunately, we have never been able to obtain a pure sample of the unidentified compound) shows

four downfield resonances at 228.7, 213.5, 152.7 and 132.7 ppm all of which belong to the unidentified species.

A similar, yet much faster reaction (complete in less than 1 h) occurs between $W(CMe)(OCMe_3)_3$ and excess 2-butyne. A good deal of polymer forms in this reaction and the color of the solution becomes emerald green (Sancho observed a green solution for all metathesis reactions involving 2-alkynes.[35]) The residue obtained from this reaction is once again a mixture of compounds. One of these is $W(\eta^5\text{-}C_5Me_5)(O)_2(OCMe_3)$ and the other exhibits a ^1H NMR spectrum that is similar to the unidentified compound obtained from the 3-hexyne reaction, but simpler. The spectrum consists of four methyl resonances at 3.95, 2.92, 2.00 and 1.95 ppm in a ratio of 1:2:1:1, respectively and two t-butoxy resonances in a 1:2 ratio. The two lowest field methyl resonances are coupled to tungsten ($^3J_{HW} \approx 5.2$ and 3.9 Hz, respectively) and the resonances at 2.00 and 1.95 ppm are quartets ($^5J_{HH'} \approx 1.2$ Hz) which presumably arise from coupling between two vicinal methyl groups. At -70°C, one of the t-butoxide resonances splits into two peaks but the rest of the spectrum remains relatively unchanged. In the ^{13}C NMR spectrum the lowest field resonances are found at 225.1, 204.0, 143.9, and 134.0 ppm.

Combining all of the above information leads us to conclude that these unidentified species have the general formula $W(C_5R_5)(OCMe_3)_3$. A tungstenacyclohexatriene complex (Figure 7) is the first structure that comes to mind. However, the NMR data are not consistent with either the localized (A) or delocalized (B) structures shown.

Recalling that we observe tungsten coupling to the two lowest field resonances (which account for a total of three methyl groups) in the

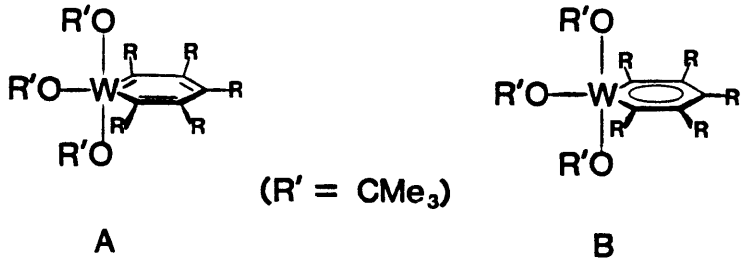


Figure 7.

^{1}H NMR spectrum of $W(C_5Me_5)(OCMe_3)_3$ suggests that there might be <u>three</u> tungsten-carbon bonds in this species. A metallabenzvalene complex (Figure 8A) or an alkyne adduct of a cyclopropenyl complex (Figure 8B) are possible descriptions for the nature of the C_5R_5 unit in this compound.

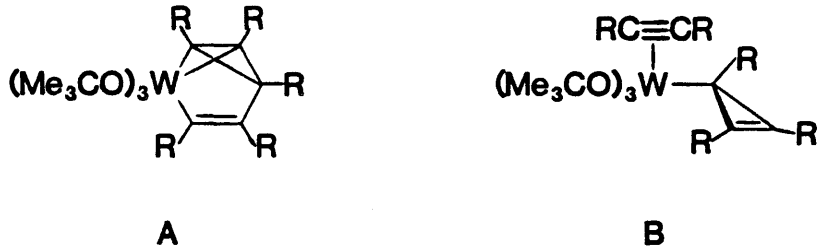


Figure 8.

A reasonable pathway leading to the formation of $W(C_5R_5)(OCMe_3)_3$ involves an irreversible reaction of alkyne with an intermediate metallacyclobutadiene complex. In agreement with what we observe, the chance of this reaction occurring in an active metathesis system should increase with increasing concentration of alkyne.

Upon heating a toluene solution of the mixture obtained from the reaction of excess 2-butyne with $W(CMe)(OCMe_3)_3$, the amount of $W(\eta^5\text{-}C_5Me_5)(O)_2(OCMe_3)$ increases as $W(C_5Me_5)(OCMe_3)_3$ disappears (followed by ^{1}H NMR using an internal standard). This suggests that $W(C_5R_5)(OCMe_3)_3$ might be the first species formed along a deactivation pathway and that the tungsten cyclopentadienyl complex observed is the final, thermodynamic product.

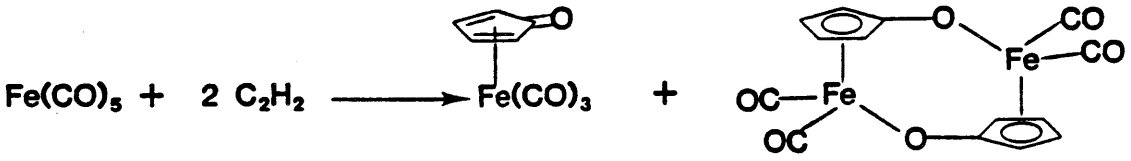
DISCUSSION

My entry into the area of chemistry discussed in this chapter stemmed from our interest in learning more about the details of homogeneous alkyne metathesis catalyzed by tungsten(VI) alkylidyne complexes. At the time we began these studies, the most important features known about these catalyst systems were: (1) some tungsten(VI) alkylidyne complexes can catalyze alkyne metathesis and are chain-carrying intermediates; and (2) alkyne metathesis reactions catalyzed by such species are first order in catalyst and alkyne. Furthermore, in general the reactivity of tungsten(VI) alkylidyne complexes with alkynes had only been pursued to the extent of screening such compounds for metathesis activity (by GC analysis of the organic products). Studying deactivation reactions available to our active catalysts had also not been explored in any detail, mainly because this was a relatively new concern. Obviously, gaining a better understanding of such processes is necessary if one hopes to slow down or completely stop such reactions (e.g., by changing appropriate variables).

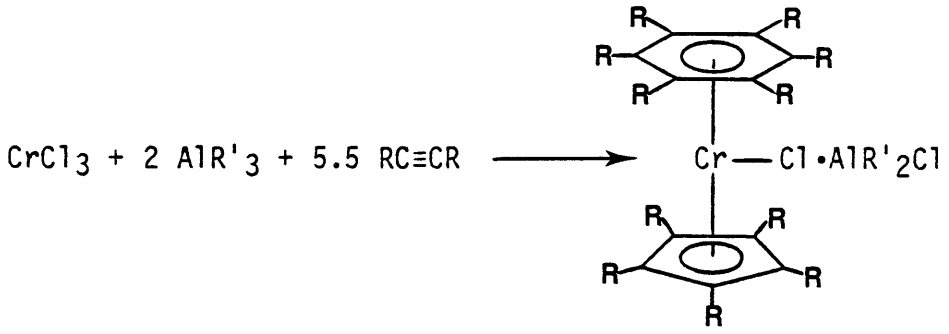
Our first experiments in this new project involved reacting trichloro-neopentylidyne complexes of tungsten with alkynes. The results of such reactions were quite surprising. When more than two equivalents of alkyne are used we found that cyclopentadienyl rings consisting of two alkyne units and the original neopentylidyne ligand (i.e., η^5-$C_5R_4CMe_3$) are formed. The reaction is quantitative and two products are obtained in equal amounts. One of the most exciting features of this reaction is that it provided us with a route to high oxidation state, peralkyl cyclopentadienyl complexes of tungsten, a class of molecules that several groups of workers, including ours, have been trying to make for some time now. The d^1 species,

$[W(\eta^5\text{-}C_5R_4CMe_3)Cl_4]_2$, has proven to be the most useful (synthetically) of the two complexes derived from this reaction.[27] Fortunately, the other product, $W(\eta^5\text{-}C_5R_4CMe_3)(RC{\equiv}CR)Cl_2$ can be converted into the tetrachloride complex in high yield with chlorine gas. An advantageous feature of this route to cyclopentadienyl complexes is that it provides one with a great deal of "synthetic flexibility". In theory, a large variety of alkynes can be used to prepare cyclopentadienyl rings with predesigned solubility, steric and electronic requirements.

Our synthesis of cyclopentadienyl rings from alkynes and transition metals is not the first to be reported. For example, the dimeric iron complex shown in eq 21 is prepared from $Fe(CO)_5$ and acetylene.[50] Another example, more closely related to our chemistry, is shown in eq 22.[51]



(21)



(22)

Completely symmetric cyclopentadienyl rings are obtained even when the alkyl groups of the aluminum reagent are different from that of the alkyne.

This suggests that a carbon-carbon triple bond is split at some point. Some $Cr(\eta^5\text{-}C_5Me_5)Cl_2$ was obtained from hydrolysis of the reaction outlined in eq 22, suggesting that the cyclopentadienyl ring might be formed first in this reaction and that this species is further reduced by the aluminum reagent to give a Cr^{II} complex that is capable of cyclotrimerizing alkynes.

Based on the above information and our group's recent endeavors, it is tempting to speculate on a mechanism for cyclopentadienyl ring formation in this system. The initial step probably involves formation of $(Cr(CR)Cl_x)_n$ (x = 2 or 3) which arises from interaction of alkyne (RC≡CR) with some form of $(CrCl_3)_n$ or $(CrCl_2)_n$ (probably involving metal-metal multiple bonds[49]). The alkylidyne species then reacts with more alkyne to give either $[Cr(\eta^5\text{-}C_5R_5)Cl_3]_n$ or $[Cr(\eta^5\text{-}C_5R_5)Cl_2]_n$.

Our interest in learning more about how cyclopentadienyl rings form from tungsten neopentylidyne ligands and alkynes led to experiments that provided us with isolable tungstenacyclobutadiene complexes (e.g., $W(CCMe_3C_2R_2)Cl_3$). Such species were not the first examples of this type of metallacyclic ring. Some triphenyl metallacyclobutadiene complexes had been prepared earlier by reacting Vaska complexes, $M(CO)(PR_3)_2Cl$ (M = Rh, Ir), with the triphenylcyclopropenium ion (e.g., $C_3Ph_3^+Cl^-$) (eq 23,[39] 24[40]). In

$$Rh(CO)(PR_3)_2Cl + C_3Ph_3^+Cl^- \xrightarrow{-CO} Rh(C_3Ph_3)(PR_3)_2Cl_2 \qquad (23)$$

$$Ir(CO)(PR_3)_2Cl + C_3Ph_3^+BF_4^- \longrightarrow [Ir(C_3Ph_3)(PR_3)_2(CO)Cl][BF_4] \qquad (24)$$

essence, these reactions involve the oxidative addition of the cyclopropenium group to the metal. The structures of these complexes have been

determined and the overall features of the metallacycle ring are quite different from what we observe in $W(CCMe_3C_2Me_2)Cl_3$. For example, even though the ring is planar in both Group VIII species (as in our complex) there is no extensive multiple bond character in $M-C_\alpha$. Furthermore, the $M-C_\beta$ distances of 2.61(2)Å and 2.582(5)Å for the Ir and Rh complexes, respectively, indicate that there is no interaction between these atoms. The carbon-carbon distances within the ring suggest that there is a good deal of $p_\pi-p_\pi$ delocalization and the $C_\alpha-C_\alpha'$ trans-annular distance of 2.156(6)Å is short enough to suggest some interaction between these atoms. A resonance structure like that shown in Figure 9 may best describe this situation.[39]

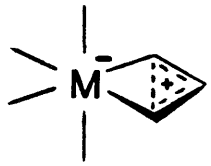


Figure 9

$W-C_\alpha$ in $W(CCMe_3C_2Me_2)Cl_3$ consists of a considerable amount of multiple bond character, a fact that makes these metallacycles more attractive (relative to the Group VIII complexes) as models for intermediates in alkyne metathesis. Probably the most interesting feature in the structure of $W(CCMe_3C_2Me_2)Cl_3$ is the strong $W-C_\beta$ interaction. Such an interaction might be related to the of metal-H_α interactions in many tantalum alkylidene complexes.[12]

Using molecular orbital theory Bursten has recently offered a quantitative description of this $W-C_\beta$ interaction.[52] He performed calculations on the model metallacycle core $[W(C_3H_3)]^{3+}$ and found that the $d\pi$ orbital in the

lowest-lying, filled, π-bonding set of orbitals is spatially directed towards the π-orbital on C_β, resulting in a strong interaction between these atoms. He suggests that it is this interaction that stabilizes these metallacycles and renders them inactive alkyne metathesis intermediates.

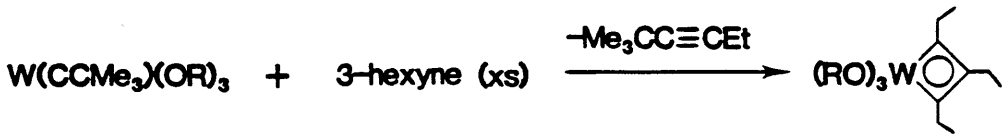
Another interesting structural feature in $W(CCMe_3C_2Me_2)Cl_3$ is the large $W\text{-}C_\alpha\text{-}CR$ (R = Me, CMe_3) angle. Such an obtuse angle suggests that for steric reasons it might be difficult to have a bulky substituent on C_β of the ring. Indeed, a very regioselective reaction occurs between $W(CCMe_3)(dme)Cl_3$ and $Me_3CC{\equiv}CMe$ to give only one product; $W[C_\alpha(CMe_3)C(Me)C_\alpha(CMe_3)]Cl_3$.

Since none of these trichloro-tungstenacyclobutadiene complexes catalyze alkyne metathesis, we focused a good deal of our attention on trying to discern the effect alkoxide ligands have on this class of tungsten compounds (i.e., what makes $W(CR)(OCMe_3)_3$ such active catalysts?). If more than one chloride ligand in $W(CCMe_3C_2R_2)Cl_3$ is substituted with a t-butoxide ligand, we find that a mixture of alkylidyne complexes and alkynes is formed. However, we have been unable to determine whether or not two t-butoxide ligands are enough to cause the metathetical cleavage of the metallacycle ring or whether $W(CCMe_3C_2R_2)(OCMe_3)_2Cl$ is simply unstable with respect to alkoxy-halide disproportionation reactions. Using a chelating diol solved the problem of isolating a stable, bis-alkoxy metallacycle complex. However, we soon learned that neither pinacol nor 2,3,3,4-tetramethyl-2,4-pentanediol were good enough at imitating two t-butoxide ligands. That is, tris-alkoxy metallacycle complexes containing these ligands could be prepared (i.e., $W(CCMe_3C_2R_2)(OCMe_2(CMe_2)_nCMe_2O)(OCMe_3)$; n = 0, 1) and showed no behavior characteristic of an alkyne metathesis intermediate

(remember that we have never isolated or observed a metallacyclobutadiene complex containing three t-butoxide ligands).

It is appropriate at this time to briefly discuss some ideas about why these chelating diol ligands do not sufficiently model two t-butoxide ligands. First, the methyl groups of these ligands are directed away from the metallacycle ring due to the fixed geometry of the chelate ring. On the other hand, a t-butoxide ligand can rotate freely about its M-O-C axis, allowing for the possibility of steric interactions with the metallacycle ring. Another important, yet maybe more subtle difference between these types of ligands concerns the π-electron donating capability of each. Indeed, t-butoxide ligands (and other non-bridging monodentate alkoxides) are very good at donating π-electron density to early transition metal complexes in high oxidation states.[53] It is reasonable to assume that as such donation increases so must the M-O-C angle, due to rehybridization of the oxygen orbitals. The geometric constraints of the chelate ring in the diol ligand (especially pinacol) places a limit on this ability to increase the M-O-C angle. Therefore, relatively speaking, these ligands cannot supply as much π-electron density to a metal as two monodentate alkoxide ligands.

Freudenberger has recently prepared a tris-alkoxy tungstenacyclobutadiene complex that contains three monodentate alkoxide ligands (eq 25).[11] Even more exciting is the fact that solutions of this metallacycle complex metathesize alkynes. This result constitutes the first piece of definitive evidence concerning the intermediacy of tungstenacyclobutadiene complexes in alkyne metathesis. Further studies are in progress to determine the exact role such species play in the metathesis reaction.



(25)

At this point it is difficult to tell whether the general stability of tungstenacyclobutadiene complexes is a result of a strong W-C_β interaction or whether some other stabilizing feature is in operation. Clearly more structural studies are necessary before such questions can be answered.

More crystallographic studies might also allow us to correlate ^{13}C NMR data with bonding trends within the metallacycle ring. At this point we can only list some of the general trends in such data. First, all three ring carbon resonances shift upfield upon replacing chloride ligands with alkoxides (Table I). In the case of $W(CCMe_3C_2R_2)(OCMe_3)Cl_2$, C_β appears to be much more chemical shift sensitive to the presence of the equatorial alkoxide ligand than does C_α (Table II); i.e., $\Delta C_\beta > \Delta C_{\alpha AV}$ (see Table II for an explanation of this nomenclature). This might be related to a weakening of the W-C_β interaction due to some "trans" influence of the t-butoxide ligand (i.e., the t-butoxide is directly aligned with C_β in the trigonal bipyramid). However, this trend is reversed (i.e., $\Delta C_\beta < \Delta C_{\alpha AV}$), when alkoxide ligands begin to occupy axial sites in these trigonal bipyramidal molecules.

Mechanistic details concerning cyclopentadienyl ring formation from tungsten alkylidynes and alkynes are not, at this time, fully understood. However, from experiments outlined in this Chapter we were able to rule out the simplest of mechanisms (Scheme I). At this point it is worthwhile to compare the two types of metallacyclobutadiene complexes that give rise to

Table II. Comparison of ^{13}C NMR Data for Tungstenacyclobutadiene Complexes.

