SYNTHESIS AND REACTIVITY OF EARLY TRANSITION METAL COMPLEXES CONTAINING MULTIPLE METAL TO CARBON, NITROGEN, OR OXYGEN BONDS

by

SCOTT M. ROCKLAGE

B.S., University of California, Berkeley

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Signature of Author ______________________________
Department of Chemistry, December 7, 1981

Certified by ______________________________
Thesis Supervisor

Accepted by ______________________________
Chairman, Department Committee

This doctoral thesis has been examined by a Committee of the Department of Chemistry as follows:

Professor Dietmar Seyferth ____________________ Chairman

Professor Richard R. Schrock ____________________ Thesis Supervisor

Professor Alan Davison ____________________

Dedicated to my wife, Julie; my son, Matthew;
and to the memory of my father, Gerald.

Man's youth is a wonderful thing:
It is so full of anguish and of magic
and he never comes to know it as it is, until
it has gone from him forever.
- Thomas Wolfe

If the man of science of our day could find the time and courage to think honestly and critically over his situation and the tasks before him and if he would act accordingly, the possibilities for a sensible and satisfactory solution to the present dangerous international situation would be considerably improved.

- Albert Einstein (1952)

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Submitted to the Department of Chemistry at the Massachusetts Institute of Technology, February, 1982, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

Chapter 1

Complexes of the type $M(CHR)L_2X_3$ (M = Nb, Ta; R = CMe_3, Ph; X = Cl, Br; L = tertiary phosphine) react with terminal olefins to give the organic products of β-hydride rearrangement of the four possible intermediate metallacyclobutane complexes. When L = THF the complex reacts with ethylene to give ~10% metathesis product, with 1-butene to give ~75% metathesis products, and with cis-2-pentene to give exclusively metathesis products. Complexes of the type $M(CHCMe_3)(OCMe_3)_{3-x}Cl_x(PMe_3)_x$ ($x = 0,1,2$) react with terminal and internal olefins to give rearrangement and metathesis products. When $x = 1$ only metathesis products are observed. The major chain termination steps in metathesis with these complexes are decomposition of intermediate alkylidene ligands and rearrangement of intermediate metallacyclobutane complexes.

Chapter 2

$M(CHCMe_3)(THF)_2X_3$ reacts with RN=CHPh (M = Ta; Nb; X = Cl, Br; R = Ph, CMe_3, Me) to give organoimido complexes, $M(NR)(THF)_2Cl_3$, and $Me_3CCH{=}CHPh$ quantitatively. The THF ligands can be displaced by phosphines to give complexes such as cis,mer-$Ta(NR)(PMe_3)_2Cl_3$. The $Ta(NR)L_2Cl_3$ complexes (L = PMe_3, 1/2 dmpe) can be reduced in the presence of L to give the Ta(III) complexes, $Ta(NR)L_4Cl$, in high yield, and these, in turn, react with ethylene or styrene to give olefin complexes, $Ta(NPh)(olefin)L_3Cl$. Several ^{15}N

labelled phenyl-imido compounds have been prepared and examined by ^{15}N NMR and IR (δ ^{15}NR = 300-350 ppm vs. NH_3, ν_{TaNR} ~ 1350 cm^{-1}). The products of the reaction between $M(CHCMe_3)(THF)_2Cl_3$ and PhCH=N-N=CHPh are $[MCl_3(THF)_2]_2(\mu\text{-}N_2)$ and two equivalents of Me_3CCH=CHPh. Phosphine complexes such as $[TaCl_3(PEt_3)_2]_2(\mu\text{-}N_2)$ can be prepared straightforwardly from the THF complexes. The organoimido complexes react with benzaldehyde to give RN=CHPh in high yield. The $\mu\text{-}N_2$ complexes react with acetone to give Me_2C=N-N=CMe_2 and with HCl to give $N_2H_4\cdot 2HCl$ in high yield.

Chapter 3

The reactions of $TaCl_3(PMe_3)_3$ Ta(III), prepared by the sodium amalgam reduction of $TaCl_5$, in the presence of excess PMe_3, are described. $TaCl_3(PMe_3)_3$ reacts with H_2 to give dimeric $[TaCl_3(PMe_3)H]_2$ and with Me_3SiN_3 to give $Ta(NSiMe_3)(PMe_3)_2Cl_3$ (Ta(V)). An imido-alkylidene complex is obtained from $Ta(CHCMe_3)(PMe_3)_4Cl$ and Me_3SiN_3. $[Ta(R)(PMe_3)_xCl]_2N_2$ (R = $CHCMe_3$, x = 2; R = C_2H_4, x = 3), dimeric μ-dinitrogen complexes, react with HCl to yield $N_2H_4\cdot 2HCl$ and with acetone to yield dimethylketazine. ^{15}N-labelled dinitrogen complexes establish an IR absorbance at ca. 850 cm^{-1} to be associated with the Ta_2N_2 bridge and display singlets at ca. 400 ppm in the ^{15}N NMR spectra.

Chapter 4

The reaction chemistry of $[W(CCMe_3)Cl_4]NEt_4$, a novel anionic tungsten alkylidyne complex, is described. The anion reacts with PEt_3 to yield $[W(CCMe_3)Cl_4(PEt_3)]NEt_4$ and with $ZnCl_2(PEt_3)$ to give neutral $W(CCMe_3)Cl_3(PEt_3)$. $[W(CCMe_3)Cl_4]NEt_4$ undergoes clean metallation reactions with H_2O, $PhNH_2$, and PhP(H)X (X = H, Me, Ph), in the presence of NEt_3 and a tertiary phosphine, to yield octahedral tungsten complexes. The reaction with H_2O provides an oxo-alkylidene species and with $PhNH_2$ an amido-alkylidyne species. The secondary-amido complex is found to transfer its proton to the alkylidyne α-carbon atom and kinetic data has been obtained. The reaction with PhP(H)X yields novel mononuclear phosphido-complexes. Preliminary structural results, provided by M. Churchill, are presented for $W(CCMe_3)(PHPh)(PEt_3)_2Cl_2$.

Chapter 5

A route to novel W(VI) σ-alkyl complexes by alkylation of $W(OMe)_3Cl_3$, in the presence of NEt_4Cl, is described. $W(OR)_3X_3$ (R = CH_3, CMe_3; X = CH_2CMe_3, CH_2SiMe_3) complexes are photosensitive and decompose to neopentylidyne species in the presence of light. $W(OMe)_3(CH_2CMe_3)_3$ reacts with Me_3SiBr to substitute a methoxide yielding an intermediate which decomposes to a dimeric W(V) neopentylidene complex. The alkylation chemistry of $W(OMe)_3(CH_2CMe_3)_3$ is complex as substitution, reduction, and α-hydrogen abstraction processes occur.

Thesis Supervisor: Richard R. Schrock
Title: Professor of Chemistry

ABBREVIATIONS

C_α	alpha carbon, directly bonded to metal
COD	cyclooctadiene
Cp	cyclopentadienyl
d	doublet
dmpe	1,2-bis(dimethylphosphino)ethane, $Me_2PCH_2CH_2PMe_2$
EPR	electron paramagnetic resonance
C_2H_4	ethylene
GLC	gas-liquid chromatography
H_α	alpha hydrogen, directly bonded to C_α
IR	infrared
L	ancillary ligand
Ln	lanthanide ion
Me	methyl
NMR	nuclear magnetic resonance
Np	neopentyl
Ph	phenyl
ppm	parts per million
q	quartet
R	alkyl or aryl
s	singlet
t	triplet
thf	tetrahydrofuran
tmeda	tetramethylethylenediamine
tms	tetramethylsilane
δ	chemical shift in ppm downfield from reference

CHAPTER 1

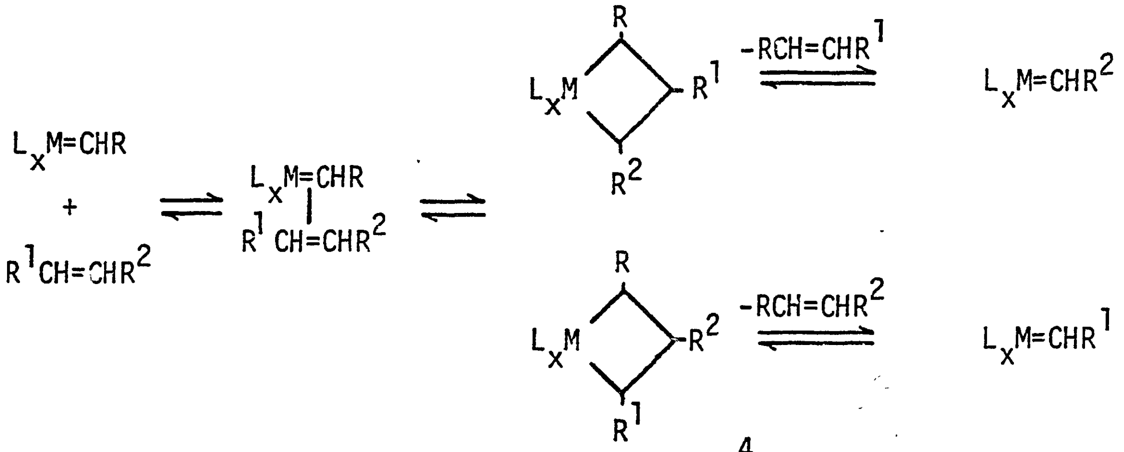
PREPARATION AND CHARACTERIZATION OF ACTIVE NIOBIUM AND TANTALUM OLEFIN METATHESIS CATALYSTS

INTRODUCTION

The olefin metathesis reaction, in which the alkylidene moieties of separate olefins are exchanged (eq 1), is one of the most remarkable

$$2R^1CH{=}CHR^2 \rightleftharpoons R^1CH{=}CHR^1 + R^2CH{=}CHR^2 \qquad (1)$$

catalytic reactions discovered in recent years. The reaction is formally, the essentially thermoneutral rupture and reformation of carbon-carbon double bonds with a thermodynamic redistribution of the alkylidene units, resulting in equilibrium concentrations of reactants and products. Banks and Bailey, in 1964, reported the catalytic metathesis of acyclic olefins by molybdenum hexacarbonyl on alumina at ca. 150°C.[1] The first homogeneous olefin metathesis catalyst, $WCl_6/EtOH/EtAlCl_2$, was reported by Calderon, et al in 1967.[2] Since the initial discovery much research has been devoted to the study of this fascinating reaction. Chauvin and Herisson were the first to propose the mechanism of the reaction to be a chain process that involves a metal-alkylidene to metallacycle interconversion as the pathway responsible for transalkylidenation[3] (eq 2). Katz and Grubbs have expanded