Compound	$C_{\alpha_{AVG}}$ [a]	$\Delta C_{\alpha_{AVG}}$ [b]	ΔC_{β} [c]
$W(CCMe_3C_2Me_2)Cl_3$	265.5		
$W(CCMe_3C_2Et_2)Cl_3$	267.2		
$W(CCMe_3C_2Me_2)(OCMe_3)Cl_2$	262.4	3.2	16.5
$W(CCMe_3C_2Et_2)(OCMe_3)Cl_2$	266.1	1.2	12.9
$W(CCMe_3C_2Me_2)(OCH(Me)CH_2Cl)Cl_2$	264.1	1.4	10.2
$W(CCMe_3C_2Me_2)(OCMe_2CMe_2O)Cl$	245.7	19.8	7.7
$W(CCMe_3C_2Et_2)(OCMe_2CMe_2O)Cl$	248.8	16.8	4.5
$W(CCMe_3C_2Me_2)(OCMe_2CMe_2CMe_2O)Cl$	245.2	20.3	11.7
$W(CCMe_3C_2Me_2)(OCMe_2CMe_2O)(OCMe_3)$	228.7	36.9	21.8
$W(CCMe_3C_2Me_2)(OCMe_2CMe_2CMe_2O)(OCMe_3)$	230.0	35.5	26.2
$W(C_3Et_3)(OCMe_2CMe_2O)(OCMe_3)$ [d]	226.5	40.7	17.4
$W(C_3Et_3)(OCH(CF_3)_2)_3$ [11,d]	242.9	24.3	3.0

a $C_{\alpha_{AVG}}$ is the average value of C_{α} ^{13}C NMR shifts.

b $\Delta C_{\alpha_{AVG}}$ is the difference between $C_{\alpha_{AVG}}$ of the appropriate parent trichloro metallacycle complex and $C_{\alpha_{AVG}}$ of the alkoxy metallacycle.

c ΔC_{β} is the difference between C_{β} of the appropriate parent trichloro metallacycle complex and C_{β} of the alkoxy metallacycle.

d Compared with $C_{\alpha_{AVG}}$ and C_{β} of $W(CCMe_3C_2Et_2)Cl_3$.

cyclopentadienyl products, namely $W(CCMe_3C_2R_2)Cl_3$ and $W(CCMe_3C_2Me_2)$-$(OCMe_2CMe_2O)(OCMe_3)$. First, both complexes lead to quantitative yields of tungsten cyclopentadienyl complexes. Second, even though the products from these reactions are different, it is reasonable that both proceed through a tungsten(IV) cyclopentadienyl intermediate. Finally, a similar mixture of isomeric cyclopentadienyl rings is obtained when the $W(CCMe_3C_2Me_2)$ derivative of each is reacted with 3-hexyne.

The fact that we get the same cyclopentadienyl isomers from these two different metallacycles does not prove that the mechanistic details of ring formation are the same for each. This consideration is mentioned because of a curious trend we observe in the reactivity of various metallacycle complexes with alkynes. For example, when one chloride ligand in $W(CCMe_3C_2R_2)Cl_3$ is replaced with a t-butoxy group, the new complex reacts much more slowly with alkynes relative to its trichloride precursor. When two oxygen groups, in the form of a pinacolate ligand are placed on the metal we observe absolutely no reactivity with alkynes, even at elevated temperatures. However, when the chloride ligand in $W(CCMe_3C_2Me_2)$-$(OCMe_2CMe_2O)Cl$ is replaced with a t-butoxy group, the new species reacts relatively quickly with alkyne to give a cyclopentadienyl product.

This reactivity trend might be indicative of some mechanistic alteration in the cyclopentadienyl ring forming reaction. Of possible importance is that a trigonal bipyramidal geometry is maintained for the first three metallacycle complexes. Based on this, we also assume that the first two alkoxy metallacycles have planar, delocalized metallacycle rings. Therefore, it would appear that some electronic factor associated with placing an increasing number of alkoxide ligands around the metal slows down and

eventually stops cyclopentadienyl ring formation. On the other hand, the structure of $W(CCMe_3C_2Me_2)(OCMe_2CMe_2O)(OCMe_3)$ is non-rigid, a point which might include the intermediacy of a distorted (e.g., non-planar) metallacycle ring (see discussion on fluxional behavior of $W(C_3Et_3)(OCMe_2CMe_2O)$-$(OCMe_3)$, Figure 5). Such a structural change might facilitate some new type of reactivity between the metallacycle ring and alkyne to once again give cyclopentadienyl products.

An interesting question that arises from the above consideration is what factor(s) are responsible for $W(CCMe_3C_2Me_2)(OCMe_2CMe_2O)(OCMe_3)$ distorting from the apparently favored trigonal bipyramidal geometry? That is, is it simply the bulk of the t-butoxy ligand that causes this structural distortion or is there some electronic effect associated with placing another alkoxide ligand on $W(CCMe_3C_2Me_2)(OCMe_2CMe_2O)Cl$? The answers to such questions might be ascertained by substituting the chloride ligand on $W(CCMe_3C_2Me_2)(OCMe_2CMe_2O)Cl$ with various alkoxide ligands and examining their structural integrity by ^1H NMR.

The final point I would like to address concerns our study of deactivation reactions of our active alkyne metathesis catalysts. I have already described the products obtained from metathesis reactions involving high concentrations of alkynes and have also discussed how such products may arise. Therefore, I would now like to concentrate on applying what we have learned to designing a longer-lived, more robust class of catalysts.

The most important point arising from these studies concerns comparing the relative rates of deactivation of the 2-butyne/W≡CMe system versus the 3-hexyne/W≡CEt system. Remember that the 2-butyne reaction is complete (i.e., all of the W≡CMe is gone) in less than one hour, whereas the 3-hexyne

reaction takes considerably longer (ca. 24 h). This suggests that a $W(C_3Me_3)$ metallacycle reacts more quickly with alkyne than $W(C_3Et_3)$. This is probably a result of intermediate $W(C_3Me_3)(OCMe_3)_3$ being more sterically accessible to alkynes than $W(C_3Et_3)(OCMe_3)_3$. The obvious ways to slow down such deactivation reactions are: (1) reduce the concentration of alkyne; and (2) stick to metathesizing larger alkynes. However, both of these suggestions would be unreasonable if such a catalyst were to be deemed useful in preparative chemistry. A reasonable alternative involves increasing the steric bulk about the metal center; i.e., use larger alkoxide ligands. For this reason, $W(CCMe_3)(OCEt_3)_3$ was prepared (Chapter 3). It should be interesting to see how this and other bulky tris-alkoxy alkylidyne complexes react with smaller alkynes compared with $W(CCMe_3)(OCMe_3)_3$ which is known to deactivate quite readily in the presence of 2-butyne.[35]

EXPERIMENTAL

For general experimental details see Chapter 1, Experimental section. $[W(CCMe_3)Cl_4][NEt_4]$,[2] $W(CCMe_3)(dme)Cl_3$,[2] $W(CCMe_3)(OCMe_3)_3$,[2] and $W(CR)(OCMe_3)_3$[49] were prepared by published methods. Pinacol was sublimed prior to use. $HOCMe_2CMe_2CMe_2OH$ was prepared from $EtOC(O)CMe_2C(O)OEt$ (Aldrich) and four equivalents of MeMgI.[54] The crude product was first distilled and then sublimed. NEt_3 was distilled from barium oxide. Alkynes were passed through alumina prior to use.

Preparation of $W(\eta^5\text{-}C_5Me_4CMe_3)(MeC{\equiv}CMe)Cl_2$ from $[W(CCMe_3)Cl_4][NEt_4]$ (II-S-24).

2-butyne (750 μl, 9.5 mmol) was added to a CH_2Cl_2 solution of $[W(CCMe_3)Cl_4][NEt_4]$ (0.50 g, 0.95 mmol). After 18 h the reaction was filtered through Celite and the volatiles were removed from the filtrate *in vacuo*. The residue was extracted with pentane, filtered and concentrated *in vacuo*. Cooling to -30°C gave 0.19 g (82%) of bright red crystals. See spectroscopic data below.

Preparation of $W(\eta^5\text{-}C_5Me_4CMe_3)(MeC{\equiv}CMe)Cl_2$ and $[W(\eta^5\text{-}C_5Me_4CMe_3)Cl_4]_2$ from $W(CCMe_3)(dme)Cl_3$ (XVI-50).

An ether suspension (50 ml) of $W(CCMe_3)(dme)Cl_3$ (4.0 g, 8.9 mmol) was cooled to -30°C and 2-butyne (3.5 ml, 44.7 mmol) was added. The solution was stirred vigorously and allowed to warm to room temperature. After 1.5 h the mixture was filtered and the orange precipitate was washed with ether (30 ml) and pentane (30 ml) and dried *in vacuo* (2.09 g). The volatiles were removed from the filtrate *in vacuo* and 300 ml of pentane was added to the residue. After stirring this solution for 3 h the mixture was

filtered, giving another 0.13 g of $W(\eta^5\text{-}C_5Me_4CMe_3)Cl_4$ (total yield 2.22 g, 99%). The pentane was removed from the filtrate in vacuo and the red crystals were dissolved in ether. Cooling to -30°C gave 1.9 g (88%) of $W(\eta^5\text{-}C_5Me_4CMe_3)(MeC{\equiv}CMe)Cl_2$.

$W(\eta^5\text{-}C_5Me_4CMe_3)(MeC{\equiv}CMe)Cl_2$: (II-S-24) ^1H NMR (C_6D_6, 250 MHz) δ ~10.9 (br), ~6.0 (br). (III-S-76) IR (Nujol mull, cm^{-1}) 1676 ($\nu_{C\equiv C}$).

$[W(\eta^5\text{-}C_5Me_4CMe_3)Cl_4]_2$: No pertinent spectroscopic data to report. IR data is in files.

Preparation of $W(\eta^5\text{-}C_5Et_4CMe_3)(EtC{\equiv}CEt)Cl_2$ from $[W(CCMe_3)Cl_4][NEt_4]$ (II-S-21).

2.2 ml (19 mmol) of 3-hexyne was added to a dichloromethane solution (25 ml) of $[W(CCMe_3)Cl_4][NEt_4]$ (1.0 g, 1.9 mmol). After stirring for 22 h the volatiles were removed in vacuo. The residue was extracted with pentane and filtered. Concentrating this solution in vacuo followed by cooling to -30°C gave two crops of bright red crystals (0.42 g, 78%).

Preparation of $W(\eta^5\text{-}C_5Et_4CMe_3)(EtC{\equiv}CEt)Cl_2$ and $[W(\eta^5\text{-}C_5Et_4CMe_3)Cl_4]_2$ from $W(CCMe_3)(dme)Cl_3$ (XIV-33).

$W(CCMe_3)(dme)Cl_3$ (1.0 g, 2.2 mmol) in ether (25 ml) was reacted with 3-hexyne (1.3 ml, 11.1 mmol). The solution was left to stand for 2 h after which point the orange precipitate was isolated by filtration. The solid was dissolved in CH_2Cl_2 and filtered through Celite to remove some polymer. Removing the volatiles in vacuo left a bright orange powder that was washed with pentane and dried in vacuo (0.48 g, 77% of theory for $[W(\eta^5\text{-}C_5Et_4CMe_3)Cl_4]_2$). This material can be recrystallized from CH_2Cl_2/ether.

The volatiles were removed from the original filtrate in vacuo. The residue was extracted with pentane (20 ml) and filtered. Concentrating in vacuo followed by cooling to -30°C gave 0.52 g of bright red $W(\eta^5\text{-}C_5Et_4CMe_3)(EtC{\equiv}CEt)Cl_2$ (82%)

$W(\eta^5\text{-}C_5Et_4CMe_3)(EtC{\equiv}CEt)Cl_2$: (III-S-69) ^1H NMR (C_6D_6, 270 MHz) δ 4.52, 2.62, 2.02 and 1.14 (br). (II-S-21) IR (Nujol mull, cm^{-1}) 1665 ($\nu_{C{\equiv}C}$).

$[W(\eta^5\text{-}C_5Et_4CMe_3)Cl_4]_2$: (III-S-69) ^1H NMR ($CDCl_3$, 250 MHz) δ 2.85, 2.53 and 2.29 (br). (XIV-65) MW (differential vapor pressure, CH_2Cl_2, 0°C); Calcd: 1118. Found: 1141 at $3x10^{-2}$ M. Anal. Calcd for $WC_{17}H_{29}Cl_4$: C, 36.52; H, 5.23; Cl, 25.37. Found: C, 36.66; H, 5.38; Cl, 26.17.

Preparation of $[W(\eta^5\text{-}C_5Me_4CMe_3)Cl_4]_2$ from $W(\eta^5\text{-}C_5Me_4CMe_3)(MeC{\equiv}CMe)Cl_2$ and Cl_2 (XIV-32).

Dry (passed through H_2SO_4) chlorine was bubbled through a pentane suspension (15 ml) of $W(\eta^5\text{-}C_5Me_4CMe_3)(MeC{\equiv}CMe)Cl_2$ (0.30 g, 0.62 mmol). The reaction was stopped when the solution became pale yellow in color. The volatiles were removed in vacuo and the remaining orange solid was washed with ether and dried in vacuo (0.27 g, 87%).

Preparation of $[W(\eta^5\text{-}C_5Et_4CMe_3)Cl_4]_2$ from $W(\eta^5\text{-}C_5Et_4CMe_3)(EtC{\equiv}CEt)Cl_2$ and Cl_2 (XV-7).

Prepared in a manner analogous to that described above. Starting with 0.62 g of $W(\eta^5\text{-}C_5Et_4CMe_3)(EtC{\equiv}CEt)Cl_2$, 0.55 g (90%) of product was obtained.

Preparation of $W(CCMe_3C_2Me_2)Cl_3$ (XV-11).

An ether solution (50 ml) of $W(CCMe_3)(dme)Cl_3$ (1.0 g, 2.2 mmol) was cooled to -20°C and treated with 2-butyne (174 µl, 2.2 mmol). The reaction

was left to stand at -30°C overnight. Violet crystals were isolated by filtration, washed with pentane and dried in vacuo. Yield 0.72 g (78%).

This complex is relatively unstable in CH_2Cl_2 and $CHCl_3$.

(XIV-3) ^1H NMR (C_6D_6, 250 MHz) δ 2.97 (s, 3, $C_\alpha Me$), 2.06 (s, 3, $C_\beta Me$), 1.22 (s, 9, $CCMe_3$). ^1H NMR (CD_2Cl_2, 250 MHz) δ 4.15 (s, 3, $C_\alpha Me$), 3.71 (s, 3, $C_\beta Me$), 1.68 (s, 9, $CCMe_3$).

(XIV-3) ^{13}C NMR (CD_2Cl_2, 67.9 MHz) δ 267.5 and 263.4 (s, $\underline{C}CMe_3$ and $\underline{C}_\alpha Me$), 150.7 (s, $\underline{C}_\beta Me$), 44.3 (s, $C\underline{C}Me_3$), 29.5 (q, J_{CH} = 128 Hz, $CC\underline{Me}_3$), 25.6 and 17.2 (q, J_{CH} = 137 Hz, C_α and $C_\beta\underline{Me}$).

Preparation of $W(CCMe_3C_2Et_2)Cl_3$ (XIV-23).

Same procedure as used for $W(CCMe_3C_2Me_2)Cl_3$. Yield, 57%.

(XIV-1) ^1H NMR (C_6D_6, 250 MHz) δ 3.53 (q, 2, ^3J_H = 7.4 Hz, $^3J_{HW} \sim 3$ Hz, $C_\alpha C\underline{H}_2CH_3$), 3.25 (q, 2, ^3J_H = 7.6 Hz, $C_\beta C\underline{H}_2CH_3$), 1.39 (t, 3, ^3J_H = 7.4 Hz, $C_\alpha CH_2C\underline{H}_3$), 1.29 (s, 9, $CCMe_3$), 0.44 (t, 3, ^3J_H = 7.6 Hz, $C_\beta CH_2C\underline{H}_3$).

(XIV-1) $^{13}C\{^1H\}$ NMR (C_6D_6, 67.9 MHz) δ 267.6 and 266.7 ($\underline{C}CMe_3$ and $\underline{C}_\alpha Et$, not respectively), 150.3 ($\underline{C}_\beta Et$), 43.8 ($C\underline{C}Me_3$), 32.0 ($C\underline{C}H_2CH_3$), 29.8 ($CC\underline{Me}_3$), 24.5 ($C\underline{C}H_2CH_3$), 14.3 and 11.9 ($CCH_2\underline{C}H_3$).

Anal. Calcd for $WC_{11}H_{19}Cl_3$: C, 29.93; H, 4.34; Cl, 24.09. Found: C, 30.23; H, 4.50; Cl, 24.39.

Preparation of $W[C_\alpha(CMe_3)C(Me)C_\alpha(CMe_3)]Cl_3$ (XV-51).

$Me_3CC{\equiv}CMe$ (158 μl, 1.3 mmol) was added to an ether solution (12 ml) of $W(CCMe_3)(dme)Cl_3$ (0.53 g, 1.2 mmol). After 14 h the volatiles were removed in vacuo leaving violet crystals. These were dissolved in a minimum of ether, filtered and concentrated in vacuo. Cooling to -30°C gave 0.30 g of product (56%).

(XV-40) ^{1}H NMR (C_6D_6, 250 MHz) δ 2.90 (s, 3, $C_\beta Me$), 1.28 (s, 18, $CCMe_3$).

(XV-51) $^{13}C\{^{1}H\}$ NMR (C_6D_6, 67.9 MHz) δ 273.0 (J_{CW} = 102 Hz, $\underline{C}CMe_3$), 148.1 ($\underline{C}_\beta Me$), 44.7 ($C\underline{C}Me$), 29.3 ($CC\underline{Me}_3$), 13.3 ($C_\beta\underline{Me}$).

Reaction of $W(CCMe_3C_2Me_2)Cl_3$ with propylene oxide.

Preparation of $W(CCMe_3C_2Me_2)(OCH(Me)CH_2Cl)Cl_2$ (isomer A) and $W(CCMe_3C_2Me_2)(OCH_2CH(Me)Cl)Cl_2$ (isomer B) (XIV-10).

Propylene oxide (75 μl, 1.2 mmol) was added to a well-stirred ether suspension (15 ml) of $W(CCMe_3C_2Me_2)Cl_3$ (0.25 g, 1.2 mmol). After 15 min the volatiles were removed in vacuo leaving orange crystals. These were dissolved in a minimum of ether and cooled to -30°C. A first crop of crystals was isolated by filtration, washed with pentane and dried in vacuo (0.11 g). A ^{1}H NMR spectrum of this material demonstrated that isomer B was the predominant component (see NMR data below). The major component in the second crop of crystals (70 mg) was isomer A.

When a similar reaction as described above is performed in an NMR tube (using C_6D_6 as the solvent in place of ether) it is seen that the reaction is quantitative and gives a mixture of isomers A and B in the ratio 44:56, respectively. This ratio does not change over a period of at least one day at room temperature.

Isomer A was prepared independently by reacting $W(CCMe_3C_2Me_2)Cl_3$ with $HOCH(Me)CH_2Cl$ in the presence of NEt_3 (XV-1) (e.g., see preparation of $W(CCMe_3C_2Me_2)(OCMe_3)Cl_2$). A ^{1}H NMR spectrum of the crude material from this reaction demonstrated that this material was identical with isomer A prepared from the route employing propylene oxide.

^{13}C NMR assignments for the alkoxide ligand in both isomers are based on a gated $\{^{1}H\}^{13}C$ NMR spectrum of a mixture of the isomers.

Isomer A (XV-1) ^{1}H NMR (C_6D_6, 250 MHz) δ 5.25 (m, 1, $OC\underline{H}(Me)CH_2Cl$), 3.52 (dd, 1, $^{2}J_{H_BH_C}$ = 10.6 Hz, $^{3}J_{H_BH_A}$ = 9.5 Hz, $OCH_A(Me)C\underline{H_B}H_CCl$), 3.33 (s, 3, $C_\alpha Me$), 3.14 (dd, 1, $^{2}J_{H_CH_B}$ = 10.6 Hz, $^{3}J_{H_CH_A}$ = 2.8 Hz, $OCH_A(Me)CH_B\underline{H_C}Cl$), 2.29 (s, 3, $C_\beta Me$), 1.40 (s, 9, $CCMe_3$), 1.09 (d, 3, $^{3}J_{HH_A}$ = 6.3 Hz, $OCH_A(\underline{Me})CH_2Cl$).

(XIV-40) $^{13}C\{^{1}H\}$ NMR (C_6D_6, 67.9 MHz) δ 267.9 and 260.2 ($\underline{C}CMe_3$ and $\underline{C}_\alpha Me$), 140.5 ($\underline{C}_\beta Me$), 84.4 ($O\underline{C}H(Me)CH_2Cl$), 50.9 ($OCH(Me)\underline{C}H_2Cl$), 29.8 ($C\underline{C}Me_3$), 20.9 (either $C_\alpha\underline{Me}$, $C_\beta\underline{Me}$ or $OCH(\underline{Me})CH_2Cl$). The other resonances for this isomer are either too small to observe (e.g., $CCMe_3$) or are masked by isomer B's resonances .

Isomer B (XV-1) ^{1}H NMR (C_6D_6, 250 MHz) δ 5.11 (dd, 1, $^{2}J_{H_AH_B}$ = 12.1 Hz, $^{3}J_{H_AH_C}$= 3.3 Hz, $OC\underline{H_A}H_BCH_C(Me)Cl$), 4.94 (dd, 1, $^{2}JH_BH_A$ = 12.1 Hz, $^{3}J_{H_BH_C}$ = 9.7 Hz, $OCH_A\underline{H_B}CH_C(Me)Cl$), 4.19 (m, 1, $OCH_2C\underline{H}(Me)Cl$), 3.31 (s, 3, $C_\alpha Me$), 2.24 (s, 3, $C_\beta Me$), 1.42 (s, 9, $CCMe_3$), 1.20 (d, 3, $^{3}J_{HH_C}$ = 6.7 Hz, $OCH_2CHC(\underline{Me})Cl$).

(XIV-40) $^{13}C\{^{1}H\}$ NMR (C_6D_6, 67.9 MHz) δ 268.5 and 260.6 ($\underline{C}CMe_3$ and $\underline{C}_\alpha Me$), 140.9 ($\underline{C}_\beta Me$), 83.3 ($O\underline{C}H_2CH(Me)Cl$), 61.4 ($OCH_2\underline{C}H(Me)Cl$), 43.3 ($C\underline{C}Me_3$), 29.8 ($CC\underline{Me}_3$), 24.0, 19.8 and 13.5 ($C_\alpha\underline{Me}$, $C_\beta\underline{Me}$ and $OCH_2CH(\underline{Me})Cl$, not respectively).

Preparation of $[W(\eta^5\text{-}C_5Me_4CMe_3)Cl_2]_n$ (XVI-51).

$[W(\eta^5\text{-}C_5Me_4CMe_3)Cl_4]_2$ (1.0 g, 1.0 mmol) was added all at once to a vigorously stirred toluene solution (30 ml) containing Na/Hg (0.41%, 22.3 g, 3.98 mmol). After ~1.5 h the reaction was filtered through Celite and the filtrate was concentrated *in vacuo*. A first crop of crystals was isolated from the concentrate (0.56 g), washed with pentane and dried *in vacuo*. The volatiles were removed from the mother liquors and the residue was dissolved in a minimum of toluene, filtered and cooled to -30°C. Another 0.13 g of product was obtained; yield 0.69 g (80%).

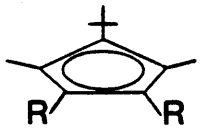
(XIV-29) ^1H NMR (C_6D_6, 270 MHz) δ 2.90 and 1.94 (s, 6 each, $\eta^5\text{-}C_5\underline{Me}_4CMe_3$), 1.31 (s, 9, $\eta^5\text{-}C_5Me_4C\underline{Me}_3$).

Preparation of $W(\eta^5\text{-}C_5Me_2Et_2CMe_3)(CCMe_3)Cl_2$ (XV-46, 47).

An ether suspension (15 ml) of $W(CCMe_3C_2Me_2)Cl_3$ (0.91 g, 2.2 mmol) was cooled to -30°C and reacted with 3-hexyne (1.0 ml, 16.8 mmol). The reaction was stirred for 3 h at room temperature and then filtered. The orange solid was washed with ether and dried *in vacuo*. The volatiles were removed from the filtrate *in vacuo* and the residue extracted with pentane. The extracts were filtered leaving more orange solid behind. The combined orange material was dissolved in CH_2Cl_2, filtered and the volatiles were removed *in vacuo*. Yield of $[W(\eta^5\text{-}C_5Me_2Et_2CMe_3)Cl_4]_2$ was 0.49 g (84%).

A toluene solution (15 ml) of $[W(\eta^5\text{-}C_5Me_2Et_2CMe_3)Cl_4]_2$ (0.30 g, 0.56 mmol) was cooled to -30°C and treated with $ZnNp_2$ (0.12 g, 0.56 mmol). The solution was warmed to room temperature and after stirring for 4 h the volatiles were removed *in vacuo*. The residue was extracted with pentane, filtered and the pentane was removed *in vacuo* leaving a purple oil. A ^1H

NMR spectrum of this oil is reported below. Assume the cyclopentadienyl ring isomers are as follows:



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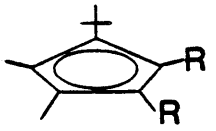


B

(XV-47) ^{1}H NMR (C_6D_6, 270 MHz) δ 3.06 to 2.29 (m, methylene resonances for ethyl groups in both ring isomers), 2.22 (s, 6, η^5-$C_5\underline{Me_2}Et_2CMe_3$ of isomer A), 2.15 and 1.93 (s, 3 each, η^5-$C_5\underline{Me_2}Et_2CMe_3$ of isomer B), 1.29, 1.23, 1.19 and 1.18 (s, 9 each, W≡CC$\underline{Me_3}$ and η^5-$C_5Me_2Et_2C\underline{Me_3}$ of isomers A and B, not respectively), 1.01 to 0.84 (m, methyl resonances of ethyl groups in both ring isomers).

Preparation of $W(CCMe_3C_2Me_2)(py)_2Cl_3$ (XVI-71).

$W(CCMe_3C_2Me_2)Cl_3$ (0.20 g, 0.48 mmol) was dissolved in cold (-30°C) CH_2Cl_2 (8 ml). Pyridine (100 µl, 1.2 mmol) was added and the reaction was warmed to room temperature. After 20 min the volatiles were removed in vacuo and the lime green solid was washed with pentane and dried in vacuo. The reaction is quantitative by ^{1}H NMR. Two isomers are present, one of which has equivalent pyridines (sym isomer) and the other has inequivalent pyridines (asym isomer). At room temperature one of the pyridines in the more asym isomer appears to be labile. Therefore, the ^{1}H NMR spectrum reported below is one taken at -20°C where the broadened pyridine resonances are now sharp. There is no further change in the spectrum down to -60°C.

(XVI-71) ^{1}H NMR (CD_2Cl_2, 250 MHz, -20°C) δ 9.02 (d, 4, py, sym), 8.62 and 8.52 (d, 2 each, py, asym), 7.80, 7.67, 7.41 and 7.15 (all other py resonances combined), 4.11 (s, 6, CMe, asym), 3.72 (s, 6, CMe, sym), 1.15 (s, 9, $CCMe_3$, asym), 0.99 (s, 9, $CCMe_3$, sym).

^{13}C NMR assignments are not separated according to isomer. The metallacycle ring carbons were picked out from a gated $\{^{1}H\}$ NMR spectrum.

(XVI-71) $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 67.9 MHz) δ 171.8, 144.6, 143.1 and 126.2 ($\underline{C}CMe_3$ and $\underline{C}Me$), 153.3, 152.6, 151.0, 140.1, 139.3, 138.3, 125.1, 124.3 and 123.4 (py), 39.2 ($C\underline{C}Me_3$), 32.3 and 32.1 ($CC\underline{Me}_3$), 30.1 ($C\underline{C}Me_3$), 16.5 and 13.6 ($C\underline{Me}$).

Preparation of $W(CCMe_3C_2Me_2)(Me_2N(CH_2)_2NMe_2)Cl_3$ (XVI-72).

Similar conditions used to make $W(CCMe_3C_2Me_2)(py)_2Cl_3$ are employed in this reaction. The reaction is very clean by ^{1}H NMR.

(XVI-71) ^{1}H NMR (CD_2Cl_2, 250 MHz, 20°C) δ 4.61 (s, 6, CMe), 2.86 and 2.69 (s with broad resonances underneath, 8 each, $\underline{Me}_2N(\underline{CH}_2)_2N\underline{Me}_2$), 1.27 (s, 9, $CCMe_3$). (-70°C) δ 4.53 and 4.36 (br s, 3 each, CMe), 2.76 and 2.61 (br s, 16 total, $\underline{Me}_2N(\underline{CH}_2)_2N\underline{Me}_2$), 1.15 (s, 9, $CCMe_3$).

Preparation of $W(CCMe_3C_2Me_2)(OCMe_3)Cl_2$ (XV-29).

A cold (-30°C) toluene solution (10 ml) of $W(CCMe_3C_2Me_2)Cl_3$ (0.52 g, 1.3 mmol) was treated with NEt_3 (175 μl, 1.3 mmol) followed by t-butanol (119 μl, 1.3 mmol). The reaction was stirred for 1 h at room temperature and the volatiles were removed in vacuo. The residue was extracted with ether, filtered and concentrated in vacuo. Cooling to -30°C gave orange crystals that were isolated by filtration, washed with pentane and dried in vacuo (2 crops, 0.38 g, 67%).

(XIV-68) ^{1}H NMR (C_6D_6, 250 MHz) δ 3.08 (s, 3, $C_\alpha Me$), 2.16 (s, 3, $C_\beta Me$), 1.75 (s, 9, $OCMe_3$), 1.39 (s, 9, $CCMe_3$).

(XIV-68) ^{13}C NMR (C_6D_6, 67.9 MHz) δ 265.6 and 259.1 (s, J_{CW} = 93 Hz and 116 Hz, $\underline{C}CMe_3$ and $\underline{C}_\alpha Me$, not respectively), 134.2 (s, $\underline{C}_\beta Me$), 87.9 (s, $O\underline{C}Me_3$), 42.7 (s, $C\underline{C}Me_3$), 31.1 (q, J_{CH} = 129 Hz, $OC\underline{Me}_3$ or $CC\underline{Me}_3$), 29.6 (q, J_{CH} = 128 Hz, $OC\underline{Me}_3$ or $CC\underline{Me}_3$), 24.3 (q, J_{CH} = 131 Hz, $C\underline{Me}$), 12.4 (q, J_{CH} = 134 Hz, $C\underline{Me}$).

Anal. Calcd for $WC_{13}H_{24}Cl_2O$: C, 34.61; H, 5.36. Found: C, 34.56; H, 5.41.

Preparation of $W(CCMe_3C_2Et_2)(OCMe_3)Cl_2$ (XIV-71).

Triethylamine (51 μl, 0.36 mmol) was added to a toluene solution (8 ml) of $W(CCMe_3C_2Et_2)Cl_3$ (0.16 g, 0.36 mmol) that had been cooled to -30°C. t-Butanol (34 μl, 0.36 mmol) in toluene (1 ml) was added dropwise and the solution was stirred for 2 h. The volatiles were removed in vacuo and the remaining solid was extracted with pentane. The extracts were filtered and concentrated in vacuo. Cooling to -30°C gave 0.13 g of orange crystals (75%).

(XIV-71) ^{1}H NMR (C_6D_6, 250 MHz) δ 3.57 (q, 2, $^{3}J_H$ = 7.4 Hz, $C_\alpha C\underline{H}_2CH_3$), 3.28 (q, 2, $^{3}J_H$ = 7.6 Hz, $C_\beta C\underline{H}_2CH_3$), 1.73 (s, 9, $OCMe_3$ or $CCMe_3$), 1.57 (t, 3, $^{3}J_H$ = 7.4 Hz, $C_\alpha CH_2C\underline{H}_3$), 1.43 (s, 9, $OCMe_3$ or $CCMe_3$), 0.68 (t, 3, $^{3}J_H$ = 7.6 Hz, $C_\beta CH_2C\underline{H}_3$).

(XIV-71) ^{13}C NMR (C_6D_6, 67.9 MHz) δ 266.4 and 265.7 (s, J_{CW} ~93 Hz and 110 Hz, $\underline{C}CMe_3$ and $\underline{C}_\alpha Et$), 137.4 (s, $\underline{C}_\beta Et$), 87.9 (s, $O\underline{C}Me_3$), 43.1 (s, $C\underline{C}Me_3$), 31.9 (t, J_{CH} = 131 Hz, $C_\alpha$or$C_\beta\underline{C}H_2CH_3$), 31.2 (q, J_{CH} = 127 Hz, $OC\underline{Me}_3$ or $CC\underline{Me}_3$), 30.4 (q, J_{CH} = 128 Hz, $OC\underline{Me}_3$ or $CC\underline{Me}_3$), 21.5 (t, J_{CH} = 135 Hz, $C_\alpha$or$C_\beta\underline{C}H_2CH_3$), 15.1 and 12.3 (q, J_{CH} ~130 Hz, $CCH_2\underline{C}H_3$).

Preparation of $W(CCMe_3C_2Me_2)(OCMe_2CMe_2O)Cl$ (XV-64).

An ether suspension (40 ml) of $W(CCMe_3C_2Me_2)Cl_3$ (1.14 g, 2.8 mmol) was cooled to -30°C and triethylamine (770 μl, 5.6 mmol) was added. Pinacol (0.33 g, 2.8 mmol) in ether (5 ml) was added dropwise. After the addition was complete the reaction was allowed to warm to room temperature and was stirred for an additional 2 h. The solution was filtered and the volatiles were removed in vacuo. The residue was extracted with ether, filtered and concentrated. Cooling to -30°C gave orange/red crystals that were isolated by filtration and dried in vacuo (2 crops, 1.17 g, 92%).

(XV-3) ^1H NMR (C_6D_6, 250 MHz) δ 3.12 (s, 3, CMe), 2.25 (s, 3, CMe), 1.57 and 1.55 (s, 6, $OCMe_2CMe_2O$), 1.36 (s, 9, $CCMe_3$), 1.16 and 1.13 (s, 6, $OCMe_2CMe_2O$).

(XV-14) ^1H NMR (d_8-tol, 250 MHz, 20°C, ~0.13 M) δ 3.20 (s, 3, CMe), 2.38 (s, 3, CMe), 1.52 and 1.51 (s, 6, $OCMe_2CMe_2O$), 1.38 (s, 9, $CCMe_3$), 1.14 and 1.11 (s, 6, $OCMe_2CMe_2O$). (57°C) δ 3.25 (s, 3, CMe), 2.51 (s, 3, CMe), 1.50 and 1.48 (s, 6, $OCMe_2CMe_2O$), 1.40 (s, 9, $CCMe_3$), 1.13 and 1.09 (s, 6, $OCMe_2CMe_2O$).

(XV-3) ^{13}C NMR (C_6D_6, 67.9 MHz) δ 250.1 and 241.3 (s, $\underline{C}CMe_3$ and $\underline{C}_\alpha Me$), 143.0 (s, $\underline{C}_\beta Me$), 98.5 and 89.7 (s, $O\underline{C}Me_2\underline{C}Me_2O$), 41.6 (s, $C\underline{C}Me_3$), 30.8 (q, J_{CH} = 128 Hz, $CC\underline{Me}_3$), 27.9 and 27.0 (q, J_{CH} ~126 Hz, $OC\underline{Me}_2C\underline{Me}_2O$), 22.5 (q, J_{CH} = 131 Hz, $C_\alpha\underline{Me}$ or $C_\beta\underline{Me}$), 13.7 (q, J_{CH} = 134 Hz, $C_\alpha\underline{Me}$ or $C_\beta\underline{Me}$).

Anal. Calcd for $WC_{15}H_{27}O_2Cl$: C, 39.28; H, 5.93. Found: C, 38.81; H, 5.88.

^{1}H NMR Spectrum of $W(CCMe_3C_2Me_2)(OCMe_2CMe_2O)Cl$ and two pyridines, in situ (XV-41).