(2)

and confirmed the above mechanistic proposal.[4]

Metathesis catalysts have been prepared from transition metals in Groups IVA-VIIIA but best results are obtained with tungsten, molybdenum, and rhenium based systems.[5] Most industrial applications of olefin metathesis use heterogeneous catalysts based on metal oxides deposited on inorganic supports.[5,6] These applications include the production of styrene from stilbene and ethylene,[7] the synthesis of polymers from cycloolefins,[8] as well as the synthesis of biologically active organic molecules.[9] An olefin metathesis catalyst, such as MoO_3 on Al_2O_3, is used in the "Shell Higher Olefins Process" to produce C_{10}-C_{20} olefins from their higher and lower molecular weight counterparts generated by ethylene oligomerization.[10]

The soluble catalysts are of two major types. One family is based on combinations of alkyl aluminum, magnesium, or lithium reagents with transition metal halides or oxy-halides.[5a] The best results have been obtained using WCl_6 or $WOCl_4$. Recently an active olefin metathesis catalyst was generated by the electroreduction of WCl_6 with an aluminum anode.[11] Systems derived from Mo and Re halides or other high-valent compounds of these metals are much less active than their W analogues. The other family is derived from Group VIA metal carbonyls such as $Mo(CO)_6$ and $W(CO)_6$ as well as ligand-substituted derivatives such as $[W(CO)_5Cl]^-$.[5b] These metal carbonyl catalysts require activation by photolysis or by addition of a Lewis acid such as an alkyl aluminum halide complex. Many mechanistic proposals exist for the generation of the active species, an alkylidene moiety, in the above systems.[5,12]

Although the reaction between an alkylidene complex and an olefin is the favorite proposed mechanism for scrambling alkylidene fragments in the olefin metathesis reaction, only Casey had demonstrated that an isolable alkylidene complex, $(CO)_5W=CPh_2$, can react with olefins to yield metathesis products.[13] When this complex was reacted with isobutylene at 100°C, a 76% yield of 1,1-diphenylethylene (metathesis) in addition to 45% $W(CO)_6$ and approximately 10% 1,1-dimethyl-2,2-diphenylcyclopropane (cyclopropanation) were obtained. Further studies on the reactions of $(CO)_5W=CPh_2$ with a variety of olefins have shown that the least substituted alkylidene fragment of an olefin is preferentially transferred to the alkylidene ligand, and that less substituted olefins are more reactive toward the alkylidene complex.[14]

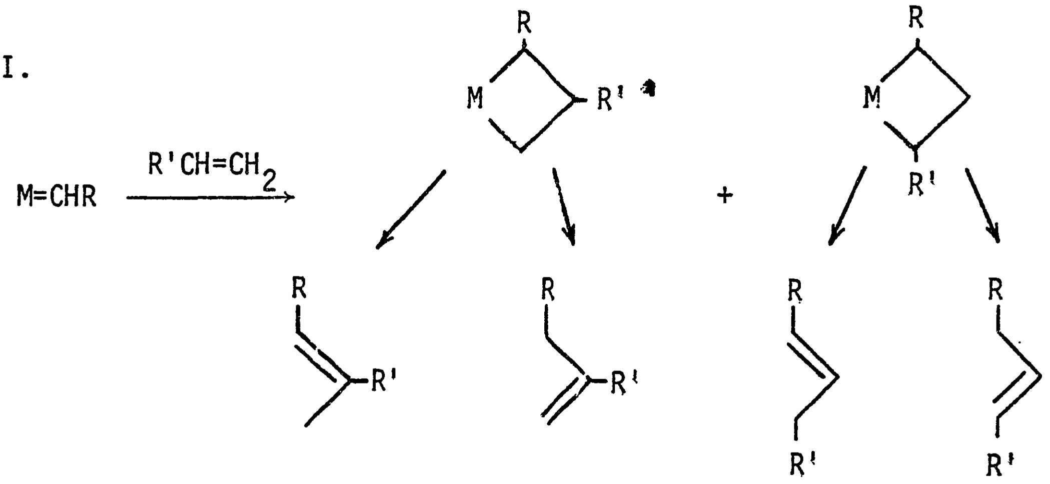
We have been interested for some time in how niobium and tantalum alkylidene complexes[15] react with olefins. The first type which contained no other potentially reactive ligands which might complicate such studies was $Ta(\eta^5\text{-}C_5H_5)(CHCMe_3)Cl_2$.[16] It reacts with terminal olefins to give a tantallacyclobutane complex which rapidly rearranges to an unobservable olefin complex by migration of a β-proton to an α-carbon atom. Two equivalents of the smaller, more strongly coordinating olefin which is present in excess then displaces this new olefin to give a tantallacyclopentane complex.[17]

Recently Rupprecht, et al have prepared other complexes which are suitable for studying this type of reaction, octahedral complexes of the type $M(CHR)L_2X_3$ (M = Ta, Nb; L = THF, tertiary phoshpine; X = Cl, Br).[18] These species also react with terminal olefins to yield organic products derived from the "rearrangement" of an intermediate metallacyclobutane complex. However, we now find that these non-cyclopentadienyl species can be modified so that the rate of rearrangement of the intermediate tantallacyclobutane ring is slow relative to metathesis. This modification to give metathesis catalysts is the subject of this chapter. Most of this work has appeared in published form.[19] G.A. Rupprecht did the reactions of $Ta(CHCMe_3)L_2Cl_3$ (L = tertiary phosphine) and $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ with ethylene, propylene, and styrene. L.W. Messerle did any work concerning tantalum benzylidene complexes. J.D. Fellmann performed the transalkylidenation reactions and prepared $Ta(CHCMe_3)(OCMe_3)(PMe_3)_2Cl_2$. The author did all other experiments.

RESULTS

Reactions of Halo/Alkylidene Complexes with Ethylene, Propylene or Styrene. G.A. Rupprecht and L.W. Messerle showed that Ta(CHR)L_2Cl_3 (R = CMe_3 or Ph, L = tertiary phosphine) reacts within a few seconds with ethylene, propylene, or styrene to give trans,mer-Ta(olefin)L_2Cl_3 and the four products of rearrangement of the two possible intermediate metallacyclobutane complexes (Scheme I; see ref. 19 for yields of organic products).

Scheme I.



Rupprecht found that Ta($CHCMe_3$)(PMe_3)$_2Cl_3$ reacted with ethylene in the presence of 1 equiv of 4,4-dimethyl-1-pentene to give a product mixture consisting of 1.1 equiv of 4,4-dimethyl-1-pentene and 0.9 equiv of trans-4,4-dimethyl-2-pentene; therefore once the olefin product dissociates from the metal it is not isomerized. In no case were any of the possible metathesis products or cyclopropanes observed.

The reaction between Ta($CHCMe_3$)(dmpe)Cl_3 and ethylene requires hours at 80-100°C. Since phosphine ligands in Ta($CHCMe_3$)(PR_3)$_2Cl_3$ are known to be labile,[18] we conclude that the olefin actually must coordinate to the metal before it can react with an alkylidene ligand.

The organic products of the reaction between Ta(CHCMe$_3$)(THF)$_2$Cl$_3$ or Ta(CHCMe$_3$)(py)$_2$Cl$_3$ and ethylene are largely rearrangement products, but the mixture contains a reproducible amount of the metathesis product, 3,3-dimethyl-1-butene (6% and 15%, respectively). We were not able to observe the methylene complex which must form when the initial metallacycle loses 3,3-dimethyl-1-butene, nor could we determine its fate.

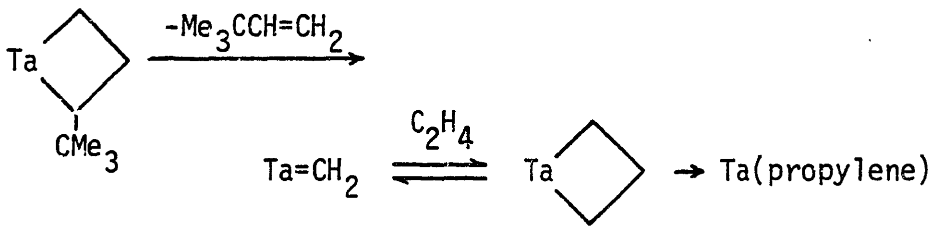
Preparation of Alkoxo Complexes and How They React with Ethylene. We turned to preparing and studying alkoxo complexes for two reasons. If metathesis by the THF or pyridine complexes can be attributed to the fact that THF and pyridine are "hard" donor ligands, then perhaps a "hard" covalently bonded ligand will promote metathesis even more effectively. Second, McLain noted that substituting a methoxide for a chloride made tantallacyclopentane complexes relatively stable toward rearrangement to an olefin by a β-hydride elimination process, one which proceeds via a tantallacyclobutane intermediate.[20]

M(CHCMe$_3$)(PMe$_3$)$_2$Cl$_3$ reacts with 2 equiv of LiOCMe$_3$ to give yellow M(CHCMe$_3$)(OCMe$_3$)$_2$(PMe$_3$)Cl in good yield (M = Nb or Ta). We suspect these molecules are trigonal bipyramids in which the neopentylidene ligand lies in the equatorial plane and the PMe$_3$ ligand is axial, on the basis of the structure of Ta(CHCMe$_3$)$_2$(mesityl)(PMe$_3$)$_2$.[21] However, we cannot choose between a molecule in which one of the inequivalent alkoxides is equatorial and one is axial and a molecule containing two equatorial alkoxides which are inequivalent by virtue of the fact that the neopentylidene ligand lies in the equatorial plane and does not rotate. We prefer the former proposal since there is one less 90° interaction between PMe$_3$ and the three tert-butyl-containing ligands. $M(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ will coordinate a second PMe_3 ligand in the presence of a large excess of PMe_3 or at low temperatures in the presence of 1 equiv of PMe_3.

A mono-tert-butoxide complex can be prepared by reacting $M(CH_2CMe_3)_2(OCMe_3)Cl_2$ with PMe_3, a version of the reaction used to prepare $M(CHCMe_3)(PMe_3)_2Cl_3$.[18] The NMR data suggest that two isomers are formed and that the PMe_3 ligands are trans and equivalent in the major isomer.

$Ta(CHCMe_3)(OCMe_3)_3$ (cf. $Ta(CHCMe_3)(CH_2CMe_3)_3$[22]) can be prepared from $Ta(CHCMe_3)(THF)_2Cl_3$[18] and $LiOCMe_3$. It is a yellow-orange oil and therefore is not readily purified. $Ta(CHCMe_3)(OCMe_3)_3$ does not form a stable PMe_3 adduct at room temperature (by ^{31}P NMR).

$Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ reacts rapidly with ethylene (30 psi) to give 1 equiv of tert-butylethylene, 1 equiv of propylene, and 0.4 equiv of $Ta(C_2H_4)(OCMe_3)_2(PMe_3)_2Cl$. We see no products arising from rearrangement of the initial metallacyclobutane complex. We believe propylene is formed by rearrangement of the unsubstituted tantallacyclobutane complex which is formed from the intermediate methylene complex and ethylene (eq 3).



(3)

Apparently, the initial complex, $Ta(C_2H_4)(OCMe_3)_2(PMe_3)Cl$, disproportionates to trans,trans-$Ta(C_2H_4)(OCMe_3)_2(PMe_3)_2Cl$ and an as yet unidentified species or mixture of species. In the presence of PMe_3 the initial reaction is slightly slower and the yield of $Ta(C_2H_4)(OCMe_3)_2(PMe_3)_2Cl$ is high.

$Ta(CHCMe_3)(OCMe_3)(PMe_3)_2Cl_2$ reacts with ethylene to give solely rearrangement products and an ethylene complex in high yield (eq 4). The major

$$Ta(CHCMe_3)(OCMe_3)(PMe_3)_2Cl_2 + C_2H_4 \xrightarrow{1\ h}$$
$$Ta(C_2H_4)(OCMe_3)(PMe_3)_2Cl_2 + t\text{-}Me_3CCH{=}CHMe\ (24\%) + Me_3CCH_2CH{=}CH_2\ (65\%) \quad (4)$$

isomer of the ethylene complex has trans, equivalent phosphine ligands.

$Ta(CHCMe_3)(OCMe_3)_3$ reacts only slowly with ethylene to give largely rearrangement products (eq 5). We could not isolate or identify in situ

$$Ta(CHCMe_3)(OCMe_3)_3 + C_2H_4 \xrightarrow{8\ h}$$
$$Me_3CCH_2CH{=}CH_2\ (57\%) + t\text{-}Me_3CCH{=}CHMe\ (29\%) + Me_3CCH{=}CH_2\ (4\%) \quad (5)$$

any organometallic product. Adding PMe_3 to the system increases the amount of metathesis product only slightly (14% metathesis, 70% rearrangement in 16 h), but now we also see 1-butene forming catalytically at a rate on the order of 0.5 equiv $Ta^{-1}\ h^{-1}$. We suspect that it forms via a tantallacyclopentane complex.[20] Propylene reacts with $Ta(CHCMe_3)(OCMe_3)_3$ to give a quantitative yield of rearrangement products (2,4,4-trimethyl-1-pentene, 70% and 2,4,4-trimethyl-2-pentene, 30%) and the propylene dimer, 2,3-dimethyl-1-butene (400%) in 24 hr.

Reactions of $M(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ with Styrene, Propenylbenzene, and Stilbene: Observation of the Transalkylidenation Reaction. Casey and Burkhardt have found that the reaction of $(CO)_5W{=}CPh_2$ with 1-methoxy-1-

phenylethylene gives a new carbene complex, $(CO)_5W{=}C(OCH_3)C_6H_5$ in 24% isolated yield.[13] Fellmann chose to look at the reaction of the di-tert-butoxy complexes with selected phenyl-substituted olefins since the product of the initial metathesis reaction could be an isolable benzylidene complex.

One equivalent of styrene reacts with $M(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ to give a good yield of the two possible initial metathesis products, most of which is 3,3-dimethyl-1-butene. trans- and cis-Stilbenes form slowly in the absence of added PMe_3, probably primarily by intermolecular decomposition of the resultant benzylidene complex. The evidence consists of the fact that the amount of stilbenes continues to grow after the initial metathesis is complete and the fact that no stilbenes form in the presence of 1 equiv of PMe_3. cis-Propenylbenzene reacts with $M(CHCMe_3)(OCMe_3)_2$-$(PMe_3)Cl$ to give almost exclusively trans-4,4-dimethyl-2-pentene as the initial metathesis product. Stilbenes again form, more rapidly when M = Nb than when M = Ta and more slowly in the presence of PMe_3. cis-Stilbene reacts fairly quickly with both the Nb and Ta complexes to give the only possible initial metathesis product in good yield. trans-Stilbene reacts much more slowly than cis-stilbene in the presence of PMe_3 as expected if the olefin must first compete with PMe_3 for a metal coordination site.

In all of the above reactions Fellmann observed lime green $M(CHPh)$-$(OCMe_3)_2(PMe_3)_2Cl$ as the major organometallic product. The yield in the presence of 1 equiv of PMe_3 when M = Ta is high, and it is easiest to isolate from the styrene reaction. It is six-coordinate, probably because the benzylidene ligand is not as sterically demanding as the neopentylidene ligand. However, the complex does lose one phosphine ligand readily in solution to give an orange complex which cannot be isolated free of stilbenes and organometallic decomposition products. By ^{13}C NMR we can show that this species is $[Ta(CHPh)(OCMe_3)_2(PMe_3)Cl]_x$. (We do not know if x = 1 or 2.) It decomposes readily to give stilbenes (eq 6). Mixtures of

$$Ta(CHCMe_3)(OR)_2(PMe_3)Cl \xrightarrow[PMe_3]{PhCH=CH_2} Ta(CHPh)(OR)_2(PMe_3)_2Cl \xrightarrow{-PMe_3}$$

$${}^1/_x[Ta(CHPh)(OR)_2(PMe_3)Cl]_x \rightarrow \text{stilbenes} \quad (6)$$

$$R = CMe_3$$

$Nb(CHPh)(OCMe_3)_2(PMe_3)_2Cl$ and $[Nb(CHPh)(OCMe_3)_2(PMe_3)Cl]_x$ can be observed in the reaction of $Nb(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ with styrene in the presence of PMe_3. The fact that we can prepare tantalum- and niobium-benzylidene complexes by a transalkylidenation reaction confirms that a new alkylidene complex forms whenever metathesis products are observed.

Metathesis of 1-Butene: Why It Does Not Work. We developed a test for productive metathesis of a terminal olefin using 1-butene as the model since we could identify all metathesis or rearrangement products of initial or intermediate metallacyclobutane complexes. These products, and how they form, are shown in Scheme II, and the results for all complexes which yield at least some metathesis products are listed in Table I. Note that (i) metathesis of 1-butene is productive only if the amount of 3-hexenes exceeds the amount of 3,3-dimethyl-1-butene and (ii) the percent initial metathesis products less the sum of all products of rearrangement of intermediate metallacyclobutane complexes (C_5^b, C_5^1, C_7^b, C_7^1) equals the amount of chain

Scheme II. Metathesis of 1-Butene

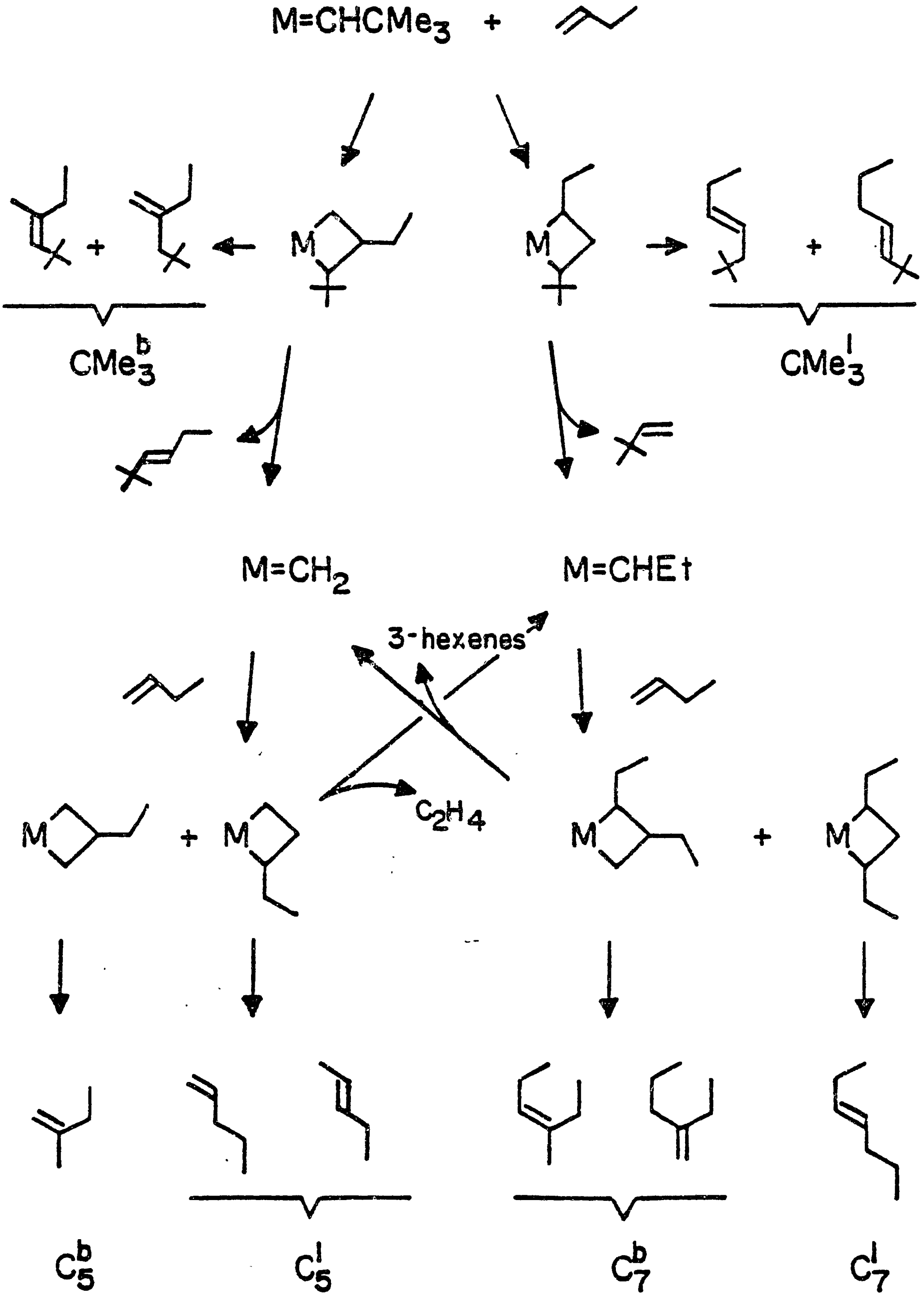


Table I. 1-Butene Test for Metathesis Activity[a]

	time, h	CMe_3[b]	CMe_3[1]	Me_3C-CH=CH_2	trans-Me_3CH-CH=CHEt	% rxn	C_5[b]	C_5[1]	C_7[b]	C_7[1]	3-hex-enes	decomp[b]	pro-ductive meta-thesis
1 $Ta(CHCMe_3)(THF)_2Cl_3$[c]	2		11	79		90			76		5	3	0
2 $Nb(CHCMe_3)(THF)_2Cl_3$	2		17	73		90			56		17	17	0
3 $Ta(CHCMe_3)(py)_2Cl_3$	2		38	51		89			20	27	0	4	0
4 $Ta(CHCMe_3)(py)_2Cl_3$ + py	48	22	53	17		92			5	7	0	5	0
5 $Ta(CHCMe_3)(OCMe_3)$-$(PMe_3)_2Cl_2$	1	7	50	32		89			15	20	<2	"-3"	0
6 $Ta(CHCMe_3)(OCMe_3)_2$-$(PMe_3)Cl$[d]	3			76	18	94	46				75	48	0
7 $Nb(CHCMe_3)(OCMe_3)_2$-$(PMe_3)Cl$	0.25			86	6	92					92	92	0
8 $Nb(CHCMe_3)(OCMe_3)_2$-$(PMe_3)Cl + 2PMe_3$[e]	1			97	1	98	55				202	43	104
9 $Ta(CHCMe_3)(OCMe_3)_3$[f]	6	7	73	17		97			9	6	<3	2	0
10 $Ta(CHCMe_3)(OCMe_3)_3$ + PMe_3[g]	6	6	31	46		83			4	2	5	40	0

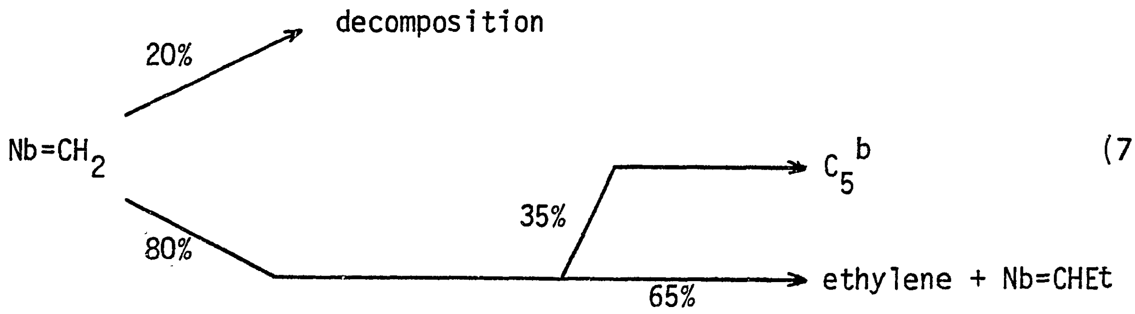
[a] The numbers are expressed as percent yield vs. the metal. Details can be found in the experimental section. [b] This number [Σ(initial metathesis products)-$\Sigma(C_5^b + C_5^1 + C_7^b + C_7^1)$] is accurate to only ca. ±5%. [c] Similar results were obtained with $Ta(CHCMe_3)(DME)Cl_3$ (DME = 1,2-dimethoxyethane). [d] 1-Butene dimers = 32%. [e] The numbers did not change on varying the PMe_3 concentration from 1 to 10 equiv. Ethylene = 33%; theory = 125% - 104% by metathesis, 21% by decomposition of methylene complexes. [f] 1-Butene dimers = 40%. [g] 1-Butene dimers = 60%.

termination by some other step which we call "decomposition".

THF- or pyridine-substituted neopentylidene complexes react with 1-butene to give more metathesis product than is formed when they react with ethylene, and it is all 3,3-dimethyl-1-butene. First, we note that when pyridine is added, the rate slows down, substantially less 3,3-dimethyl-1-butene is formed, and rearrangement of the α,β-disubstituted metallacycle (to give CMe_3^b) becomes important. Interestingly, metathesis of the initial α,β-disubstituted metallacyle does not compete with its rearrangement. Second, one or both of the two intermediate metallacycles which form from the intermediate propylidene complex and 1-butene mostly rearrange to C_7^b and C_7^1. When L = THF, metathesis of the α,β-diethylmetallacyclobutane complex competes with its rearrangement to give 5% (M = Ta) and 17% (M = Nb) 3-hexenes. Metathesis of the α,α'-diethylmetallacycle probably also competes with its rearrangement, but this process is degenerate. Third, the sum of C_7 rearrangement products and 3-hexenes approximately equals the amount of 3,3-dimethyl-1-butene, as it should if the metathesis chain never develops.

$Ta(CHCMe_3)(OCMe_3)(PMe_3)_2Cl_2$ reacts with 1-butene to yield some rearrangement and some metathesis products (run 5). The metathesis product is almost exclusively $Me_3CCH{=}CH_2$ and the new alkylidene therefore the propylidene complex. We have never been able to observe it by NMR since it apparently reacts too rapidly with more 1-butene to give the C_7 metallacycles which rearrange exclusively to the branched and linear C_7 olefins. These data suggest that the α-tert-butyl-α'-ethylmetallacyclobutane complex forms and metathesizes or rearranges more rapidly than the α-tert-butyl-β-ethylmetallacyclobutane complex. Note, however, that the rate of formation and rearrangement of the α,α'-diethylmetallacycle is about the same as that of the α,β-diethylmetallacycle.

The di-tert-butoxide complexes react with 1-butene to give only metathesis products (mostly $Me_3CCH=CH_2$; runs 6-8). First, note that intermediate C_7 metallacycles do not rearrange but metathesize exclusively to give 3-hexenes and an intermediate methylene complex. Second, one of the C_5 metallacycles which forms when the methylene complex reacts with 1-butene rearranges to a branched C_5 olefin, except in run 7 where decomposition of the $Nb=CH_2$ complex (we propose bimolecularly) is the fastest termination step. Third, by adding PMe_3 to the Nb catalyst, we can slow bimolecular decomposition so that some methylene complex survives to complete the catalytic metathesis cycle (run 8). If we say that 20% of the methylene complex decomposes each time and of the 80% that survives, 35% is converted into branched C_5 rearrangement products and 65% into ethylene and a propylidene complex by productive metathesis (eq 7), then after ten



(7)

cycles all alkylidene complexes would be consumed. The yields of decomposition, rearrangement, and productive metathesis products would be 42%, 58%, and 108%, respectively. This is what we observe. We do observe some ethylene in solution, but no propylene, the likely product of rearrangement of a propylidene ligand. Apparently, this rearrangement is considerably slower than the other termination steps in this system (cf. metathesis of cis-2-pentene).

$Ta(CHCMe_3)(OCMe_3)_3$ reacts with 1-butene (run 9) to give mostly rearrangement products of the initial metallacycles and intermediate C_7 metallacycles. In the presence of PMe_3 (run 10) the amount of metathesis product increases but rearrangement of intermediate metallacycles still occurs.

Metathesis of cis-2-Pentene. Unlike the phosphine complexes, the THF and py complexes react (slowly) with cis-2-pentene. $Ta(CHCMe_3)(THF)_2Cl_3$ in the presence of THF yields one of the initial metathesis products, trans-2,2-dimethyl-3-hexene (30%). The other probably also forms but we cannot see it by GLC due to the presence of free THF in the mixture. 2-Butenes and 3-hexenes form catalytically but only about 6 equiv of each before the purple solution turns brown and the system deactivates (eq 8). We cannot be

$$Ta(CHCMe_3)(THF)_2Cl_3 \xrightarrow[\text{2.5THF, ether, 4h}]{\text{cis-2-pentene}}$$

$$0.30 t\text{-}Me_3CCH{=}CHEt + \sim 6 \text{ 3-hexenes} + \sim 6 \text{ 2-butenes} \quad (8)$$

certain, on the basis of these data alone, that none of the initial metallacycle rearranges, but for us to see about 6 equiv of productive metathesis products, a significant percentage (>90%) of the initial and intermediate trisubstituted metallacyclobutane complexes must metathesize rapidly relative to the rate at which they rearrange. Messerle has shown that the reaction between $Ta(CHPh)(THF)_2Cl_3$ (generated in 25% yield in situ from $Ta(CH_2Ph)_2Cl_3$ and THF in ether) and cis-2-pentene shows more clearly that the initial metallacycles metathesize in high yield and that 5-6 equivalents of 3-hexenes form (vs. $Ta(CHPh)(THF)_2Cl_3$ formed) before the reaction stops (eq 9). In this case, as well as the above, we do not know what the

$$Ta(CH_2Ph)_2Cl_3 \xrightarrow[\text{4THF, ether}]{\text{cis-2-pentene}} 0.25\text{toluene} + 0.21\text{t-PhCH=CHMe} + 0.05\text{t-PhCH=CHEt} + 1.4\ \text{3-hexenes} \quad (9)$$

major chain-terminating reaction(s) is (are). However, we suspect that the intermediate propylidene and ethylidene complexes are prone to decompose biomolecularly since even $Ta(CHPh)(PMe_3)_2Cl_3$ decomposes fairly readily in this manner[18] and $Ta(CHPh)(THF)_2Cl_3$ has not yet been isolated.

The red-purple glyme adduct, $Ta(CHCMe_3)(DME)Cl_3$ (DME = 1,2-dimethoxyethane), reacts with cis-2-pentene to quickly cleave the neopentylidene moiety (80% cleavage in 90 min) but gave only a poor yield of productive metathesis products (~200%) after 6 hr. A dark precipitate began depositing from solution as soon as the olefin was added. In the presence of 1,2-dimethoxyethane the solution remained homogeneous but the reaction slowed considerably as only 30% of the cleavage products were observed after 28 hr.

Although $Ta(CHCMe_3)(PMe_3)_2Cl_3$ does not react with cis-2-pentene the mono-tert-butoxy complex, $Ta(CHCMe_3)(OCMe_3)(PMe_3)_2Cl_2$, reacts slowly to give a low yield of initial cleavage products (40%) and productive metathesis products (125%) after 24 hr at ca. 25°C in toluene.

cis-2-Pentene (100 equiv) reacts with $Nb(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ in the presence of PMe_3 to give the two initial metathesis products (90% combined yield) in 25 min (Figure 1). At the same time 2-butenes and 3-hexenes begin forming so that after 25 min 5-6 equiv of each are present (Figure 2). After 2 h about 15 equiv have formed and after 24 h about 34 equiv. cis-2-Pentene is rapidly isomerized during the metathesis reaction to trans-2-pentene (Figure 2). After 24 h the catalyst is no longer active; any added cis-2-pentene is neither metathesized nor isomerized.