^{1}H NMR (C_6D_6, 250 MHz, ~0.15 M) δ 8.55 (d, py), 7.05 (m, py), 6.72 (m, py), 3.15 (s, 3, CMe), 2.36 (s, 3, CMe), 1.52 and 1.41 (s, 6, $OCMe_2CMe_2O$), 1.40 (s, 9, $CCMe_3$), 1.14 and 1.13 (s, 6, $OCMe_2CMe_2O$).

Preparation of $W(CMe_3C_2Et_2)(OCMe_2CMe_2O)Cl$ (XV-26).

A toluene solution (8 ml) of $W(CCMe_3C_2Et_2)Cl_3$ (0.15 g, 0.34 mmol) was cooled to -30°C, followed by addition of triethylamine (95 μl, 0.68 mmol). A toluene solution (1 ml) of pinacol (0.04 g, 0.34 mmol) was added dropwise. After warming to room temperature the reaction was stirred for 1 h and the volatiles were removed in vacuo. The residue was extracted with pentane, filtered, and concentrated in vacuo until crystallization had begun. Cooling to -30°C gave orange-red crystals (0.10 g, 60%).

(XV-26) ^{1}H NMR (C_6D_6, 250 MHz) δ 3.75 to 3.12 (m, 4, $CC\underline{H_2}CH_3$), 1.58, 1.52, 1.16 and 1.13 (s, 3 each, $OCMe_2CMe_2O$) 1.56 (t, 3, ^3J_H = 7.4 Hz, $C_\alpha CH_2C\underline{H_3}$), 1.42 (s, 9, $CCMe_3$), 0.71 (t, 3, ^3J_H = 7.5 Hz, $C_\beta CH_2C\underline{H_3}$).

(XV-26) ^{13}C NMR (C_6D_6, 67.9 MHz) δ 248.8 and 248.7 (s, $CCMe_3$ and C_αEt), 145.8 (s, $\underline{C_\beta}$Et), 98.5 and 89.9 (s, $O\underline{C}Me_2\underline{C}Me_2O$), 41.7 (s, $C\underline{C}Me_3$), 31.5 (q, J_{CH} ≈ 127 Hz, $CC\underline{Me_3}$), 30.4 (t, J_{CH} ≈ 134 Hz, $C\underline{C}H_2CH_3$), 28.5, 27.8 and 27.0 (q, J_{CH} ≈ 125 Hz, $OC\underline{Me_2}C\underline{Me_2}O$), 22.5 (t, J_{CH} = 134 Hz, $C\underline{C}H_2CH_3$), 15.5 and 12.9 (q, J_{CH} ≈ 129 Hz, $CCH_2\underline{C}H_3$).

Preparation of $W(CCMe_3C_2Me_2)(OCMe_2CMe_2O)(OCMe_3)$ (XV-24).

A cold (-30°C) ether solution (12 ml) of $W(CCMe_3C_2Me_2)(OCMe_2CMe_2O)Cl$ (0.25 g, 0.55 mmol) was reacted with $LiOCMe_3$ (44 mg, 0.55 mmol). LiCl precipitated as the reaction warmed to room temperature and after 1 h the

volatiles were removed in vacuo. The residue was extracted with pentane and filtered through a pad of Celite. The filtrate was concentrated in vacuo and cooled to -30°C. Orange crystals were isolated the following day by filtration (80 mg). The volatiles were removed from the mother liquors in vacuo and the resulting solid was sublimed (25°C, 10^{-3} μ). The product is extremely soluble in pentane and is best isolated by sublimation.

(XV-24) ^{1}H NMR (C_6D_6, 250 MHz, 20°C) δ 3.30 (s, 3, $C_\alpha Me$), 2.50 (s, 3, $C_\beta Me$), 1.44 and 1.33 (s, 9 each, $OCMe_3$ and $CCMe_3$, not respectively). The pinacol methyl resonances are broad and are centered at ~1.30 ppm. (d_8-tol, -35°C) δ 3.24 (s, 3, $C_\alpha Me$), 2.30 (s, 3, $C_\beta Me$), 1.61 and 1.53 (s, 3 each, $OC\underline{Me}_2C\underline{Me}_2O$), 1.48 (s, 9, $CCMe_3$), 1.20 (br s, 6, $OC\underline{Me}_2C\underline{Me}_2O$). ($C_6D_6$, 50°C) δ 3.35 (s, 3, $C_\alpha Me$), 2.61 (s, 3, $C_\beta Me$), 1.43 (s, 9, $OCMe_3$ or $CCMe_3$), 1.28 (s, 6, $OC\underline{Me}_2C\underline{Me}_2O$), 1.25 (s, 15, $OCMe_3$ or $CCMe_3$ and the other $OC\underline{Me}_2C\underline{Me}_2O$ resonance). See discussion on fluxional behavior of $W(C_3Et_3)(OCMe_2CMe_2O)(OCMe_3)$ for explanation of these observations.

$^{13}C\{^1H\}$ NMR (C_6D_6, 67.9 MHz) δ 232.1 and 225.2 (J_{CW} = 122 Hz and 134 Hz, $\underline{C}CMe_3$ and $\underline{C}_\alpha Me$), 128.9 ($\underline{C}_\beta Me$), 88.3 ($O\underline{C}Me_2\underline{C}Me_2O$), 75.9 ($O\underline{C}Me_3$), 40.4 ($C\underline{C}Me_3$), 31.9, 31.7 and 27.6 ($OC\underline{Me}_3$, $CC\underline{Me}_3$ and $OC\underline{Me}_2C\underline{Me}_2O$, not assignable), 22.0 and 13.0 ($C\underline{Me}$).

Molecular ion found at 496 in mass spectrum.

Preparation of $W(\eta^5\text{-}C_5Me_4CMe_3)(O)_2(OCMe_3)$ (XV-37).

A pentane solution (2 ml) of $W(CCMe_3C_2Me_2)(OCMe_2CMe_2O)(OCMe_3)$ (0.10 g, 0.20 mmol) was reacted with 2-butyne (80 μl, 1.0 mmol). After 2 h the volatiles were removed in vacuo leaving a colorless oil. A ^{1}H NMR spectrum of this material was very clean, indicating that the reaction proceeds in

high yield (essentially quantitatively). The reaction may also be followed by ^{1}H NMR. 2,3-Dimethyl-2-butene was identified by ^{1}H and ^{13}C NMR.

$Me_2C{=}CMe_2$: (XV-37) ^{1}H NMR (C_6D_6, 250 MHz) δ 1.60 (s). (XV-37) $^{13}C\{^{1}H\}$ NMR (C_6D_6, 67.9 MHz) δ 123.3 ($Me_4\underline{C}_2$), 20.4 ($\underline{Me}_4C_2$).

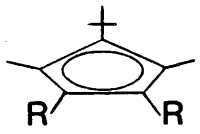
$W(\eta^5\text{-}C_5Me_4CMe_3)(O)_2(OCMe_3)$: (XV-37) ^{1}H NMR (C_6D_6, 250 MHz) δ 2.17 and 1.72 (s, 6 each, $\eta^5\text{-}C_5\underline{Me}_4CMe_3$), 1.37 (s, 9, $\eta^5\text{-}C_5Me_4\underline{CMe}_3$), 1.27 (s, 9, $OCMe_3$).

(XV-37) $^{13}C\{^{1}H\}$ NMR (C_6D_6, 67.9 MHz) δ 124.7, 122.3 and 119.7 ($\eta^5\text{-}\underline{C}_5Me_4CMe_3$), 79.7 ($O\underline{C}Me_3$), 35.4 ($\eta^5\text{-}C_5Me_4\underline{C}Me_3$), 31.9 and 30.3 ($\eta^5\text{-}C_5Me_4C\underline{CMe}_3$ and $OC\underline{Me}_3$, not respectively), 14.3 and 10.7 ($\eta^5\text{-}C_5\underline{Me}_4CMe_3$).

Preparation of $W(\eta^5\text{-}C_5Me_2Et_2CMe_3)(O)_2(OCMe_3)$ (XV-42).

$W(CCMe_3C_2Me_2)(OCMe_2CMe_2O)(OCMe_3)$ was reacted with excess 3-hexyne in an NMR tube. After 24 h the reaction was near completion.

Assume once again that the cyclopentadienyl isomers are as follows:



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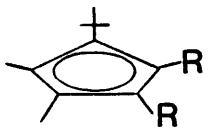


B

(XV-42) ^{1}H NMR (C_6D_6, 250 MHz) δ 2.92, 2.49 and 2.32 (m, methylene proton of ethyl groups for both isomers), 2.24 (s, 6, $\eta^5\text{-}C_5\underline{Me}_2Et_2CMe_3$ of isomer A), 2.14 and 1.75 (s, 3 each, $\eta^5\text{-}C_5\underline{Me}_2Et_2CMe_3$ of isomer B), 1.41, 1.36, 1.28(4) and 1.27(7) (s, 9 each, $OCMe_3$ and $CCMe_3$ of both isomers), 1.06 to 0.87 (m, methyl resonances of ethyl groups for both isomers).

Preparation of $W(CCMe_3C_2Me_2)(OCMe_2CMe_2CMe_2O)Cl$ (XV-25).

A toluene suspension (8 ml) of $W(CCMe_3C_2Me_2)Cl_3$ (0.19 g, 0.46 mmol) was cooled to -30°C. NEt_3 (128 μl, 0.92 mmol) was then added, followed by a toluene solution of $HOCMe_2CMe_2CMe_2OH$ (0.07 g, 0.46 mmol). The reaction was stirred at room temperature for 1 h and the volatiles were removed *in vacuo*. The residue was extracted with ether, filtered and concentrated. Cooling to -30°C gave 0.13 g (57%) of orange crystals.

(XV-25) ^1H NMR (C_6D_6, 270 MHz) δ 3.27 (s, 3, $C_\alpha Me$), 2.33 (s, 3, $C_\beta Me$), 1.67, 1.56, 1.12, 1.11, 0.94 and 0.90 (s, 3 each, $OCMe_2CMe_2CMe_2O$), 1.42 (s, 9, $CCMe_3$).

(XV-25) ^{13}C NMR (C_6D_6, 67.9 Hz) δ 251.5 and 238.9 (s, $\underline{C}CMe_3$ and $\underline{C}_\alpha Me$), 139.0 (s, $\underline{C}_\beta Me$), 87.2 and 81.1 (s, $O\underline{C}Me_2CMe_2\underline{C}Me_2O$), 44.2 and 41.7 ($OCMe_2\underline{C}Me_2CMe_2O$ and $C\underline{C}Me_3$, not assignable), 30.8 (q, $J_{CH} \approx 126$ Hz, $CC\underline{Me}_3$), 30.0, 29.8, 29.7 and 29.5 (q, $J_{CH} \approx 125$ Hz, $OC\underline{Me}_2CMe_2C\underline{Me}_2O$), 22.5 (q, $J_{CH} \approx 129$ Hz, $C_\alpha\underline{Me}$, $C_\beta\underline{Me}$, or $OCMe_2C\underline{Me}_2CMe_2O$), 22.2 and 22.0 (q, $J_{CH} \approx 125$ Hz, $C_\alpha\underline{Me}$, $C_\beta\underline{Me}$, or $OCMe_2C\underline{Me}_2CMe_2O$), 13.6 (q, $J_{CH} \approx 134$ Hz, $C_\alpha\underline{Me}$ or $C_\beta\underline{Me}$).

Preparation of $W(CCMe_3C_2Me_2)(OCMe_2CMe_2CMe_2O)(OCMe_3)$ (XV-32).

An ether solution (10 ml) of $W(CCMe_3C_2Me_2)(OCMe_2CMe_2CMe_2O)Cl$ (0.15 g, 0.30 mmol) was cooled to -30°C and treated with $LiOCMe_3$ (24 mg, 0.30 mmol). After stirring at room temperature for 1.5 h the volatiles were removed *in vacuo*. The residue was extracted with pentane and filtered. The pentane was removed *in vacuo*, leaving a red/orange oil that was pure by ^1H NMR.

(XV-32) ^1H NMR (C_6D_6, 250 MHz) δ 3.47 (s, 3, $C_\alpha Me$), 2.55 (s, 3, $C_\beta Me$), 1.42 (s, 9, $OCMe_3$ or $CCMe_3$), 1.29 and 1.24 (br s, total of 12, $OC\underline{Me}_2CMe_2C\underline{Me}_2O$), 1.19 (s, 9, $OCMe_3$ or $CCMe_3$), 1.03 (s, 6, $OCMe_2C\underline{Me}_2CMe_2O$).

(XV-32) $^{13}C\{^{1}H\}$ NMR (C_6D_6, 67.9 MHz) δ 238.6 and 221.4 (J_{CW} = 113 Hz and 145 Hz, $\underline{C}CMe_3$ and $\underline{C}_{\alpha}Me$), 124.5 ($\underline{C}_{\beta}Me$), 80.5 (br, $O\underline{C}Me_2CMe_2\underline{C}Me_2O$), 74.8 ($O\underline{C}Me_3$), 44.2 ($OCMe_2\underline{C}Me_2CMe_2O$), 40.4 ($C\underline{C}Me_3$), 32.0, 31.4, and 30.1 ($OC\underline{Me}_3$, $CC\underline{Me}_3$ and $OC\underline{Me}_2CMe_2C\underline{Me}_2O$, not respectively), 22.0 ($OCMe_2C\underline{Me}_2CMe_2O$ and $C\underline{Me}$), 12.9 ($C\underline{Me}$).

Preparation of $W(CHCMe_3)(OCMe_2CMe_2O)(OCMe_3)_2$ (XV-62).

Pinacol (130 mg, 1.1 mmol) in 2 ml of toluene was added dropwise to a toluene solution (10 ml) of $W(CCMe_3)(OCMe_3)_3$ (0.53 g, 1.1 mmol). After 5 min the volatiles were removed in vacuo leaving a red/orange oil. A ^{1}H NMR spectrum of this material was very clean. The oil can be sublimed at room temperature and 10^{-3} μ.

(XV-62) ^{1}H NMR (C_6D_6, 250 MHz) δ 6.76 (s, 1, $^{2}J_{HW}$ = 11.5 Hz, $C\underline{H}CMe_3$), 1.39 (s, 18, $OCMe_3$), 1.25 and 1.24 (s, total of 21, $CHC\underline{Me}_3$ and $OCMe_2C\underline{Me}_2O$, not respectively).

(XV-62) ^{13}C NMR (C_6D_6, 67.9 MHz) δ 237.5 (d, J_{CH} = 130 Hz, J_{CW} = 186 Hz, $\underline{C}HCMe_3$), 92.3 and 80.9 (s, $O\underline{C}Me_2\underline{C}Me_2O$ and $O\underline{C}Me_3$), 39.5 (s, $CH\underline{C}Me_3$), 36.1, 30.9, and 26.2 (q, J_{CH} ~ 125 Hz, $OC\underline{Me}_2C\underline{Me}_2O$, $OC\underline{Me}_3$ and $CHC\underline{Me}_3$, not respectively).

Preparation of $W(C_3Et_3)(OCMe_2CMe_2O)(OCMe_3)$ (XV-74).

A toluene solution (20 ml) of $W(CEt)(OCMe_3)_3$ (1.47 g, 3.3 mmol) was cooled to -20°C and 3-hexyne was added (376 μl, 3.3 mmol). Pinacol (0.39 g, 3.3 mmol) in toluene (8 ml) was added dropwise to the reaction over a 5 min period. The reaction was left to stir at this temperature for another 5 min and then warmed to room temperature. The volatiles were removed in vacuo,

leaving a red oil. This was dissolved in pentane, treated with DARCO, filtered and the volatiles were removed in vacuo. The resultant oil was distilled through a short path apparatus at 50°C and 10^{-3} μ. The product was collected in a flask that was maintained at -78°C. Yield 1.21 g (74%).

(XV-44) ^{1}H NMR (d_8-tol, 250 MHz, 20°C) δ 3.87 to 3.57 (m, 4, $C_\alpha\underline{H_2}CH_3$), 3.05 (q, 2, ^3J_H = 7.5 Hz, $C_\beta\underline{H_2}CH_3$), 1.54 (t, 6, ^3J_H = 7.4 Hz, $C_\alpha CH_2\underline{CH_3}$), 1.33 (s, 9, $OCMe_3$), 0.74 (t, 3, ^3J_H = 7.5 Hz, $C_\beta CH_2\underline{CH_3}$). (-40°C) δ 3.83 to 3.52 (m, 4, $C_\alpha\underline{H_2}CH_3$), 2.88 (q, 2, ^3J_H = 7.6 Hz, $C_\beta\underline{H_2}CH_3$), 1.61 (t, 6, ^3J_H = 7.4 Hz, $C_\alpha CH_2\underline{CH_3}$), 1.59 (s, 6, $OC\underline{Me_2}CMe_2O$), 1.42 (s, 9, $OCMe_3$), 1.19 (s, 6, $OCMe_2C\underline{Me_2}O$), 0.65 (t, 3, ^3J_H = 7.5 Hz, $C_\beta CH_2\underline{CH_3}$). (70°C) δ 3.90 to 3.65 (m, 4, $C_\alpha\underline{H_2}CH_3$), 3.14 (q, 2, $C_\beta\underline{H_2}CH_3$), 1.51 (t, 6, $C_\alpha CH_2\underline{CH_3}$), 1.29 and 1.27 (s, 21 total, $OCMe_3$ and $OCMe_2CMe_2O$), 0.79 (t, 3, $C_\beta CH_2\underline{CH_3}$).

(XV-44) $^{13}C\{^1H\}$ NMR (C_6D_6, 67.9 MHz) δ 226.5 ($\underline{C}_\alpha CH_2CH_3$), 132.9 ($\underline{C}_\beta CH_2CH_3$), 75.6 ($O\underline{C}Me_3$), 31.8 ($OC\underline{Me}_3$), 29.3 ($C\underline{C}H_2CH_3$), 27.6 ($OC\underline{Me}_2C\underline{Me}_2O$), 23.2 ($C\underline{C}H_2CH_3$), 16.0 and 12.9 ($CCH_2\underline{C}H_3$).

Molecular ion found at 496 in mass spectrum.