An important finding is that propylene and ethylene appear early in the reaction along with the initial metathesis products (Figure 1). They must be formed by rearrangement of the intermediate propylidene and ethylidene complexes to propylene and ethylene complexes, respectively. Since at least 0.7 equiv form, bimolecular decomposition of intermediate alkylidene complexes and rearrangement of intermediate metallacycles both must be fairly slow; i.e., rearrangement of intermediate alkylidene complexes must now be the major metathesis chain termination step. Casey, et al have observed this formal β-hydrogen shift in their attempts to prepare $(CO)_5W{=}C(CH_3)C_6H_5$.[23] They observed a 47% yield of styrene as well as 26% cis- and trans-1-methyl-1,2-diphenylcyclopropane (formally the cyclopropanation product of $(CO)_5W{=}C(CH_3)C_6H_5$ and styrene) upon the thermal decomposition of the tungsten alkylidene complex at -78°C.

The trimethylsilyl substituted alkylidene complex, $Nb(CHSiMe_3)(OCMe_3)_2(PMe_3)Cl$ reacts only very slowly with cis-2-pentene, in the presence of PMe_3,

Figure 1. Cleavage and alkylidene rearrangement products in the metathesis of cis-2-pentene with $Nb(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ in the presence of PMe_3 in mesitylene at 25°C. (The mole percents of ethylene and propylene are inaccurate and low, especially initially, due to loss of these products in the gas phase during sampling.)

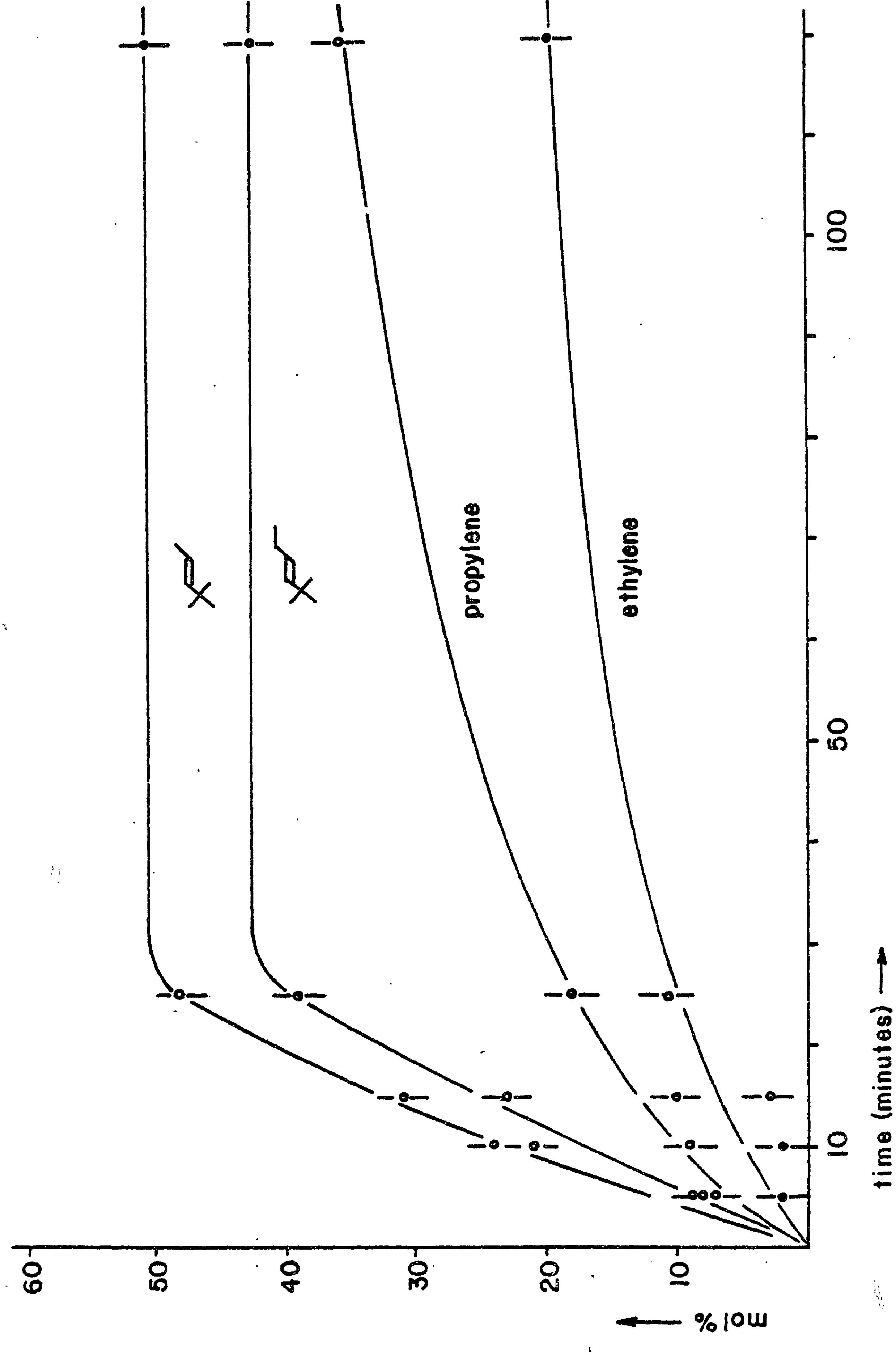
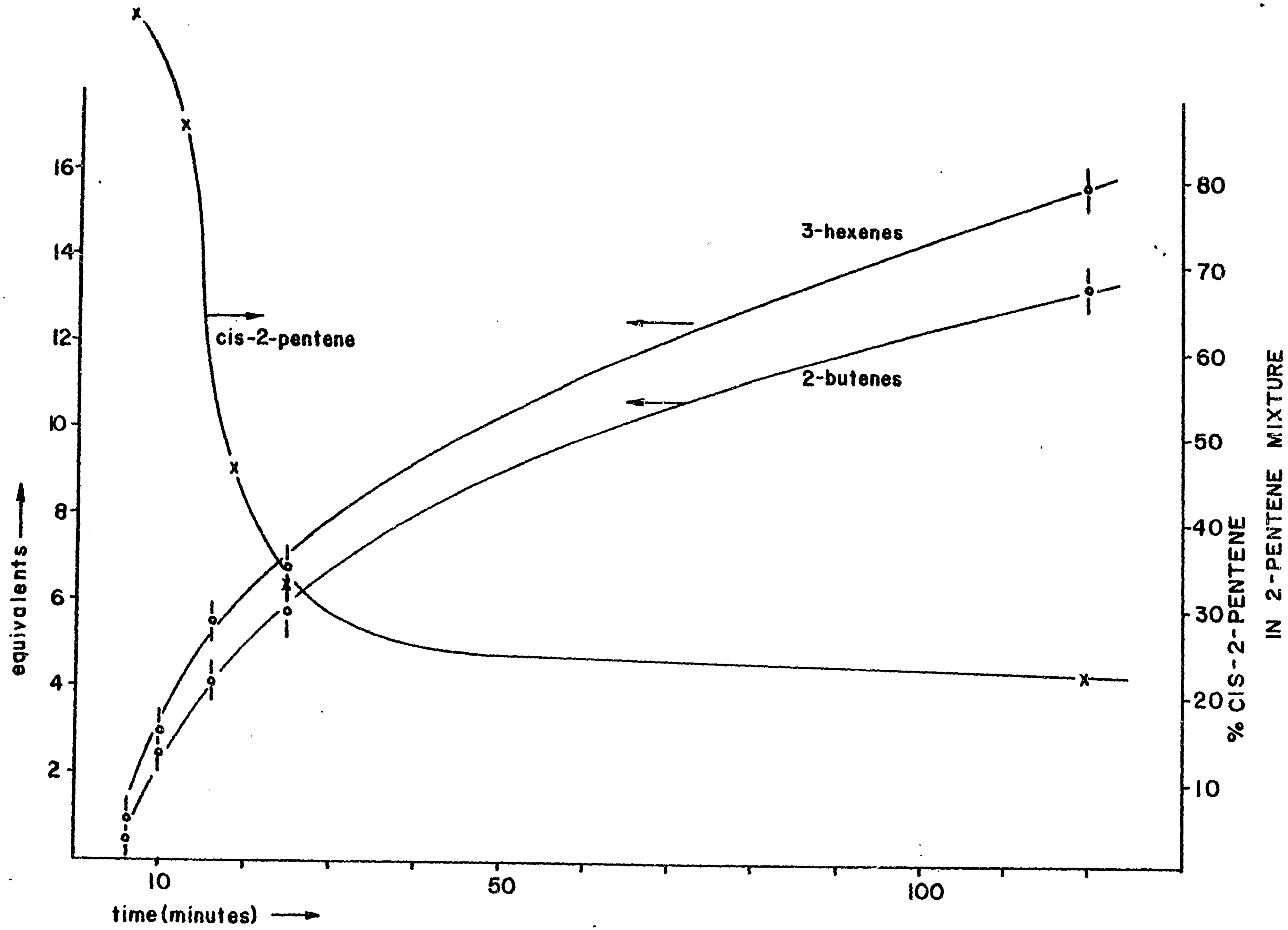

mol% ⟵
60
50
40
30
20
10
time (minutes) ⟶
10
50
100
propylene
ethylene

Figure 2. Metathesis of cis-2-pentene by $Nb(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ in the presence of PMe_3 in mesitylene at 25°C. (Equivalents of 2-butene are low due to loss in the gas phase. After 24 h, 34 equiv of 3-hexenes and 29 equiv of 2-butenes had formed.)


cis-2-pentene
3-hexenes
2-butenes
equivalents
16
14
12
10
8
6
4
2
time (minutes)
10
50
100
% CIS-2-PENTENE
IN 2-PENTENE MIXTURE
80
70
60
50
40
30
20
10

to give only 80% productive metathesis (3-hexenes) after 4 hr at room temperature.

$Ta(CHCMe_3)(OCMe_3)_3$ reacts quickly with cis-2-pentene to give initial and productive metathesis products, but the system deactivates after about seven turnovers (Table II). Adding monodentate tertiary phosphines increases the number of turnovers while adding a chelating phosphine (dmpe) appears to slow the formation of initial as well as productive metathesis products. We do not see any significant amount of ethylene or propylene nor any significant amount of metallacyclobutane rearrangement products. Therefore if there is no chain-terminating decomposition step we do not yet know about, bimolecular decomposition must be the primary chain termination step.