Reaction of $W(C_3Et_3)(OCMe_2CMe_2O)(OCMe_3)$ with 3-hexyne to give $W(\eta^5\text{-}C_5Et_5)(O)_2(OCMe_3)$

The reaction was carried out in an NMR tube using an excess of 3-hexyne. After standing overnight the reaction was complete by ^{1}H NMR. The presence of 2,3-dimethyl-2-butene was confirmed by ^{1}H and ^{13}C NMR comparison with an authentic sample (also by coinjection in a reaction examined by GC analysis).

This reaction can be done on a preparative scale by reacting a pentane solution of $W(C_3Et_3)(OCMe_2CMe_2O)(OCMe_3)$ with excess (~2 or 3 equiv) 3-hexyne. The product can be recrystallized from pentane.

Complete analytical details are reported here although crystals used for C and H analysis and a mass spectrum were obtained from the reaction of $W(CEt)(OCMe_3)_3$ with excess 3-hexyne (vide infra).

^1H NMR (C_6D_6, 250 MHz) δ 2.45 (q, 10, ^3J_H = 7.7 Hz, η^5-($CC\underline{H}_2CH_3)_5$), 1.26 (s, 9, $OCMe_3$), 1.03 (t, 15, ^3J_H = 7.7 Hz, η^5-($CCH_2C\underline{H}_3)_5$).

^{13}C NMR (C_6D_6, 67.9 MHz) δ 123.6 (η^5-$\underline{C}_5Et_5$), 79.7 ($O\underline{C}Me_3$), 30.3 ($OC\underline{H}_3$), 19.3 (η^5-($CCH_2\underline{C}H_3)_5$), 15.7 (η^5-($CCH_2\underline{C}H_3)_5$).

Molecular ion observed at 494 in mass spectrum. Anal. Calcd for $WC_{19}H_{34}O_3$: C, 46.17; H, 6.93. Found: C, 45.78; H, 6.80.

Preparation of $W(\eta^5\text{-}C_5Me_2Et_3)(O)_2(OCMe_3)$ (XVI-1).

A pentane solution (12 ml) of $W(CCMe_3C_2Me_2)(OCMe_2CMe_2O)(OCMe_3)$ (1.0 g, 2.0 mmol) was reacted with 2-butyne (800 μl, 10.2 mmol). After 12 h the volatiles were removed in vacuo and the residue was extracted with pentane. The extracts were treated with DARCO and then filtered. The pentane was removed in vacuo leaving an oily solid. A ^1H NMR spectrum showed the presence of only one cyclopentadienyl compound which we assume has the structure shown in eq 19.

(XVI-1) ^1H NMR (C_6D_6, 250 MHz) δ 2.49 to 2.31 (m, 6, $C\underline{H}_2CH_3$), 1.89 (s, 6, η^5-$C_5\underline{Me}_2Et_3$), 1.22 (s, 9, $OCMe_3$), 1.02 to 0.90 (m, 9, $CH_2C\underline{H}_3$).

Reaction of $W(CEt)(OCMe_3)_3$ with excess 3-hexyne (XV-19).

$W(CEt)(OCMe_3)_3$ (0.20 g, 0.45 mmol) was added to 3-hexyne (1.02 ml, 8.98 mmol) and the reaction was left to stand for 63.5 h. The volatiles were removed in vacuo leaving an orange/red oil that was dissolved in a minimum of pentane and cooled to -30°C. White crystals of

$W(\eta^5\text{-}C_5Et_5)(O)_2(OCMe_3)$ [see reaction of $W(C_3Et_3)(OCMe_2CMe_2O)(OCMe_3)$ with 3-hexyne for spectroscopic and analytical details] were isolated by filtration and dried in vacuo. The volatiles from the mother liquors were removed in vacuo and the residue was shown to consist of a mixture of $W(\eta^5\text{-}C_5Et_5)(O)_2(OCMe_3)$ and $W(C_5Et_5)(OCMe_3)_3$ (vide supra) by NMR. Although all of our spectra are of mixtures of these compounds, only the resonances for $W(C_5Et_5)(OCMe_3)_3$ are reported below for the sake of clarity.

(XV-19) ^1H NMR (C_6D_6, 270 MHz) δ 4.30 (q, 2, J_H = 6.9 Hz, CH_2CH_3), 3.55 (q, 4, J_H = 7.5 Hz, CH_2CH_3), 2.60 (q, 2, J_H = 7.6 Hz, CH_2CH_3), 2.27 (q, 2, J_H = 7.3 Hz, CH_2CH_3), 1.40 (s, 9, $OCMe_3$), 1.35 to 1.16 (m, CH_2CH_3), 1.14 (s, 9, $OCMe_3$), 1.12 to 1.00 (m, CH_2CH_3).

(XV-19) $^{13}C\{^1H\}$ NMR (C_6D_6, 67.9 MHz) δ 228.7, 213.5, 152.7 and 132.7 (C_5Et_5), 77.8 and 76.8 ($OCMe_3$), 32.6 and 30.1 ($OCMe_3$), 29.7, 28.2, 27.2 and 26.8 (CH_2CH_3), 14.5, 14.2, 13.6 and 11.8 (CH_2CH_3).

Reaction of $W(CMe)(OCMe_3)_3$ with excess 2-butyne (XV-33).

1.16 ml (14.8 mmol) of 2-butyne was cooled to -30°C and $W(CMe)(OCMe_3)_3$ (0.32 g, 0.74 mmol) was added. The solution became bright green and polymer began to form. After shaking for 10 min at room temperature, the reaction was filtered and the polymer was washed with pentane. The volatiles were removed in vacuo leaving a solid that was sublimed at room temperature and 10^{-3} μ. An orange/red crystalline solid was obtained and the ^1H and ^{13}C NMR spectra of this material are reported below. However, for the sake of clarity the resonances of $W(\eta^5\text{-}C_5Me_5)(O)_2(OCMe_3)$ and $W(C_5Me_5)(OCMe_3)_3$ are reported separately.

$W(\eta^5\text{-}C_5Me_5)(O)_2(OCMe_3)$: (XV-35) ^1H NMR (C_6D_6, 250 MHz) δ 1.84 (s, 15, $\eta^5\text{-}C_5Me_5$), 1.25 (s, 9, $OCMe_3$). (XV-35) $^{13}C\{^1H\}$ NMR (C_6D_6, 67.9 MHz) δ 118.5 ($\eta^5\text{-}\underline{C}_5Me_5$), 79.5 ($O\underline{C}Me_3$), 30.4 ($OC\underline{Me}_3$), 10.4 ($\eta^5\text{-}C_5\underline{Me}_5$).

$W(C_5Me_5)(OCMe_3)_3$: (XV-35) ^1H NMR (C_6D_6, 250 MHz) δ 3.95 (s, 3, $^3J_{HW} \approx$ 5.2 Hz, CMe), 2.92 (s, 6, $^3J_{HW} \approx$ 3.9 Hz, CMe), 2.01 and 1.95 (q, 3 each, $^5J_H \approx$ 1 Hz, CMe), 1.34 (s, 9, $OCMe_3$), 1.06 (s, 18, $OCMe_3$). (XV-35) $^{13}C\{^1H\}$ NMR (C_6D_6, 67.9 MHz) δ 225.1, 204.0, 143.9 and 134.0 ($\underline{C}_5Me_5$), 78.8 and 76.5 ($O\underline{C}Me_3$), 32.6 and 30.0 ($OC\underline{Me}_3$), 24.2, 20.8, 20.1 and 17.7 ($C_5\underline{Me}_5$).

CHAPTER 3

Preparation of Some Miscellaneous Tungsten(VI) Alkylidyne Complexes

INTRODUCTION

Jeff Wengrovius was the first to prepare a tungsten(VI) neopentylidyne complex (i.e., $[W(CCMe_3)Cl_4][HPEt_3]$[2]) with features that rendered it a potentially useful precursor to a large class of alkylidyne complexes. However, the rather circuitous route to this species (starting from $W(O)(OCMe_3)_4$ and $Ta(CHCMe_3)(PEt_3)_2Cl_3$) would undoubtedly have proven to be a sufficient barrier to stifle any major progress in such synthetic endeavors. Fortunately, in the meantime Sancho had found a new, high-yield route[2] to an "old" molecule, $W(CCMe_3)Np_3$. Shortly thereafter he found that this neopentylidyne species could be transformed into $[W(CCMe_3)Cl_4][NEt_4]$ in high yields and on large scales (eq 1).[2] In this author's opinion it was this

$$W(CCMe_3)Np_3 + 3\ HCl + NEt_4Cl \xrightarrow[-3\ C_5H_{12}]{CH_2Cl_2} [W(CCMe_3)Cl_4][NEt_4] \qquad (1)$$

sequence of events which opened the door to an extremely exciting and fruitful area of organometallic chemistry, namely, the synthesis and reactivity of high oxidation state, Group VI transition metal alkylidyne complexes.

From $[W(CCMe_3)Cl_4][NEt_4]$, a large class of neopentylidyne complexes have been prepared, many of which were recently reported.[2] In this chapter I describe the synthesis of some more tungsten(VI) alkylidyne complexes. The reasons for undertaking such experiments, if not described within, should be evident from our studies in Chapter 2.

RESULTS AND DISCUSSION

Preparation of $W(CCMe_3)(dme)Cl_3$.

$[W(CCMe_3)Cl_4][NEt_4]$ has proven to be an invaluable starting material in the development of tungsten(VI) neopentylidyne chemistry. However, in some cases its solubility properties have limited its usefulness. Being ionic, this derivative is soluble only in select solvents such as dichloromethane and tetrahydrofuran. There came a time when it became necessary to find a complementary trichloroneopentylidyne complex with a greater solubility range (e.g., ether, toluene, etc.). Therefore, the new species should be neutral and preferably monomeric. To satisfy these requirements we chose to experiment with the neutral, chelating, 1,2-dimethoxyethane ligand.

Our first approach involved removing the chloride ligand from $[W(CCMe_3)Cl_4][NEt_4]$ using $ZnCl_2$ in the presence of 1,2-dimethoxyethane (eq 2). The reaction proceeds as described and NMR data of the purple crystal-

$$[W(CCMe_3)Cl_4][NEt_4] + ZnCl_2(dioxane) \xrightarrow{dme} W(CCMe_3)(dme)Cl_3 + [ZnCl_3][NEt_4] \qquad (2)$$

line product suggest that the complex is octahedral with three chloride ligands cis to the neopentylidyne ligand. The coordinated 1,2-dimethoxyethane ligand does not exchange with free 1,2-dimethoxyethane on the NMR time scale.

The success of this reaction prompted us to proceed one step further and prepare this species directly from $W(CCMe_3)Np_3$. Thus, when a pentane solution of $W(CCMe_3)Np_3$ containing 1,2-dimethoxyethane is reacted with three equivalents of HCl, product precipitates from solution in greater than 85% yield.

Preparation of Tris-alkoxy Alkylidyne Complexes

As a result of our studies in Chapter 2 we became interested in examining the effect other alkoxide ligands (besides t-butoxide and pinacolato) have on alkyne metathesis systems. We began such studies by synthesizing a variety of tris-alkoxy alkylidyne complexes of tungsten(VI).

Jose Sancho prepared $W(CCMe_3)(OCMe_3)_3$ by the reaction outlined in eq 3.[2]

$$[W(CCMe_3)Cl_4][NEt_4] + 3\ LiOCMe_3 \xrightarrow{-NEt_4Cl} W(CCMe_3)(OCMe_3)_3 \qquad (3)$$

However, attempts to make other alkoxide derivatives using methoxy, ethoxy, isopropoxy and phenoxy ligands were unsuccessful.[35] NEt_4Cl did not precipitate from these reactions, suggesting that ionic complexes are being formed (however, no pure samples of such species were ever obtained).

Based on these observations, the immediate problem with preparing neopentylidyne complexes containing smaller alkoxides (relative to t-butoxide) appeared to stem from the ability of such species to bind other ligands (e.g., Cl^-). We reasoned that the bidentate nature of the 1,2-dimethoxyethane ligand in $W(CCMe_3)(dme)Cl_3$ might preclude it from remaining bound to a metal center containing a neopentylidyne group and three alkoxide ligands. Indeed, when an ether solution of $LiOPr^i$ is reacted with $W(CCMe_3)(dme)Cl_3$, pale yellow, sublimable, $[W(CCMe_3)(OPr^i)_3]_2$ is isolated in high yield. At room temperature the isopropoxy ligands are equivalent by ^1H NMR. However, at -40°C two types of isopropoxy groups are observed (1:2 ratio). This information is consistent with a dimeric structure containing bridging alkoxide ligands (Figure 1). Similar structures for $[W(CMe)(OCMe_3)_3]_2$[55] and $[Mo(NO)(OPr^i)_3]_2$[56] have been confirmed by x-ray structural analyses.

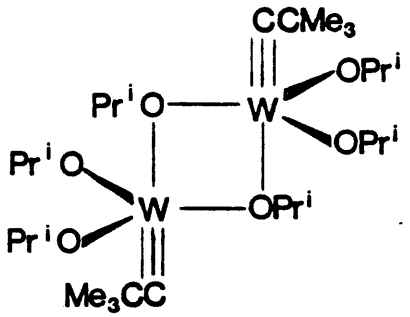


Figure 1

A monomeric tris-isopropoxy complex can be prepared by adding quinuclidene (1-azabicyclo[2.2.2]octane) to a pentane solution of $[W(CCMe_3)(OPr^i)_3]_2$. By NMR all three alkoxide ligands are equivalent and presumably located in the equatorial plane of a trigonal bipyramid (cf. $[W(CCMe_3)(OPr^i)_3]_2$).

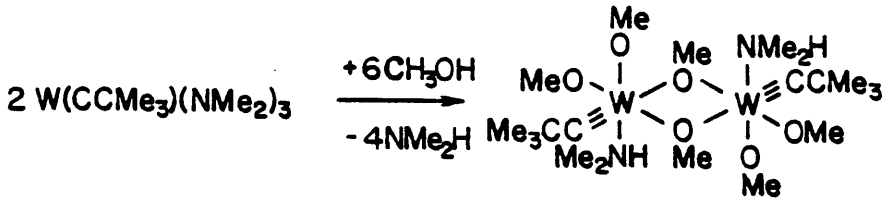
We were also interested in preparing tris-isopropoxy complexes that contain unbranched alkylidyne ligands (e.g., W≡CMe, W≡CEt, etc.). Recall that t-butoxy derivatives of such species are most conveniently prepared by reacting symmetric alkynes with $(Me_3CO)_3W{\equiv}W(OCMe_3)_3$.[49] Although $(Pr^iO)_3W{\equiv}W(OPr^i)_3$ is unknown, nitrogen base adducts (pyridine[57] and dimethylamine[58]) of this complex have been reported. Conveniently, Listemann had already found that the addition of such bases to solutions of $W_2(OCMe_3)_6$ and alkynes actually accelerates these metathesis-like reactions.[59] Therefore, starting with $(Me_2NH)(Pr^iO)_3W{\equiv}W(OPr^i)_3(HNMe_2)$, we were able to prepare $[W(CEt)(OPr^i)_3]_2$ as shown in eq 4. The dimeric formulation is based on comparison with $[W(CCMe_3)(OPr^i)_3]_2$.

$$[W(OPr^i)_3(HNMe_2)]_2 + 4 \text{ pyridine} + 3\text{-hexyne} \longrightarrow [W(CEt)(OPr^i)_3]_2 \quad (4)$$

Analogous to $[W(CCMe_3)(OPr^i)_3]_2$, $[W(CCMe_3)(ONp)_3]_2$ can be prepared from $W(CCMe_3)(dme)Cl_3$ and LiONp. NMR spectra of the crude product are fairly clean, indicating that this material is formed in good yield. Unfortunately, the physical properties of this complex are far from ideal, making it difficult to obtain in a pure state. For example, upon evaporating solutions of this material to dryness, oily foams are obtained. Attempts at crystallizing this substance from pentane have been unsuccessful. When using ether/acetonitrile as a crystallizing medium, large amounts of $[W(N)(ONp)_3]_2$ (Appendix III) are obtained. Extensive decomposition occurs upon sublimation; however, enough compound may be procured to characterize it by NMR. Similar to $[W(CCMe_3)(OPr^i)_3]_2$, a ^1H NMR spectrum of this material at room temperature shows only one type of neopentyloxy group. Upon cooling, two types of neopentyloxy resonances appear, suggesting that this complex is also dimeric.

$W(CCMe_3)(dme)Cl_3$ reacts with LiOEt in tetrahydrofuran to give a yellow, pentane-soluble solid. In the ^1H NMR spectrum at least two t-butyl resonances, in non-integral ratios, are observed, indicating that a mixture of compounds are present. We have not been able to separate these species by crystallization. Furthermore, addition of quinuclidine to a pentane solution of this material does not lead to adduct formation (cf. $W(CCMe_3)(OPr^i)_3$(quinuclidine)). However, the ratio of products in this mixture does change, suggesting that the quinuclidine is capable of temporarily breaking up W-O(Et)-W bridges. It appears that in the long run, however, ethoxide bridges are favored over nitrogen base ligation.

Well-defined tris-methoxy and phenoxy neopentylidyne complexes can be prepared from the appropriate alcohol and $W(CCMe_3)(NMe_2)_3$ (eq 5). The



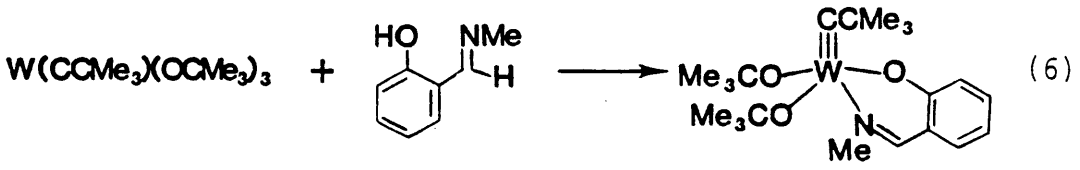
(5)

methoxy compound was shown to be a dimer by molecular weight measurements and by NMR there are three different methoxide ligands. A logical and consistent structure is shown in eq 5. The phenoxy complex also has three different phenoxide ligands (by ^{13}C NMR) and most likely has an analogous structure.

When methanol is reacted with $W(CCMe_3)(NPr^i_2)_3$ a yellow, toluene-soluble solid is obtained. A ^1H NMR spectrum of this material exhibits six methoxide and two t-butyl resonances. However, there are no diisopropylamine ligands, indicating that this bulkier amine is not capable of remaining in the coordination sphere. The structure of this new methoxy compound is unknown but presumed to be polynuclear.

For reasons discussed in Chapter 2 we prepared $W(CCMe_3)(OCEt_3)_3$ in a straightforward manner from $W(CCMe_3)(dme)Cl_3$ and $LiOCEt_3$. Based on the fact that $W(CCMe_3)(OCMe_3)_3$ is a monomer in dichloromethane[2] we presume that this complex is also monomeric.

One final example of a tris-alkoxy neopentylidyne complex comes from a project that focused on attaching well-defined alkylidyne complexes to functionalized silica surfaces. One of these surfaces contained chelating Schiff base ligands, a feature that we felt should lend stability to the attached alkylidyne complex. It was first necessary to prepare a homogeneous model which was accomplished by the reaction outlined in eq 6.



(6)

The square pyramidal structure shown in eq 6 is consistent with the fact that two different t-butoxy ligands are observed by ^1H NMR at 0°C. At room temperature the t-butoxy resonances are equivalent in the ^1H NMR spectrum (in $CDCl_3$). A reasonable mechanism that accounts for this observation involves passing through a trigonal bipyramidal intermediate that contains axial neopentylidyne and methylimine ligands. An alternative process might involve dissociation of the methylimine function from the metal.

Preparation of some dialkylamido neopentylidyne complexes.

During the course of the surface project I mentioned above it was of interest to prepare some dialkylamido neopentylidyne complexes. Such species were attractive because metal-dialkylamido ligands generally react irreversibly with hydroxyl functions to give metal alkoxides and the free amine.[43] Furthermore, a large number of functionalized silica surfaces contain dialkylamine groups.

Rocklage has prepared $[W(CCMe_3)(OCMe_3)Cl_3][NEt_4]$ by equilibrating $W(CCMe_3)(OCMe_3)_3$ and $[W(CCMe_3)Cl_4][NEt_4]$.[26] This methodology might also work with analogous dialkylamido complexes (i.e., $W(CCMe_3)(NR_2)_3$). However, the yields of $W(CCMe_3)(NR_2)_3$ are lower than for $W(CCMe_3)(OCMe_3)_3$, making this route less attractive. Therefore, we set out to prepare mono-dialkylamido complexes of the type $[W(CCMe_3)(NR_2)Cl_3][NEt_4]$, directly from

$[W(CCMe_3)Cl_4][NEt_4]$. Excess diisopropyl or diethylamine reacts with $[W(CCMe_3)Cl_4][NEt_4]$ as shown in eq 7. $[W(CCMe_3)(NEt_2)Cl_3][NEt_4]$ is prepared

$$[W(CCMe_3)Cl_4][NEt_4] + 10\ HNR_2 \xrightarrow[-R_2NH_2Cl]{CH_2Cl_2} [W(CCMe_3)(NR_2)Cl_3][NEt_4] \qquad (7)$$

$(R = Et, Pr^i)$

more conveniently from $[W(CCMe_3)Cl_4][NEt_4]$ and commercially available Me_3SiNEt_2. The synthetic ease and high yield (>90%) associated with the preparation of this particular compound make it an attractive starting material for other tungsten(VI) alkylidyne chemistry.[23] A square pyramidal geometry with the neopentylidyne group occupying the apex is a reasonable structure for these complexes based on the fact that all isoelectronic metal nitrido complexes with the general formula $X_3LM{\equiv}N$ or $[X_4M{\equiv}N]^-$ adopt a similar structure.[60] By ^{13}C NMR the alkyl groups on the dialkylamido ligand are different, suggesting that the C-N-C core is coplanar with the $W{\equiv}CCMe_3$ group. Similar structures are very common in a number of five-coordinate dialkylamido ditungsten and dimolybdenum complexes containing metal-metal triple bonds.[61]

A dimethylamido complex can be prepared from $W(CCMe_3)(PEt_3)Cl_3$ and Me_3SiNMe_2 (eq 8). This reaction proceeds quite rapidly, affording bright

$$W(CCMe_3)(PEt_3)Cl_3 + Me_3SiNMe_2 \xrightarrow[CH_2Cl_2]{-Me_3SiCl} W(CCMe_3)(PEt_3)(NMe_2)Cl_2 \qquad (8)$$

yellow crystals. The methyl groups of the dimethylamido ligand are different by NMR and are coupled to phosphorus, suggesting that the amido

group is trans to the phosphine ligand and in the base of a square pyramid (cf. $[W(CCMe_3)(NR_2)Cl_3][NEt_4]$).

These monodialkylamido complexes are attractive starting materials for the synthesis of a potentially large class of mixed tris-dialkylamido derivatives (e.g., $W(CCMe_3)(NR_2)(NR'_2)_2$) and alkoxy/amido complexes (e.g., $W(CCMe_3)(NR_2)(OR)_2$). One example of this latter type of compound is shown in eq 9.

$$[W(CCMe_3)(NPr^i_2)Cl_3][NEt_4] + 2\ LiOCMe_3 \xrightarrow{-NEt_4Cl} W(CCMe_3)(OCMe_3)_2(NPr^i_2) \qquad (9)$$

EXPERIMENTAL

See the experimental section of Chapter 1 for general experimental details. $[W(OPr^i)_3(HNMe_2)]_2$ was prepared as described by Chisholm[58] except only 12 equivalents of isopropanol were used instead of the gross excess they call for. $[W(CCMe_3)Cl_4][NEt_4]$,[2] $W(CCMe_3)(OCMe_3)_3$[2] and $W(CCMe_3)(PEt_3)Cl_3$[2] were prepared by published methods. $2\text{-}(HO)C_6H_4CHNMe$ was prepared by treating an ethanol solution of salicylaldehyde ($2\text{-}(HO)C_6H_4CHO$) with excess dimethylamine. The reaction is essentially instantaneous and quantitative. The product was distilled under reduced pressure to give a yellow liquid that was pure by ^1H NMR. Methanol was dried with magnesium methoxide.[62] Diethyl and diisopropylamine were distilled from barium oxide.

Preparation of $W(CCMe_3)(dme)Cl_3$

(a) From $[W(CCMe_3)Cl_4][NEt_4]$ and $ZnCl_2$(dioxane) (III-S-72).

$ZnCl_2$(dioxane) (0.94 g, 3.8 mmol) was added to a CH_2Cl_2 solution (40 ml) containing $[W(CCMe_3)Cl_4][NEt_4]$ (2.0 g, 3.8 mmol) and 1,2-dimethoxyethane (1.2 ml, 11.4 mmol). After stirring for 3 h, 20 ml of ether was added (to aid in the precipitation of $ZnCl_3^-$) and the reaction was filtered. The volatiles were removed from the filtrate *in vacuo* and the residue was extracted with ether. The extracts were filtered and concentrated *in vacuo* and cooled to -30°C. Purple crystals were isolated by filtration, washed with pentane, and dried *in vacuo* (2 crops, 1.64 g, 96%).

(b) From $W(CCMe_3)Np_3$ and HCl (XIV-49).

A pentane solution (60 ml) containing $W(CCMe_3)Np_3$ (10.0 g, 21.4 mmol) and dimethoxyethane (5.8 g, 64.4 mmol) was cooled in an ice bath and a 3.3 M solution of HCl in ether (25 ml, 83 mmol) was added dropwise (5 minutes). A blue-purple precipitate formed near the end of the addition. The reaction was stirred for 0.5 h and the solid was filtered off, washed with pentane, and dried in vacuo (7.92 g). Cooling the filtrate (containing the pentane washings) to -30°C gave a second crop of purple crystals (0.86 g) for a total yield of 8.78 g (91%).

(III-S-72) ^1H NMR (C_6D_6, 250 MHz) δ 3.66 and 3.27 (s, 6, $\underline{Me}OCH_2CH_2O\underline{Me}$), 3.02 and 2.92 (m, 4, $MeOCH_2CH_2OMe$), 1.26 (s, 9, $CCMe_3$).

(III-S-72) $^{13}C\{^1H\}$ NMR (C_6D_6, 67.9 MHz) δ 335.1 (s, J_{CW} = 224 Hz, $\underline{C}CMe_3$), 78.4 (t, J_{CH} = 151 Hz, $MeO\underline{C}H_2CH_2OMe$), 76.3 (q, J_{CH} = 149 Hz, $\underline{Me}OCH_2CH_2OMe$), 69.6 (t, J_{CH} = 146 Hz, $MeOCH_2\underline{C}H_2OMe$), 59.3 (q, J_{CH} = 146 Hz, $MeOCH_2CH_2O\underline{Me}$), 47.7 (s, $C\underline{C}Me_3$), 33.7 (q, J_{CH} = 128 Hz, $CC\underline{Me}_3$).

Anal. Calcd. for $WC_9H_{19}Cl_3O_2$: C, 24.05; H, 4.26. Found: C, 24.26; H, 4.25.

Preparation of $[W(CCMe_3)(OPr^i)_3]_2$ (XVI-19).

$W(CCMe_3)(dme)Cl_3$ (1.0 g, 2.2 mmol) was added as a solid (in portions) to an ether solution (20 ml) of $LiOPr^i$ (0.44 g, 6.6 mmol). After 1 h the volatiles were removed in vacuo and the residue was extracted with pentane. The extracts were filtered and the pentane was removed in vacuo leaving 0.88 g (92%) of yellow crystals (pure by ^1H NMR). The product can be sublimed in vacuo at 10^{-3} μ and 40-50°C.

(XVI-19) ^{1}H NMR (d_8-tol, 250 MHz, 20°C) δ 5.52 (h, 3, $^{3}J_H$ = 6.1 Hz, OC$\underline{H}$Me$_2$), 1.47 (d, 18, $^{3}J_H$ = 6.1 Hz, OCH$\underline{Me}_2$), 1.23 (s, 9, CCMe$_3$). (-40°C) δ 5.62 (h, 2, $^{3}J_H$ = 5.9 Hz, OC$\underline{H}$Me$_2$ terminal), 5.42 (m, 1, OC$\underline{H}$Me$_2$ bridge), 1.67 (d, 6, $^{3}J_H$ = 6.0 Hz, OCH$\underline{Me}_2$ bridge), 1.42 (br t, 12, OCH$\underline{Me}_2$ terminal), 1.27 (s, 9, CC$\underline{Me}_3$).

(XVI-19) $^{13}C\{^{1}H\}$ NMR (C_6D_6, 67.9 MHz) δ 278.6 (J_{CW} = 293.5, $\underline{C}$CMe$_3$), 85.9 (br, O$\underline{C}$HMe$_2$), 49.5 (C$\underline{C}$Me$_3$), 34.7 (CC$\underline{Me}_3$), 27.1 (OCH$\underline{Me}_2$).

Molecular ion in mass spectrum found at 430.

Preparation of W(CCMe$_3$)(OPr^i)$_3$(quinuclidine).

This complex is prepared by adding slightly more than one equivalent of quinuclidine to a pentane solution of [W(CCMe$_3$)(OPr^i)$_3$]$_2$. The product may be recrystallized from concentrated pentane solutions (-30°C) to give colorless cubes.

^{1}H NMR (C_6D_6, 270 MHz) δ 5.58 (h, 3, $^{3}J_H$ = 6.2 Hz, OC$\underline{H}$Me$_2$), 2.98 (br t, 6, $H_{\alpha\ quin}$), 1.42 (d, 18, $^{3}J_H$ = 6.1 Hz, OCH$\underline{Me}_2$), 1.31 (s, 9, CC$\underline{Me}_3$). The other two quinuclidine resonances are underneath the t-butyl resonance.

$^{13}C\{^{1}H\}$ NMR (C_6D_6, 67.9 MHz) δ 272.4 ($\underline{C}$CMe$_3$), 87.9 (O$\underline{C}$HMe$_2$), 48.5 (C$\underline{C}$Me$_3$), 45.9 (NC$_\alpha$), 35.0 (CC$\underline{Me}_3$), 27.7 (OCH$\underline{Me}_2$), 26.6 (NC$_\beta$), 21.3 (NC$_\gamma$).

Preparation of [W(CEt)(OPr^i)$_3$]$_2$ (XVI-27).

3-hexyne (12 μ, 0.11 mmol) was added to a cold (-20°C) pentane solution (5 ml) containing [W(OPr^i)$_3$(HNMe$_2$)]$_2$ (80 mg, 0.11 mmol) and pyridine (18 μl, 0.22 mmol). After warming to room temperature and stirring for 0.5 h the volatiles were removed in vacuo. The residue was sublimed at 25-40°C (10^{-3} μ).

(XVI-27) ^{1}H NMR (C_6D_6, 270 MHz) δ 5.43 (h, 3, $^{3}J_H$ = 6.1 Hz, $OC\underline{H}Me_2$), 3.93 (q, 2, $^{3}J_H$ = 7.3 Hz, $CC\underline{H}_2CH_3$), 1.45 (d, 18, $^{3}J_H$ = 6.1 Hz, $OCH\underline{Me}_2$), 1.05 (t, 3, $^{3}J_H$ = 7.3 Hz, $CCH_2C\underline{H}_3$).

(XVI-27) $^{13}C\{^{1}H\}$ NMR (C_6D_6, 67.9 MHz) δ 270.3 ($\underline{C}Et$), 83.4 (br, $O\underline{C}HMe_2$), 39.1 ($^{2}J_{CW}$ = 46 Hz, $C\underline{C}H_2CH_3$), 27.1 ($OCH\underline{Me}_2$), 18.2 ($CCH_2\underline{C}H_3$).

Preparation of $[W(CCMe_3)(ONp)_3]_2$ (XVI-32).

This complex was prepared in a manner analogous to $[W(CCMe_3)(OPr^i)_3]_2$ starting with LiONp. The product can be sublimed at 50°C and 10^{-3} μ; however, extensive decomposition takes place.

(XVI-32) ^{1}H NMR (C_6D_6, 270 MHz) δ 5.12 (s, 6, $OC\underline{H}_2CMe_3$), 1.22 (s, 9, $CCMe_3$), 1.13 (s, 27, $OCH_2C\underline{Me}_3$).

(XVI-32) $^{13}C\{^{1}H\}$ NMR (d_8-tol, 67.9 MHz) δ 284.4 ($\underline{C}CMe_3$), 96.3 ($O\underline{C}H_2CMe_3$), 50.6 ($C\underline{C}Me_3$), 35.3 ($CC\underline{Me}_3$), 27.3 ($OCH_2C\underline{Me}_3$).

Preparation of $[W(CCMe_3)(OEt)_3]_x$ (XVI-66).

$W(CCMe_3)(dme)Cl_3$ (0.50 g, 1.1 mmol) was added as a solid (in portions) to a THF suspension (10 ml) of LiOEt (0.18 g, 3.3 mmol). After stirring for 10 min the volatiles were removed in vacuo. The residue was extracted with ether, filtered and the filtrate was evaporated to dryness (in vacuo) leaving a yellow solid (0.40 g, 96%). Yellow crystals can be obtained from pentane. See files for spectroscopic information.

Preparation of $[W(CCMe_3)(OMe)_3(HNMe_2)]_2$ (II-S-52).

A toluene solution (8 ml) of methanol (116 μl, 2.9 mmol) was cooled to -30° and a solution of $W(CCMe_3)(NMe_2)_3$ (0.37 g, 0.96 mmol) in toluene (2 ml) was added dropwise. After 2 h at room temperature the volatiles were removed in vacuo leaving yellow crystals which were recrystallized from ether at -30° (0.34 g, 90%).

(II-S-52) ^1H NMR (C_6D_6, 270 MHz) δ 5.26, 5.04 and 4.68 (s, 3 each, OMe), 2.94 (d, 3, $^3J_{H_AH}$ = 5.9 Hz, $HNMe_AMe_B$), 2.45 (d, 3, $^3J_{H_BH}$ = 5.9 Hz, $HNMe_AMe_B$), 1.15 (s, 9, $CCMe_3$).

(II-S-73) $^{13}C\{^1H\}$ NMR (C_6D_6, 67.9 MHz) δ 286.0 (s, $\underline{C}CMe_3$), 72.1 (q, J_{CH} = 139 Hz, OMe), 71.1 (q, J_{CH} = 139 Hz, OMe), 67.0 (q, J_{CH} = 140 Hz, OMe), 48.7 (qd, J_{CH} = 139 Hz, $^2J_{C_AH} \approx$ 6 Hz, $HNMe_AMe_B$), 48.5 (s, $C\underline{C}Me_3$), 42.7 (qd, $J_{CH} \approx$ 137 Hz, $^2J_{C_BH} \approx$ 6 Hz, $HNMe_AMe_B$), 35.7 (q, J_{CH} = 130 Hz, $CC\underline{Me}_3$).

MW (CH_2Cl_2, differential vapor pressure, 0°C): Calcd 782. Found 837 at 4.4×10^{-2} M. Anal. Calcd for $WC_{10}H_{25}NO_3$: C, 30.71; H, 6.44. Found: C, 30.99; H, 6.32.

Preparation of $[W(CCMe_3)(OPh)_3(HNMe_2)]_2$ (II-S-57).

Analogous to synthesis of $[W(CCMe_3)(OMe)_3(HNMe_2)]_2$; sublimed phenol used.

(II-S-57) ^1H NMR (C_6D_6, 270 MHz) δ 7.62 (d, 2, OPh), 7.30 to 6.84 (m, 13, OPh), 6.26 (m, 1, $\underline{H}NMe_2$), 2.92 (d, 3, $^3J_{H_AH}$ = 5.5 Hz, $HNMe_AMe_B$), 2.49 (d, 3, $^3J_{H_BH}$ = 5.5 Hz, $HNMe_AMe_B$), 0.61 (s, 9, $CCMe_3$).