Metathesis of Functionalized Olefins

The metathesis of olefins substituted with polar functional groups was pioneered by Boelhouwer, et al in 1972.[24] These workers reported the metathesis of the ester, methyl oleate, with a homogeneous catalyst based on a 1/1.4 molar combination of $WCl_6/SnMe_4$ in chlorobenzene. At 70°C and an ester/W molar ratio of 33, near thermodynamic equilibrium was attained and the ester was converted to equal amounts of 9-octadecene and the dimethyl ester of 9-octadecene-1,18-dioic acid. Boelhouwer subsequently reported the successful metathesis of methyl esters of the polyunsaturated linoleic and linolenic acids using the $WCl_6/SnMe_4$ catalyst system.[25] The use of $SnMe_4$ as cocatalyst is unique as $Sn(C_2H_5)_4$, $Sn(C_4H_9)_4$, and $Sn(Ph)_4$ were inactive as cocatalysts in the metathesis of fatty acid esters.[26]

Table II. Metathesis of cis-2-Pentene by Ta(CHCMe$_3$)(OCMe$_3$)$_3$[a]

added ligands[b]	time	initial cleavage products	cis/trans-2-butenes	cis/trans-3-hexenes
none	30 min	85	530	700[d]
THF	30 min	90	540	700[d]
PMe$_2$Ph	30 min	91	985	1060[d]
PEt$_3$	30 min	98	800	860[d]
PMe$_3$	2 h	73	815	1200
	16 h	78	970	1600
	18 h	86	1200	1700[d]
dmpe[e]	30 min	28	300	270
	1 h	38	375	370
	2 h	44	540	550
	10 h	60	750	810[d]

[a] 50 mg of complex in toluene at ca. 25°C plus ca. 50 equiv of cis-2-pentene. The numbers are expressed as percent yield vs. the metal. The yield of 2-butenes is generally low due to escape during sampling. [b] Ca. 2-5 mol equiv. [c] Roughly equal amounts of cis/trans-4,4-dimethyl-2-pentene and trans-2,2-dimethyl-3-hexene. [d] No substantial further activity. [e] dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$.

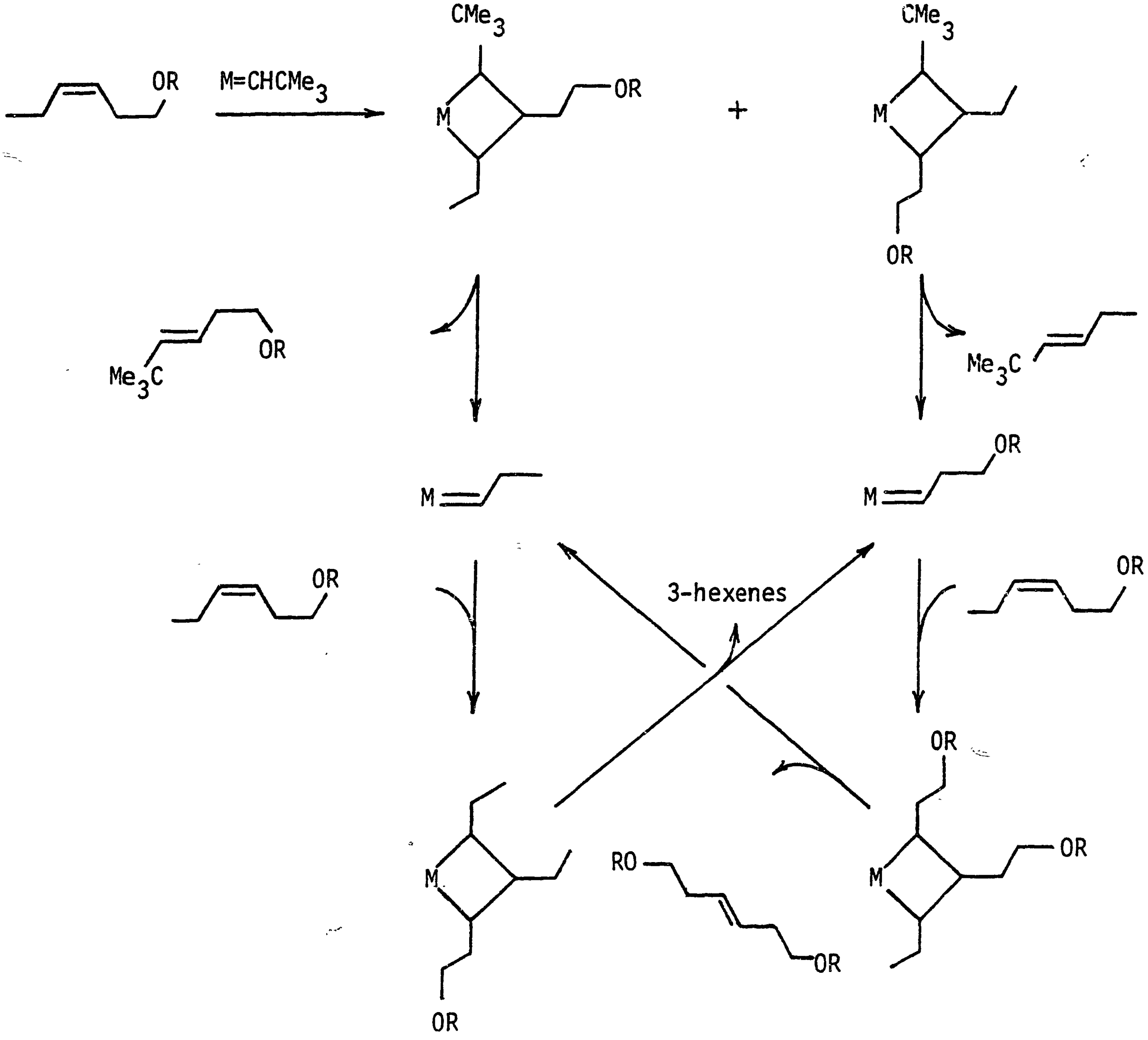
Nakamura, et al reported that catalyst systems derived from WCl_6, $MoCl_5$, $Mo(OC_2H_5)_2Cl_3$, and $W(CO)_6$ in combination with $(CH_3)_3Al_2Cl_3$ effected the disproportionation of a variety of fatty acid esters as well as the first reported metathesis involving alkenyl nitriles, ketones, ethers, amides, and oxysilanes, albeit in low yields (2-10%).[27] This catalyst system failed with unsaturated carboxylic acids, alcohols, primary amines, and unsubstituted amides.

Basset and co-workers found that alkenyl amines such as allyl amine or the N,N-dimethyl derivative failed to be metathesized but that unsaturated quaternary ammonium salts were metathesized in moderate yield (11-33%) with W(mesitylene)$(CO)_3$ activated with $EtAlCl_2$ and O_2.[28]

Heterogeneous rhenium based metathesis systems exhibit good activity, but maybe more importantly, a high degree of selectivity (>96%). The combination of Re_2O_7-Al_2O_3/$SnMe_4$ in CCl_4 at an olefin/Re/Sn molar ratio of 220/6/1 converted terminal alkenyl ethers, esters, halides, and ketones to metathesis products.[29]

The metathesis of functionalized olefins presents a special difficulty with our catalysts since nucleophilic metal alkylidene moieties are known to react with organic functionalities such as carbonyl, alcohol, and nitrile.[15] Alkenyl halides, ethers, and substituted amines may be less reactive and could be metathesized by our catalysts. Scheme III outlines the metathesis course of cis-3-hexene alkyl ethers involving -OR substituted alkylidenes and metallacyclobutanes. These species may react differently than their hydrocarbon counterparts. $Nb(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ was chosen as the catalyst for these studies since it was the most active catalyst with cis-2-pentene.

Scheme III. Metathesis of cis-$CH_3CH_2CH{=}CHCH_2CH_2OR$



The metathesis of cis-3-hexene trimethylsilyl ether and cis-3-hexene methyl ether should yield cis/trans-3-hexenes and 1,6-disubstituted-3-hexene alkyl ethers as productive metathesis products. In Table III we can see that cis-$CH_3CH_2CH{=}CHCH_2CH_2OSiMe_3$ is metathesized quickly to give a good yield of 3-hexenes (175%) and $Me_3SiOCH_2CH_2CH{=}CHCH_2CH_2OSiMe_3$ (120%) but the reaction stops immediately. The reaction solution turned from yellow to orange-brown in less then 5 min. The alcoxy-substituted alkylidene complex, $Nb(CHCH_2CH_2OSiMe_3)(OCMe_3)_2(PMe_3)_xCl$, apparently survives long enough to react with the alkenyl substrate to produce some alkenyl diether. In the presence of free PMe_3 the reaction slows considerably and after 24 hr only 140% 3-hexenes are observed. When cis-$CH_3CH_2CH{=}CHCH_2CH_2OCH_3$ reacts with $Nb(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ only a modest yield of cis-3-hexenes are produced. Free PMe_3 is observed by GLC which may indicate that the cis-3-hexene methyl ether is coordinating to the metal through the methoxy group. When excess PMe_3 is added the yield of metathesis product increases but the reaction is very slow. The trimethylsilyl-substituted ether may be metathesized more readily due to the Si-O interaction which can pull electron density away from the oxygen or to the sterically large $SiMe_3$ group which can effectively block the oxygen interaction with the catalyst. $Nb(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ reacts with 1-dimethylamino-cis-2-pentene in mesitylene in 1 hr to give 32% 3-hexenes and 56% trans-2,2-dimethyl-3-hexene. No further activity was observed and the addition of free PMe_3 did not increase the yield of metathesis products.

Table III. Metathesis of cis-$CH_3CH_2CH{=}CHCH_2CH_2OR$ by $Nb(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$[a]

R	time (hr)	added ligand[b]	t-$Me_3CCH{=}CHCH_2CH_3$	c/t-3-hexenes
1 $SiMe_3$	1	none	55[c]	175[d,e]
2 $SiMe_3$	1	PMe_3	10	30
	24		35	140[e]
3 CH_3	1	none	9	23[e]
4 CH_3	2	PMe_3	f	41
	24		f	165[e]

[a] 100 mg of complex in mesitylene at ca. 25°C plus ca. 10 equiv of cis-3-hexene alkyl ether. The numbers are expressed as percent yield vs. the metal. [b] Ca. 2-5 equiv. [c] The other cleavage product, $Me_3CCH{=}CHCH_2CH_2OSiMe_3$, is observed in 40% yield. [d] The other metathesis product, $Me_3SiOCH_2CH_2CH{=}CHCH_2CH_2OSiMe_3$, is observed in 120% yield. [e] No substantial further activity. [f] Not recorded.

DISCUSSION

The only olefin metathesis catalysts which contain niobium or tantalum are heterogeneous catalysts.[30] The scarcity of homogeneous catalysts might be ascribed to a failure to generate the initial alkylidene ligand by using techniques which are successful for preparing homogeneous group VI metal catalysts. However, even if an alkylidene complex were generated, it now seems likely that the metathesis chain, as we have found here, would be terminated by bimolecular decomposition of alkylidene complexes (especially of methylene complexes), rearrangement of metallacyclobutane rings to olefins, and rearrangement of alkylidene ligands to olefins. While we cannot be certain that similar steps terminate the metathesis chain in classical metathesis systems, all have been mentioned as possible termination steps[5,12] and the probability that at least one of them is an important chain termination step seems high. The fact that we never see cyclopropanes, however, augurs poorly for them as chain termination products in the classical systems.