(II-S-57) $^{13}C\{^1H\}$ NMR ($CDCl_3$, 7.9 MHz) δ 299.7 ($\underline{C}CMe_3$), 168.1, 167.3 and 164.4 (ipso OPh), 129.0, 128.6, 128.0, 122.6, 121.6, 121.1, 120.3, 119.7 and 119.1 (OPh), 50.0 ($HNMe_AMe_B$), 49.3 ($C\underline{C}Me_3$), 44.1 ($HNMe_AMe_B$), 33.6 ($CC\underline{Me}_3$).

Preparation of $[W(CCMe_3)(OMe)_3]_x$ (XV-69).

$W(CCMe_3)(NPr^i_2)_3$ (0.58 g, 1.0 mmol) was added to a cold (-30°C) toluene solution (10 ml) of methanol (127 μl, 3.1 mmol). The reaction was warmed to room temperature and stirred for 2 h. The volatiles were removed in vacuo and the residue was extracted with ether/toluene followed by filtration. The volatiles were removed in vacuo from the filtrate leaving a yellow powder. This was washed with pentane and dried in vacuo (0.16 g, 44%).

(XV-69) ^1H NMR (C_6D_6, 250 MHz) δ 5.91, 5.57, 5.36, 5.33, 4.79 and 4.27 (s, ~3 each, OMe), 1.24 and 1.23 (s, total area ~18, $CCMe_3$).

(XV-69) $^{13}C\{^1H\}$ NMR (C_6D_6, 67.9 MHz) δ 295.8 and 285.6 ($\underline{C}CMe_3$), 92.5, 74.9, 72.6, 71.8 and 61.5 (OMe), 48.4 ($C\underline{C}Me_3$), 35.9 and 35.2 ($CC\underline{Me}_3$).

Preparation of $W(CCMe_3)(OCEt_3)_3$ (XVI-29).

$W(CCMe_3)(dme)Cl_3$ (0.50 g, 1.1 mmol) was added to an ether solution (10 ml) of $LiOCEt_3$ (0.40 g, 3.3 mmol). After 2 h the volatiles were removed in vacuo and the residue was extracted with pentane. The extracts were filtered and the pentane was removed in vacuo. The remaining oily solid was dissolved in a minimum of ether, triturated with acetonitrile and cooled to -30°C. Colorless crystals were obtained (0.40 g, 60%).

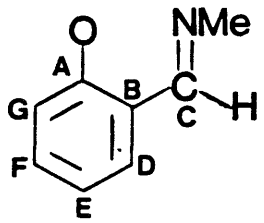
(XVI-29) ^1H NMR (C_6D_6, 270 MHz) δ 1.75 (q, 18, ^3J_H = 7.5 Hz, $OC(C\underline{H}_2CH_3)_3$), 1.32 (s, 9, $CCMe_3$), 0.89 (t, 27, ^3J_H = 7.5 Hz, $OC(CH_2C\underline{H}_3)_3$).

(XVI-29) $^{13}C\{^1H\}$ NMR (C_6D_6, 67.9 MHz) δ 274.5 (J_{CW} = 294 Hz, $\underline{C}CMe_3$), 84.6 (s, $O\underline{C}Et_3$), 50.0 (s, $C\underline{C}Me_3$), 34.1 (q, J_{CH} = 126 Hz, $CC\underline{Me}_3$), 31.9 (t, J_{CH} = 125 Hz, $OC(\underline{C}H_2CH_3)_3$), 8.56 (q, J_{CH} = 125 Hz, $OC(CH_2\underline{C}H_3)_3$).

Preparation of $W(CCMe_3)(OCMe_3)_2(2\text{-}(O)C_6H_4CHNMe)$ (III-S-5).

A toluene solution (2 ml) of the methylimine (0.15 g, 1.1 mmol) was added dropwise to a toluene soluton (10 ml) of $W(CCMe_3)(OCMe_3)_3$ (0.50 g, 1.1 mmol) that had been cooled to -30°C. The reaction was warmed to room temperature and stirred for 4 h. Removing the volatiles in vacuo left a yellow solid that was extracted with toluene. The extracts were treated with DARCO, filtered and concentrated in vacuo. Cooling to -30°C gave bright yellow crystals that were isolated by filtration and dried in vacuo; 3 crops (0.48 g, 85%).

The following labelling scheme is used for reporting the ^{13}C NMR data:



(II-S-74) ^1H NMR (C_6D_6, 270 MHz) δ 7.61 (s, 1, MeN=CHPh), 7.21, 6.89 and 6.65 (m, 4, Ph), 3.31 (d, 3, ^4J_H = 1.5 Hz, MeN=CHPh), 1.66 and 1.52 (br, s, 18, $OCMe_3$), 0.87 (s, 9, $CCMe_3$).

(III-S-5) ^1H NMR ($CDCl_3$, 250 MHz, 23°C) δ 8.30 (s, 1, MeN=CHPh), 7.36, 7.28, 6.96 and 6.74 (m, 4, Ph), 3.72 (d, 3, ^4J_H = 1.1 Hz, MeN=CHPh), 1.47 (s, 18, $OCMe_3$), 0.72 (s, 9, $CCMe_3$). (2°C) δ 8.30 (s, 1, MeN=CHPh), 7.36, 7.28, 6.96 and 6.74 (m, 4, Ph), 3.71 (s, 3, MeN=CHPh), 1.47 (s, 9, $OCMe_3$), 1.45 (s, 9, $OCMe_3$), 0.68 (s, 9, $CCMe_3$).

(III-S-5) $^{13}C\{^1H\}$ NMR ($CDCl_3$, 67.9 MHz) δ 296.4 (s, $CCMe_3$), 168.7 (s, C_B), 165.4 (d, J_{CH} = 163.0 Hz, C_C), 133.9, 131.3, 119.1 and 117.5 (d, J_{CH} ≈ 155 Hz, $C_{D,E,F,G}$, not assignable), 123.0 (s, C_A), 77.7 (s, $OCMe_3$), 54.5

(q, J_{CH} ≈ 138 Hz, NMe), 49.7 (s, $C\underline{C}Me_3$), 32.6 (q, J_{CH} ≈ 125 Hz, $OC\underline{Me}_3$), 32.3 (q, J_{CH} ≈ 125 Hz, $CC\underline{Me}_3$).

Anal. Calcd for $WC_{21}H_{35}NO_3$: C, 47.29; H, 6.61. Found: C, 46.96; H, 6.68.

Preparation of $[W(CCMe_3)(NPr^i_2)Cl_3][NEt_4]$ (I-S-49).

Diisopropylamine (2.7 ml, 19 mmol) was added to a CH_2Cl_2 solution (30 ml) of $[W(CCMe_3)Cl_4][NEt_4]$ (1.0 g, 1.9 mmol). After 18 h the volatiles were removed in vacuo and the residue was extracted with toluene. The extracts were filtered through Celite and the filtrate was concentrated in vacuo, followed by cooling to -30°C. Yellow crystals were isolated by filtration, washed with ether and dried in vacuo (3 crops, 0.82 g, 73%).

(I-S-49) $^{13}C\{^1H\}$ NMR ($CDCl_3$, 67.9 MHz) δ 295.5 (J_{CW} = 250 Hz, $\underline{C}CMe_3$), 53.6 and 52.8 ($N(\underline{C}HMe_2)_2$), 52.3 ($N(\underline{C}H_2CH_3)_4$), 49.3 ($C\underline{C}Me_3$), 31.8 and 28.5 ($CC\underline{Me}_3$ and $N(CH\underline{Me}_2)_2$, not assignable), 15.6 ($N(CH\underline{Me}_2)_2$), 7.4 ($N(CH_2\underline{C}H_3)_4$).

Preparation of $[W(CCMe_3)(NEt_2)Cl_3][NEt_4]$

(a) From $[W(CCMe_3)Cl_4][NEt_4]$ and diethylamine (I-S-31).

Analogous to $[W(CCMe_3)(NPr^i_2)Cl_3][NEt_4]$, starting with diethylamine.

(b) From $[W(CCMe_3)Cl_4][NEt_4]$ and Me_3SiNEt_2 (II-S-72).

Me_3SiNEt_2 (365 μl, 1.9 mmol) was added to a CH_2Cl_2 solution (20 ml) of $[W(CCMe_3)Cl_4][NEt_4]$ (1.0 g, 1.9 mmol). After 12 h the volatiles were removed in vacuo and the yellow solid was extracted with toluene. The extracts were filtered and concentrated in vacuo. Trituration with ether followed by cooling to -30°C gave 1.03 g (96%) of bright yellow crystals.

(II-S-72) ^{1}H NMR (d_8-tol, 270 MHz) δ 4.80 (q, 2, $^{3}J_H$ = 7.3 Hz, $N(C\underline{H}_2CH_3)_2$), 3.69 (q, 2, $^{3}J_H$ = 7.3 Hz, $N(C\underline{H}_2CH_3)_2$), 2.95 (br q, 8, $N(C\underline{H}_2CH_3)_4$), 1.54 (t, 3, $^{3}J_H$ = 7.3 Hz, $N(CH_2C\underline{H}_3)_2$), 1.45 (s, 9, $CCMe_3$), 1.43 (t, 3, $^{3}J_H$ = 7.3 Hz, $N(CH_2C\underline{H}_3)_2$), 0.98 (br t, 12, $N(CH_2C\underline{H}_3)_4$).

(II-S-72) $^{13}C\{^{1}H\}$ NMR (d_8-tol, 67.9 MHz) δ 297.1 (J_{CW} = 252.8, $\underline{C}CMe_3$), 66.9 ($N(\underline{C}H_2CH_3)_2$), 53.1 ($N(\underline{C}H_2CH_3)_4$), 50.5 ($C\underline{C}Me_3$), 49.5 ($N(\underline{C}H_2CH_3)_2$), 32.3 ($CC\underline{Me}_3$), 16.1 and 10.5 ($N(CH_2\underline{C}H_3)_2$), 8.2 ($N(CH_2\underline{C}H_3)_4$).

Preparation of $W(CCMe_3)(NMe_2)(PEt_3)Cl_2$ (II-S-47).

Me_3SiNMe_2 (150 μl, 0.96 mmol) was added to a CH_2Cl_2 solution (10 ml) of $W(CCMe_3)(PEt_3)Cl_3$ (0.25 g, 0.48 mmol). After 1 h the volatiles were removed in vacuo. The residue was dissolved in ether/CH_2Cl_2 (5/2 ml), filtered and concentrated in vacuo. Cooling to -30°C gave bright yellow needles (0.18 g, 71%).

(II-S-47) ^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.19 (d, 3, $^{4}J_{HP}$ = 2.9 Hz, $NMe_A\underline{Me}_B$), 5.15 (d, 3, $^{4}J_{HP}$ = 2.6 Hz, $NMe_A\underline{Me}_B$), 3.96 (m, 6, $P(C\underline{H}_2CH_3)_3$), 3.17 (s, 9, $CCMe_3$), 3.13 (m, 9, $P(CH_2C\underline{H}_3)_3$).

(II-S-47) $^{13}C\{^{1}H\}$ NMR (C_6D_6, 67.9 MHz) δ 313.3 ($^{2}J_{CP}$ = 15 Hz, $\underline{C}CMe_3$), 64.9 and 45.6 (NMe_2), 51.9 ($C\underline{C}Me_3$), 31.9 ($CC\underline{Me}_3$), 18.6 (J_{CP} = 29 Hz, $P(\underline{C}H_2CH_3)_3$), 8.6 ($P(CH_2\underline{C}H_3)_3$).

Preparation of $W(CCMe_3)(NPr^i_2)(OCMe_3)_2$ (II-S-67).

$[W(CCMe_3)(NPr^i_2)Cl_3][NEt_4]$ (0.30 g, 0.51 mmol) was dissolved in THF (10 ml) and the solution was cooled to -30°C. $LiOCMe_3$ (81 g, 1.0 mmol) was added and the reaction was warmed to room temperature. After stirring for 4 h the reaction was filtered and the volatiles were removed in vacuo.

The residue was dissolved in a minimum of ether, triturated with acetonitrile and cooled to -30°C. 80 mg of white crystals were isolated by filtration, washed with CH_3CN and dried *in vacuo*. The volatiles were removed from the mother liquors and the residue was sublimed (~40°C, 10^{-3} μ) to give another 70 mg of product (59%).

(II-S-67) ^1H NMR (C_6D_6, 270 MHz) δ 3.62 (h, 2, ^3J_H = 6.6 Hz, $N(C\underline{H}Me_2)_2$), 1.46 (s, 18, $OCMe_3$), 1.45 (s, 9, $CCMe_3$), 1.41 and 1.00 (br, 6 each, $N(CH\underline{Me_2})_2$).

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APPENDIX I.

Organization of Notebooks and Spectra

The experimental data for this research was contained in sixteen notebooks. The first ten were labelled I-X. The next three are labelled I-S, II-S and III-S. The S refers to surface chemistry. The last three notebooks are labelled XIV-XVI. NMR and IR spectra are listed by notebook and page number. For example, XV-1 refers to a spectrum arising from an experiment recorded on page 1 of notebook 15.

APPENDIX II.

Synthesis of Some Miscellaneous Tungsten(VI) Neopentylidene Complexes.

RESULTS AND DISCUSSION

In Chapter 3 I briefly mentioned some work we did in the area of attaching well-characterized alkyne metathesis catalysts to surfaces. Naturally, we were also interested in the possibility of "anchoring" metal alkylidene complexes to surfaces. One approach we took was to prepare an alkylidene complex that contained a silicon coupling functionality[63] (e.g., $-SiCl_3$, $-Si(OR)_3$, or $-Si(NR_2)_3$). This was accomplished (eqs 1 and 2) by

$$[W(CCMe_3)Cl_4][NEt_4] + 2\ PEt_3 + H_2N(CH_2)_3R \xrightarrow[-NEt_3HCl]{NEt_3} W(CCMe_3)(HN(CH_2)_3R)(PEt_3)_2Cl_2 + NEt_4Cl \quad (1)$$

$(R = H,\ Si(OEt)_3)$

$$W(CCMe_3)(HN(CH_2)_3R)(PEt_3)_2Cl_2 \xrightarrow{\Delta} W(CHCMe_3)(N(CH_2)_3R)(PEt_3)_2Cl_2 \quad (2)$$

employing a technique used by Rocklage and Schrock for preparing imido alkylidene complexes from tungsten alkylidynes and amines.[19] Since no alkylimido complexes had been prepared by this alkylidyne/amine route, we initially modeled this reaction with propylamine (eqs 1 and 2). Both reactions proceed in high yield and the alkylidene product exhibits no unusual spectroscopic or chemical behavior compared with their well-characterized phenylimido alkylidene analogues (Chapter 1).

Recently Osborn and co-workers reported on the preparation and olefin metathesis activity of some bis-alkoxy neopentylidene complexes (e.g., $W(CHCMe_3)(ONp)_2Cl_2$).[64] The route to such complexes is rather circuitous and we felt that we might be able to prepare similar species more conveniently from tungsten neopentylidyne complexes. The first reaction we tried is shown in eq 3. The new neopentylidene species obtained from this

$$W(CCMe_3)(dme)Cl_3 + 2\ Me_3COH \xrightarrow[-NEt_3HCl]{NEt_3} W(CHCMe_3)(OCMe_3)_2Cl_2 \qquad (3)$$

reaction is formed in essentially quantitative yield. More recently, Freudenberger has prepared a whole series of similar alkylidene complexes by reacting $W(CR)(OCMe_3)_3$ with a variety of acids.[11]

In Chapter 2 I reported that all of our attempts to prepare a pinacolato alkylidyne complex of the type $W(CR)(OCMe_2CMe_2O)(X)$ have failed. One of the simplest, yet most promising reactions involved reacting pinacol with $W(CCMe_3)(OCMe_3)_3$. However, instead of forming the desired alkylidyne complex, a quantitative yield of the neopentylidene complex, $W(CHCMe_3)$-$(OCMe_2CMe_2O)(OCMe_3)_2$ was obtained (eq 16, Chapter 2). For similar reasons we also reacted $W(CCMe_3)(NPr^i_2)_3$ with pinacol (eq 4). NMR data on the

$$W(CCMe_3)(NPr^i_2)_3 + \text{pinacol} \longrightarrow W(O)(CHCMe_3)(OCMe_2CMe_2O)(HNPr^i_2) \qquad (4)$$

yellow crystalline product obtained from this reaction indicated that we had prepared another neopentylidene complex. The oxo neopentylidene formulation (eq 4) is proposed for two reasons. First, there is only one diisopropylamine group per pinacol ligand, ruling out $W(CHCMe_3)(OCMe_2CMe_2O)(NPr^i_2)_2$, the analog of the product obtained from $W(CCMe_3)(OCMe_3)_3$ and pinacol.

Second, the mother liquors from which the yellow crystals were obtained contained predominantly starting material by NMR, suggesting that a second equivalent of pinacol was used to make this complex. This extra pinacol ligand might give rise to the proposed oxo group.

EXPERIMENTAL

$W(CCMe_3)(NPr^i_2)_3$[2] was prepared by a published method. $(EtO)_3Si-(CH_2)_3NH_2$ (Petrarch) was used as received. Propylamine was distilled from barium oxide.

Preparation of $W(NHCH_2CH_2CH_3)(CCMe_3)(PEt_3)_2Cl_2$ (VIII-57).

A CH_2Cl_2 solution (50 ml) containing $[W(CCMe_3)Cl_4][NEt_4]$ (5.0 g, 9.5 mmol) and PEt_3 (2.25 g, 19.0 mmol) was cooled to -30°C and NEt_3 (0.97 g, 9.5 mmol) was added. n-Propylamine in CH_2Cl_2 (10 ml) was added dropwise. After completing the addition the reaction was warmed to room temperature and stirred for 4 h. The volatiles were removed in vacuo and the residue was extracted with ether, filtered and concentrated in vacuo. Cooling to -30°C gave yellow/orange crystals (yield is ~75%).

(VIII-54) ^1H NMR (C_6D_6, 250 MHz) δ 12.2 (br s, 1, $NH(CH_2CH_2CH_3)$, 4.13 (m, 2, $NH(CH_2CH_2CH_3)$), 1.75 (m, 12, $P(CH_2CH_3)_3$), 1.36 (m, 2, $NH(CH_2CH_2CH_3)$), 1.17 (s, 9, $CCMe_3$), 1.02 (m, 18, $P(CH_2CH_3)_3$), 0.77 (t, 3, $NH(CH_2CH_2CH_3)$).

(VIII-57) $^{13}C\{^1H\}$ NMR (C_6D_6, 22.5 MHz) δ 296.5 ($^2J_{CP}$ = 11 Hz, $CCMe_3$), 72.0 ($NH(CH_2CH_2CH_3)$), 49.2 ($CCMe_3$), 32.7 ($CCMe_3$), 26.5 ($NH(CH_2CH_2CH_3)$, 17.6 (J_{CP} = 13 Hz, $P(CH_2CH_3)_3$), 11.7 ($NH(CH_2CH_2CH_3)$), 8.2 ($P(CH_2CH_3)_3$).

(VIII-57) $^{31}P\{^1H\}$ NMR (C_6D_6) 16.6 (s, J_{PW} = 288 Hz).

Preparation of $W(N(CH_2CH_2CH_3))(CHCMe_3)(PEt_3)_2Cl_2$ (VIII-65).

A toluene solution of $W(NH(CH_2CH_2CH_3))(CCMe_3)(PEt_3)_2Cl_2$ (1.2 g, 1.9 mmol) was heated at 65°C for 10 h. The volatiles were removed in vacuo and the residue was extracted with ether, filtered, and the ether was

removed in vacuo leaving a waxy solid. ^{1}H and ^{31}P NMR of this material shows that the reaction goes cleanly to completion.

(VIII-54) ^{1}H NMR (C_6D_6, 250 MHz) δ 12.0 (t, 1, $^{3}J_{HP} \approx 4$ Hz, $CHCMe_3$), 3.66 (m, 2, $N(CH_2CH_2CH_3)$), 2.06 to 1.81 (m, 14 total, $P(CH_2CH_3)_3$ and $N(CH_2CH_2CH_3)$), 1.18 (s, 9, $CHCMe_3$), 0.99 (m, 18, $P(CH_2CH_3)_3$), 0.77 (t, 3, $N(CH_2CH_2CH_3)$).

(VIII-54) $^{31}P\{^{1}H\}$ NMR (C_6D_6) δ 15.2 (s, J_{PW} = 278.3 Hz).

Preparation of $W(NH(CH_2)_3Si(OEt)_3)(CCMe_3)(PEt_3)_2Cl_2$ and $W(N(CH_2)_3Si(OEt)_3)(CHCMe_3)(PEt_3)_2Cl_2$ (IX-46).

Analogous to procedures for propylamide and propylimide derivatives.

$W(NH(CH_2)_3Si(OEt)_3)(CCMe_3)(PEt_3)_2Cl_2$: (IX-6) ^{1}H NMR (C_6D_6, 250 MHz) δ 11.8 (br s, 1, $NH(CH_2)_3Si(OEt)_3$), 4.20 (m, 2, $NH(CH_2CH_2CH_2)$), 3.75 (q, 6, $Si(OCH_2CH_3)_3$), 1.96 (m, 12, $P(CH_2CH_3)_3$), 1.67 (m, 2, $NH(CH_2CH_2CH_3)$), 1.15 (s, 9, $CCMe_3$), 1.13 (t, 9, $Si(OCH_2CH_3)_3$), 1.01 (m, 18, $P(CH_2CH_3)_3$), 0.59 (m, 3, $NH(CH_2CH_2CH_2)$).

$W(N(CH_2)_3Si(OEt)_3)(CHCMe_3)(PEt_3)_2Cl_2$: (IX-12) ^{1}H NMR (C_6D_6, 250 MHz) δ 12.0 (br, 1, $CHCMe_3$), 3.88 to 3.78 (m, 8 total, $N(CH_2CH_2CH_2)$ and $Si(OCH_2CH_3)_3$), ~2.19 (m, 2, $N(CH_2CH_2CH_2)$), 1.99 (m, 12, $P(CH_2CH_3)_3$), 1.21 (s with m underneath, 18 total, $CHCMe_3$ and $Si(OCH_2CH_3)_3$), 1.02 (m, 18, $P(CH_2CH_3)_3$), 0.70 (m, 3, $N(CH_2CH_2CH_2)$).

Preparation of $W(CHCMe_3)(OCMe_3)_2Cl_2$ (XIV-58).

A toluene solution (10 ml) of $W(CCMe_3)(dme)Cl_3$ (0.50 g, 1.1 mmol) was cooled to -30°C and NEt_3 (320 μl, 2.2 mmol) was added. t-butanol (0.16 g, 2.2 mmol) was added and the solution was allowed to warm to room temperature. After 2 h the volatiles were removed in vacuo and the residue was

extracted with pentane. The extracts were filtered and the pentane was removed in vacuo leaving yellow crystals that were pure by NMR.

(XIV-58) ^{1}H NMR (C_6D_6, 250 MHz) δ 10.62 (s, 1, $^{2}J_{HW}$ = 12.0 Hz, $CHCMe_3$), 1.44 and 1.40 (s, 9 each, $OCMe_3$), 1.13 (s, 9, $CHCMe_3$).

(XIV-58) $^{13}C\{^{1}H\}$ NMR (C_6D_6, 67.9 MHz) δ 289.9 (J_{CH} = 138 Hz from gated $\{^{1}H\}$ NMR spectrum, J_{CW} = 156.9 Hz, $CHCMe_3$), 92.0 and 90.4 ($OCMe_3$), 42.5 ($CHCMe_3$), 32.7, 29.8 and 29.7 ($OCMe_3$ and $CHCMe_3$).

Preparation of $W(O)(CHCMe_3)(OCMe_2CMe_2O)(HNPr^{i}_2)$ (XV-20).

Pinacol (43 mg, 0.36 mmol) was added to a cold (-30°C) pentane solution (8 ml) of $W(CCMe_3)(NPr^{i}_2)_3$ (0.20 g, 0.36 mmol). After warming to room temperature and stirring for 1 h the volatiles were removed in vacuo. The residue was extracted with pentane, filtered and concentrated in vacuo. Cooling to -30°C gave yellow/orange crystals.

(XV-20) ^{1}H NMR (C_6D_6, 250 MHz) δ 5.24 (s, 1, $^{2}J_{HW}$ = 13.2 Hz, $CHCMe_3$), 4.00 (br, 2, $HN(CHMe_2)_2$), 1.34 and 1.30 (s, 6 each, $OCMe_2CMe_2O$), 1.28 (s, 9, $CHCMe_3$), 1.20 and 1.08 (d, 6 each, J_H = 6.4 Hz, $HN(CHMe_2)_2$).

(XV-20) $^{13}C\{^{1}H\}$ NMR (C_6D_6, 67.9 MHz) δ 258.4 (d, J_{CH} = 95 Hz, J_{CW} = 162.8 Hz, $CHCMe_3$), 93.1 (s, $OCMe_2CMe_2O$), 53.9 (d, J_{CH} = 131 Hz, $HN(CHMe_2)_2$), 46.0 (s, $CHCMe_3$), 32.2, 28.5 and 26.6 (q, J_{CH} = 131, 128 and 128 Hz, $CHCMe_3$ and $OCMe_2CMe_2O$, not assignable), 24.5 and 22.3 (br, $HN(CHMe_2)_2$).

APPENDIX III.

Reactions of Tungsten(VI) Alkylidyne and Metallacyclobutadiene Complexes with Nitriles. Reaction of $[W(N)(OCMe_3)_3]_x$ with Alkynes.

RESULTS AND DISCUSSION

In Chapter 2 I reported on a variety of reactions that occur between tungsten(VI) alkylidyne complexes and alkynes. Naturally, we also became interested in what types of reactions take place between alkylidynes and nitriles. However, for a while such studies were "put on the shelf" because it was discovered early on that our primary alkyne metathesis catalyst, $W(CCMe_3)(OCMe_3)_3$, did not react with nitriles (at least under non-forcing conditions).[35] In fact, the best medium for crystallizing this species is ether/acetonitrile. Based on the historic concept that N^{3-} is the strongest π-donor ligand known,[65] this result was surprising. However, we later found that steric factors play an important role in this reaction. That is, the smaller, unbranched alkylidyne complex, $W(CEt)(OCMe_3)_3$, reacts with excess acetonitrile to give $W(N)(OCMe_3)_3$ and 2-pentyne (eq 1). This

$$W(CEt)(OCMe_3)_3 \xrightarrow[-2\text{-pentyne}]{CH_3CN(xs)} W(N)(OCMe_3)_3 \qquad (1)$$

new tungsten(VI) nitrido complex was later prepared by reacting nitriles with $W_2(OCMe_3)_6$.[49] Chisholm and co-workers have recently reported on the structure of this molecule.[55] It is a linear polymer consisting of alternating short and long W-N distances which correspond to localized triple and weak dative bonds, respectively.

We have also found that the reaction between an alkylidyne and a nitrile may be facilitated by employing smaller alkoxide ligands. For example, $[W(CCMe_3)(ONp)_3]_2$ reacts with acetonitrile to give $[W(N)(ONp)_3]_2$. The dimeric formulation is based on NMR data and the fact that this species is pentane-soluble ($[W(N)(OCMe_3)_3]_x$ is virtually insoluble in all common organic solvents). A reasonable structure for this complex involves bridging alkoxide ligands analogous to that found in $[W(CCMe_3)(OPr^i)_3]_2$ (Figure 1, Chapter 3). It appears that alkoxide bridges are favored over W≡N-W bridges and only in cases where rather bulky alkoxides are used (e.g., $OCMe_3$) does this latter mode of bonding take place.

Although tungsten(VI) nitrides can be prepared from alkylidynes and nitriles, the reaction is much slower than any stoichiometric alkyne metathesis reaction involving $W(CR)(OCMe_3)_3$. A logical explanation for this decreased reactivity involves the differences in metal-ligand bonding between alkynes and nitriles. In metal-alkyne complexes the alkyne is bound "side-on" since the bonding electrons are localized in the carbon-carbon triple bond. This in effect activates the alkyne triple bond, a condition which may be necessary for metallacyclobutadiene formation. On the other hand, nitriles typically bond to metals "end-on" via the lone pair on nitrogen.[66] Only a handful of documented examples of "side-on" bound nitriles are known.[66]

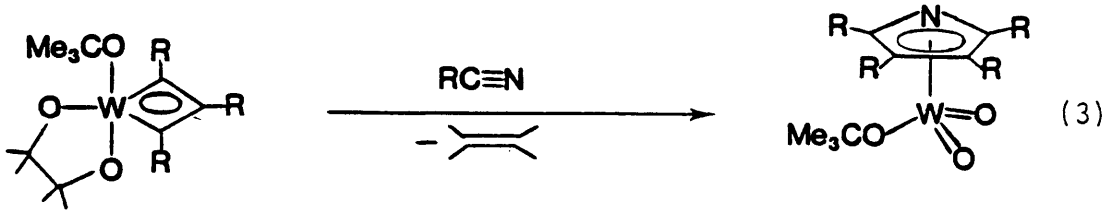
A dichloromethane solution of pure $W(N)(OCMe_3)_3$ (prepared from $WNCl_3$ and 3 $LiOCMe_3$) slowly (~12 h) metathesizes 3-heptyne to equilibrium. This reaction is of course much slower than when one starts with $W(CR)(OCMe_3)_3$. However, it does demonstrate that small concentrations of alkylidynes can be generated from metal nitrides and alkynes. At this time we do not know

whether this transformation is inherently slow for thermodynamic reasons (i.e., when W≡N is greatly favored over W≡CR) or for kinetic reasons associated with the inaccessibility of the tungsten-nitride group in polymeric $[W(N)(OCMe_3)_3]_x$ (vide supra). Along these lines, it would be interesting to prepare some tris-alkoxy nitrido complexes containing bulkier alkoxide ligands (e.g., $OCEt_3$) to see if monomeric nitrido species could be isolated.

Although the reaction between a tungsten alkylidyne and a nitrile is a unique method for forming carbon-carbon triple bonds, it certainly could not be considered practical for any large scale synthesis of alkynes. However, it might prove useful in preparing small quantities of selectively labelled ^{13}C-containing acetylenes (eq 2; remember that a large variety of R groups in $W(CR)(OCMe_3)_3$ can be prepared from alkyne plus $W_2(OCMe_3)_6$[49]).

$$R^{13}C{\equiv}N + W(CR')(OCMe_3)_3 \longrightarrow R^{13}C{\equiv}CR' + W(N)(OCMe_3)_3 \qquad (2)$$

Many of the tungstenacyclobutadiene complexes discussed in Chapter 2 react with alkynes to give cyclopentadienyl complexes. We felt it would be interesting to see if a similar reaction involving a nitrile would lead to products containing pyrolate rings (eq 3). This reaction did not work with $W(CCMe_3C_2Me_2)(OCMe_2CMe_2O)(OCMe_3)$ and excess acetonitrile. However, varying the reaction conditions (e.g., heating or photolysis) might lead to the desired products.



(3)

EXPERIMENTAL

Preparation of $[W(N)(OCMe_3)_3]_x$ from $W(CEt)(OCMe_3)_3$ and CH_3CN

A general method involves adding excess acetonitrile to a pentane solution of $W(CEt)(OCMe_3)_3$. After standing overnight a white powder is deposited. This is collected by filtration, washed with pentane and dried *in vacuo*. The reaction can probably be done with one equivalent of nitrile by heating a toluene solution of the alkylidyne and nitrile. See reference 67 for spectroscopic data.

Preparation of $[W(N)(ONp)_3]_2$ (XVI-29).

Crude (see experimental in Chapter 2) $[W(CCMe_3)(ONp)_3]_2$ was dissolved in a minimum of ether and acetonitrile was added. The solution began to darken immediately and was cooled to -30°C. After standing overnight some white needles were deposited. These were isolated on a cold frit and washed with cold pentane, followed by drying *in vacuo*.

(XVI-29) ^1H NMR (C_6D_6, 250 MHz) δ 5.13 and 4.84 (d, 2 each, ^2J_H = 10.4 Hz, OCH_2CMe_3 terminal), 4.49 (s, 2, OCH_2CMe_3 bridge), 1.18 (s, 18, OCH_2CMe_3 terminal), 1.03 (s, 9, OCH_2CMe_3 bridge).

(XVI-29) IR (Nujol mull, cm^{-1}) ~1060 ($\nu_{W\equiv N}$).

Metathesis of 3-heptyne with $[W(N)(OCMe_3)_3]_x$ (XIV-48).

A CH_2Cl_2 solution (2 ml, passed through Al_2O_3 immediately prior to use) of $[W(N)(OCMe_3)_3]_x$ (30.5 mg, 0.073 mmol, prepared from reaction of $WNCl_3$ and 3 $LiOCMe_3$) was treated with 3-heptyne (186 µl, 1.46 mmol, also passed through Al_2O_3 immediately prior to use). The reaction was sampled after 1 h 50 min and some metathesis had occurred (by GC analyses, the sample was

quenched with H_2O prior to analysis). After 12 h 50 min equilibrium had been reached. At this point another 20 equiv of 3-heptyne was added. After 1.5 h this had been metathesized to equilibrium, indicating that some active catalyst was still present.

ACKNOWLEDGEMENTS

I thank Dick Schrock for allowing me to pursue my "instincts". Certainly they were not always correct, but the experience has been a rewarding one. Thanks also for supplying some well-timed encouragement and support (moral and financial) over the past few years. This man's exciting attitude about chemistry has also laid the foundation for a very stimulating work environment. Thanks, Dick.

I am indebted to Scott Rocklage for showing me the "ins and outs" of the Schrock group and for simply being there. He always had (and still has) the time to listen to my ramblings and throw in many good words of advice. To both Scott and Julie Rocklage, thanks for your invaluable friendship and for providing a warm family atmosphere on many occasions.

Thanks to Gary Smith and José Sancho, two of my lab mates in the "Main" lab, for all their help and patience in my first few months at MIT, and for providing a very enjoyable atmosphere to work in. Lock McCullough, the last of the "Main Labbers" deserves special recognition for proofing my thesis and putting up with me for the past 2.5 years. Thanks, Lock, for always being there to talk about chemistry or anything else. To Scott Edwards and Steve Holmes, thanks for your comradery over the past few years and for promoting and maintaining a competition-free environment. Thanks to Robert Murray and Klaus Theopold, my most recent lab mates, for putting up with my rather variable behavior as of late. Thanks also goes to the rest of the Schrock group, past and present, who have provided many hours of stimulating discussions, and good times at the Muddy and elsewhere.

I am truly grateful to Professor Herb Kaesz, Art Cabral and Gordon Jarvinen for introducing me to organometallic chemistry and encouraging me to pursue such studies at the graduate level.

Thanks to Ginny Siggia for doing an excellent job of typing this thesis and putting up with my pickiness. Furthermore, Ginny deserves a lot of credit for always dealing with the MIT bureaucratic matters that normally drive a graduate student right up the wall (or at least outside and away from the lab).

I thank the Dow Chemical Company for providing me with a fellowship for the past 2.5 years.

My parents deserve a special type of acknowledgement, for without their support, encouragement, and love over the years I would not be writing this thesis. Thanks, mom, for all the help and encouragement when it came to those "tough" homework assignments, all the way from Brentwood Elementary to Uni High. Thanks, dad, for teaching me how to use my hands and my mind to build anything from a nightstand to a house. I know that it is this wisdom above all others that has allowed me to pursue a career in synthetic chemistry. Synthesizing a molecule is no different than building a piece of furniture. First, you have to choose the appropriate starting materials, and then let your existing knowledge and creativity take its course.

My final acknowlegement was saved for the end because it deserves a special place in this thesis. This is to thank Julie Leary, a woman who has provided me with much happiness and love. Her smile and thoughtful words have always succeeded in chasing away the blues. The wisdom and support she has offerred has provided me with the impetus to expand my horizons and realize that nothing is impossible if you want it badly enough. Thanks, Julie.