There are two conclusions concerning the formation and metathesis of metallacyclobutane complexes we feel are justified. The first is that α,α'-disubstituted metallacycles form and metathesize faster than α,β-disubstituted metallacycles. This is one of the two possible ways methylene groups in terminal olefins can scramble rapidly relative to productive metathesis, a phenomenon which has been known for several years in classical metathesis systems.[5,12] Unfortunately, this result does not help settle the debate as to whether formation and metathesis of α,α'-disubstituted metallacycles or β-monosubstituted metallacycles is the faster means of scrambling methylene groups. The second conclusion is that α,β,α'-trisubstituted metallacycles rearrange much more slowly relative to the rate they metathesize than di- or monosubstituted metallacycles.

One of the most important points of our results is that replacing chloride ligands with alkoxide ligands tends to slow down (but not completely stop) the rate of rearrangement of a metallacyclobutane ring relative to metathesis. We stress that this is only a trend. Obviously, other factors such as coordination number, types of donor ligands, and structures of metallacycles will also be important. (Almost certainly, this is why the behavior of $Ta(CHCMe_3)(OCMe_3)_3$ is somewhat inconsistent compared to that of $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ and $Ta(CHCMe_3)(OCMe_3)(PMe_3)_2Cl_2$.) The important question is whether the rate of rearrangement of a metallacyclobutane ring slows down absolutely. We believe it does on the basis of the fact that the rate of rearrangement of a tantallacyclopentane ring to an olefin (a β-hydride elimination process which leads to a tantallacyclobutane ring which subsequently rearranges[20]) slows by a factor of $\sim 2 \times 10^{-2}$ on replacing one chloride ligand in the olefin dimerization catalyst by a methoxide ligand. Since rearrangement of metallacycles to olefins involves formally a reduction of the metal, it is reasonable that an alkoxide, which is compatible with a d^0 metal, should "stabilize" a d^0 metallacycle toward rearrangement to a d^2 olefin complex. Although there are few data concerning how general a phenomenon in early transition-metal organometallic chemistry this "alkoxide effect" might be, it is worth noting that some of the earliest stable d^0 metal alkyls (e.g., $Ti(O\text{-}i\text{-}Pr)_3Ph$, 1952[31]) contain alkoxide ligands.[32] More recently this effect has been used to prepare novel d^0 tungsten alkyls such as $W(OCH_3)_3(CH_2CMe_3)_3$ and $W(OCH_3)_3(CH_2SiMe_3)_3$.[33]

Wengrovius and Pedersen have found that Group VIA alkylidene complexes containing ligands which stabilize high oxidation states, such as oxo[19,34] or imido,[35] also metathesize olefins.[34] Therefore, in the systems we have worked with, the metathesis catalysts are d^0 complexes (counting the alkylidene ligand as a dianion) in which there are "hard" π-electron donor ligands to sustain the d^0 oxidation state. Other recent results by Osborn[36] and Goddard,[37] as well as earlier work by Basset[38] and Muetterties,[39] are consistent with this proposal.

Our work with simple functionalized olefins has shown, as expected, that these oxophilic tantalum and niobium alkylidene complexes are not good catalysts for these substrates. These Lewis acid complexes probably interact with the "basic" substituents such as -OR or $-NR_2$ in the functionalized olefins. Sancho has observed similar results in his attempts to dimerize functionalized olefins (such as allyl methyl ether) with known tantalum based olefin dimerization catalysts.[20,40]

Addendum

(1) Since covalent "hard" donor ligands such as alkoxides appear to alter the course of the reaction of olefins with alkylidene complexes it would be interesting to compare the effect of amides as ligands in such reactions. The reaction of $Ta(CHCMe_3)(THF)_2Cl_3$ with lithium amide salts was attempted but no tractable products resulted (messy brown oils were obtained). Both $LiN(SiMe_3)_2$ and $LiN(CHMe_2)_2$ were used. The silyl amide is probably too

large but the isopropyl amide is much smaller (but still fairly large). Although it was not performed, the reaction can probably be cleaned up by using $Ta(CHCMe_3)(PMe_3)_2Cl_3$ and 2 equiv of $LiN(CHMe_2)_2$ in ether at -30°C (II-9, 11, 13, 15, 16, 19).

(2) Thiolate complexes can be prepared by the addition of $3LiSBu^t$ to $Ta(CHCMe_3)(PMe_3)_2Cl_3$ at -30°C. Very soluble $Ta(CHCMe_3)(SBu^t)_3PMe_3$ is obtained in good yield (C_α at 272, J_{CH} = 86 Hz). It reacted slowly with 1-butene in mesitylene to give ~35% metathesis and 40% rearrangement products in 1 hr. No 3-hexene was observed (IV-5, 9, 61).

(3) Attempts to prepare methoxide complexes with either 2 or 3 equiv of LiOMe added to $Ta(CHCMe_3)(PMe_3)_2Cl_3$ at -30°C gave messy untractable brown oils (IV-17).

General Experimental Details

All experiments were performed under an inert atmosphere by either standard Schlenk techniques or in a Vacuum Atmospheres HE43-2 drybox. Solvents were rigorously purified and dried under N_2 by standard techniques and transferred into the drybox without exposure to air. Commercial grade pentane was extracted with H_2SO_4 containing 5% HNO_3 three times and then with distilled H_2O in order to remove olefinic impurities and then distilled from sodium/benzophenone ketyl. All other solvents (toluene, benzene, chlorobenzene, mesitylene, diethyl ether, tetrahydrofuran, methylene chloride, chloroform) were reagent grade and were rigorously purified and dried under N_2 by standard techniques and transferred into the drybox without exposure to air. Olefins, deuterated solvents, and n-alkanes were deaerated with nitrogen and passed through alumina prior to use: 1-Butene, ethylene, hydrogen, and carbon monoxide were used as received.

NMR spectra were run at ca. 35°C on a Jeol FX-90Q or at ca. 25°C on a Bruker WM-250 spectrometer unless otherwise noted. ^{1}H and ^{13}C spectra are referenced to tetramethylsilane and ^{31}P spectra are referenced to H_3PO_4. Coupling constants are given in Hz. ^{15}N spectra were run at 9.04 MHz with a pulse delay of ~5 seconds and are referenced as downfield shifts from liquid NH_3. Infrared spectra were obtained on a Perkin-Elmer 283B instrument in Nujol mulls using KBr plates.

GLC samples were analyzed with an HP5730A chromatograph and 3380A recorder on an 8-ft. 10% SE-30 on 100/120 Gas Chrom Q or 8-ft. Carbowax 20M column. Organic products from reactions were identified by coinjection with authentic samples. The organic products from the metathesis reactions involving 1-butene and cis-2-pentene were identified by GC/MS. Yields were determined versus internal standards with measured or calculated response factors. Reactions involving gases (ethylene, 1-butene, H_2, CO) were done in glass pressure bottles (Lab Glass) connected to a metal head via an O-ring seal. Compounds were analyzed by Schwartzkopf Microanalytical Laboratories using drybox techniques.

CHAPTER 1 EXPERIMENTAL

General

$M(CHCMe_3)L_2X_3$ (M = Ta, Nb; L = THF, pyr, tertiary phosphine; X = Cl, Br) were prepared by published methods.[18] The description of the reactions of $M(CHR)(PMe_3)_2Cl_3$ (M = Ta, Nb; R = CMe_3, Ph) with olefins; the preparation and characterization of $M(CHCMe_3)(OCMe_3)_x(PMe_3)_yCl_{3-x}$ (M = Ta, Nb; x = 1, 2; y = 1, 2); the transalkylidenation reactions involving $M(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ (M = Ta, Nb) (including yields of organic products) can be found in ref. 19b.

Reactions of Alkylidene Complexes with Olefins

A minimum of ca. 0.5 mmol of complex was dissolved in 5 mL of an appropriate solvent (toluene, benzene, mesitylene) containing an internal GLC standard (e.g., heptane or nonane) and treated with cis-2-pentene, ethylene, propylene, or 1-butene in a pressure bottle. Samples were withdrawn with a cold syringe and air oxidized before being analyzed by GLC. Samples from reactions involving tert-butoxide complexes were passed down a short alumina column (followed by solvent rinses) to free them of tert-butyl alcohol since it interfered with the GLC analysis of 3,3-dimethyl-1-butene.

Preparation of $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$. $LiOCMe_3$ (0.80 g, 10 mmol) in 10 mL of ether was added dropwise to a stirred solution of $Ta(CHCMe_3)(PMe_3)_2Cl_3$ (2.55 g, 5 mmol) in 20 mL of ether at -30°C. As the purple reaction mixture was allowed to warm to 25°C, LiCl precipitated and the solution became yellow. After 2 h at 25°C the mixture was filtered and the ether was removed from the filtrate in vacuo to give a yellow solid (2.4 g). The solid was dissolved in pentane, and the solution was treated with activated charcoal and filtered. Concentrating and cooling the pentane solution to -30°C gave light yellow crystals of $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ (1.65 g, 65%). Samples sometimes contain $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)_2Cl$ which can be converted to $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ by exhaustively removing excess PMe_3 in vacuo from a toluene solution before recrystallizing from pentane.

$Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ (0.25 mmol) reacted immediately with a twofold excess of sieve-dried reagent acetone to give 0.8 equiv of 2,4,4-trimethyl-2-pentene.

The NMR, IR, molecular weight, and microanalytical data can be obtained from ref. 19b.

Preparation of $Nb(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$. The bright yellow Nb complex can be prepared by a procedure analogous to that used to prepare $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ in slightly lower yield (55%). The spectroscopic data can be found in ref. 19b.

Observation of $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)_2Cl$. Addition of excess PMe_3 to a sample of $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ yielded $Ta(CHCMe_3)(OCMe_3)(PMe_3)_2Cl$ in situ at low temperature. At room temperature the ratio of $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl$ to $Ta(CHCMe_3)(OCMe_3)_2(PMe_3)_2Cl$ depended upon the amount of excess PMe_3, sample concentration, etc.

^1H NMR (tol-d_8, -45°C, 270 MHz, ppm): 9.15 (t, 1, $^3J_{HP}$ = 3.4, $C\underline{H}CMe_3$), 1.48 (s, 9, $OC\underline{Me}_3$), 1.45 (s, 9, $OC\underline{Me}'_3$), 1.27 (t, 18, $^2J_{HP}$ = 3.0, PMe_3), 1.21 (s, 9, $\mathrm{CHC\underline{Me}_3}$). ^{13}C NMR (tol-$d_8$, -45°C, 67.89 MHz, ppm): 275.1 (dt, $J_{CH} \approx 123$, $^2J_{CP} = 8$, $\mathrm{\underline{C}HCMe_3}$), 79.8 (s, $\mathrm{O\underline{C}Me_3}$), 78.8 (s, $\mathrm{O\underline{C}Me_3'}$), 43.1 (s, $\mathrm{CH\underline{C}Me_3}$), 36.0 (q, $J_{CH} = 130$, $\mathrm{CHC\underline{Me}_3}$), 32.9 (q, $J_{CH} = 123$, $\mathrm{OC\underline{Me}_3}$), 32.3 (q, $J_{CH} = 123$, $\mathrm{OC\underline{Me}_3'}$), 16.3 (qt, $J_{CH} = 133$, $J_{CP} = 11.5$, $\mathrm{PMe_3}$). ^{31}P{^{1}H} NMR (tol-d_8, -60°C): -14 (s).

At 25°C $\mathrm{PMe_3}$ is not exchanging rapidly with coordinated $\mathrm{PMe_3}$ in either $\mathrm{Ta(CHCMe_3)(OCMe_3)_2(PMe_3)_2Cl}$ or $\mathrm{Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl}$ by ^{31}P NMR, but only a trace of $\mathrm{Ta(CHCMe_3)(OCMe_3)_2(PMe_3)_2Cl}$ is present, and at -60°C $\mathrm{Ta(CHCMe_3)(OCMe_3)_2(PMe_3)_2Cl}$ is by far the major component; it is the only one if several equivalents of $\mathrm{PMe_3}$ have been added. This property causes some problems if $\mathrm{Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl}$ is crystallized at low temperatures in the presence of $\mathrm{PMe_3}$. Only by slowly removing all volatiles at room temperature can one obtain a pure sample of $\mathrm{Ta(CHCMe_3)(OCMe_3)_2(PMe_3)Cl}$ consistently.

Observation of $\mathrm{Nb(CHCMe_3)(OCMe_3)_2(PMe_3)_2Cl}$. The sample behavior is the same as that noted for Ta above.

^{1}H NMR (tol-d_8, -45°C, 270 MHz, ppm): 11.55 (t, 1, $^3J_{HP} = 4.2$, $\mathrm{C\underline{H}CMe_3}$), 1.48 (s, 18, $\mathrm{OC\underline{Me}_3}$), 1.21 (t, 18, $^2J_{HP} = 2.7$, $\mathrm{PMe_3}$), 1.14 (s, 9, $\mathrm{CHC\underline{Me}_3}$). ^{13}C{^{1}H} NMR (tol-d_8, 67.89 MHz, -25°C): 293 (br, $\mathrm{\underline{C}HCMe_3}$), 80.4 (s, $\mathrm{O\underline{C}Me_3}$), 79.4 (s, $\mathrm{O\underline{C}Me_3'}$), 44.4 (s, $\mathrm{CH\underline{C}Me_3}$), 33.5 (s, $\mathrm{CHC\underline{Me}_3}$), 32.7 (s, $\mathrm{OC\underline{Me}_3}$), 32.2 (s, $\mathrm{OC\underline{Me}_3'}$), 16.1 (t, $J_{CP} = 8.9$, $\mathrm{PMe_3}$). ^{31}P{^{1}H} NMR (tol-d_8, -80°C): -19 (br s).

Preparation of $\mathrm{Ta(CHCMe_3)(OCMe_3)_3}$. $\mathrm{Ta(CHCMe_3)(THF)_2Cl_3}$ (3.0 g, 6.0 mmol) was dissolved in 25 mL of ether and cooled to -20°C. A cold solution of $\mathrm{LiOCMe_3}$ (1.44 g, 17.9 mmol) in ether was added while the mixture was being stirred. The reaction immediately turned orange, and after about 1 h, it turned yellow. After the solution was stirred for 8 h the LiCl was filtered off and the ether removed in vacuo to yield an orange oil that was extracted with pentane (25 mL), filtered, and the pentane removed in vacuo yielding pure product.

^{1}H NMR (C_6D_6, 60 MHz, ppm): 4.10 (s, 1, $C\underline{H}CMe_3$), 1.30 (s, 9, $CHC\underline{Me}_3$), 1.25 (s, 27, $OC\underline{Me}_3$). ^{13}C NMR (C_6D_6, 22.5 MHz, ppm): 210.2 (d, J_{CH} = 96, $\underline{C}HCMe_3$), 78.1 (s, $O\underline{C}Me_3$), 42.2 (s, $CH\underline{C}Me_3$), 36.6 (q, J_{CH} = 125, $CHC\underline{Me}_3$), 32.3 (q, J_{CH} = 125, $OC\underline{Me}_3$).

Preparation of $Ta(CHCMe_3)(DME)Cl_3$. 1,2-Dimethoxyethane (2 mol equiv) is added to a stirring CH_2Cl_2 solution of $Ta(CH_2CMe_3)_2Cl_3$ (2.15 g, 5 mmol). The yellow-orange reaction slowly turns purple-red after 5 days. The solvent is removed in vacuo yielding 2.1 g (94% yield) of purple-pink microcrystals.

^{1}H NMR (C_6D_6, 60 MHz, ppm): 3.43 (s, 1, $C\underline{H}CMe_3$), 3.18 - 3.75 (br s, 10, $C\underline{H}_3OC\underline{H}_2C\underline{H}_2OC\underline{H}_3$), 1.20 (s, 9, $CHC\underline{Me}_3$). ^{13}C NMR (C_6D_6, 22.5 MHz, ppm): 252.5 ($\underline{C}HCMe_3$), 75.7, 74.2, 70.6, 61.1 ($CH_3OCH_2CH_2OCH_3$), 45.0 ($CH\underline{C}Me_3$), 33.7 ($CHC\underline{Me}_3$).

Preparation of cis-$CH_3CH_2CH{=}CHCH_2NMe_2$ (IV-3, 4). In a dry 100 mL Schlenk flask were placed 100 mg of 5% $Pd/BaSO_4$ and $CH_3CH_2C{\equiv}CCH_2NMe_2$ (5.56 g, 50 mmol) in dry quinoline (50 mL). H_2 was passed through the brown slurry with a gas dispersion tube at RT. After 1 hr no alkyne was present by GLC. The mixture was filtered through Celite and the alkene was distilled out of the quinoline at 90°C. The ^{1}H NMR confirms the material to be the cis-alkene.

Preparation of cis-$CH_3CH_2CH{=}CHCH_2CH_2OCH_3$ (IV-32). Cis-3-hexene-1-ol was stirred with 50% aqueous NaOH containing $(nBu)_4NBr$. 1.2 mol equiv of CH_3I was added and the reaction stirred overnight. The mixture was extracted with ether, dried over anhydrous $MgSO_4$, and the product distilled at 130°C. Identification and purity were determined by NMR and GLC.

Preparation of cis-$CH_3CH_2CH{=}CHCH_2CH_2OSiMe_3$ (IV-31). 1 mol equiv of $(CH_3)_3SiCl$ (freshly distilled) and 1 mol equiv of Et_3N were added to a stirring THF solution of cis-3-hexene-1-ol. The reaction was heated gently overnight. The amine salt was filtered off and the silyl ether distilled at 170°C. Identification and purity were determined by NMR and GLC.

CHAPTER 2

THE PREPARATION OF ORGANOIMIDO AND μ-DINITROGEN COMPLEXES OF TANTALUM AND NIOBIUM FROM NEOPENTYLIDENE COMPLEXES

INTRODUCTION

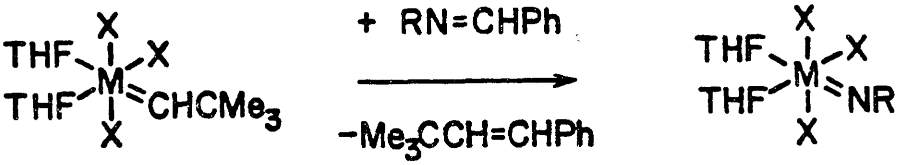
In Chapter 1, we observed that simple alkylidene complexes such as $M(CHCMe_3)(THF)_2Cl_3$ (M = Ta, Nb) react with internal olefins to give several turnovers of metathesis products. Therefore we became interested in the possibility of developing a metathesis-like reaction of organic imines (RN=CHR) with the alkylidene complexes to prepare simple organoimido analogues, $M(NR)(THF)_2Cl_3$. Organoimido complexes are known for all of the Group IV through VIII transition metals except technetium.[41] $Ta(NEt)(NEt_2)_3$ was one of the first organoimido complexes reported (1962).[42] However, little progress on Group V imido complexes has appeared since.

Sharpless has developed the use of osmium alkylimido complexes in the oxyamination[43] and diamination[44] of olefins. Imido complexes have been implicated as intermediates in the Haber ammonia process[45] and the ammoxidation of propylene to acrylonitrile.[45] The higher oxidation states of molybdenum and tungsten can be stabilized with the imido,[35,46] as well as, oxo ligand.[46]

After our initial success with simple imines, it became apparent that a metathesis reaction between a diimine, PhCH=NN=CHPh, and 2 equivalents of $M(CHCMe_3)(THF)_2Cl_3$ could lead to molecules having an M=N-N=M linkage; i.e., μ-dinitrogen complexes. In this chapter we discuss the synthesis, characterization (multi-nuclear NMR, IR, and X-ray analysis), and a few reactions of alkylimido and μ-dinitrogen complexes prepared by metathesis-like reactions. Simplicity and high yields make these unique routes attractive as entries into alkylimido[47] and μ-dinitrogen[48] chemistry of niobium and tantalum.

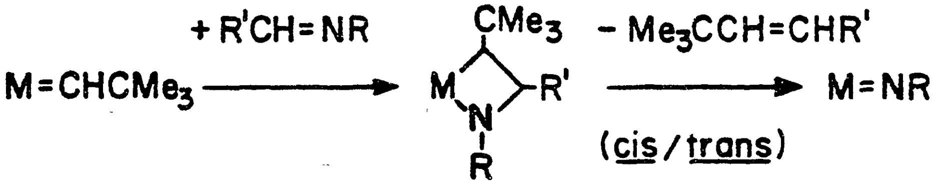
RESULTS

Preparation and Reactions of $M(NR)L_2X_3$ (M = Ta, Nb; L = THF, tertiary phosphine; X = Cl, Br, CH_2CMe_3). When RN=CHPh is added to $M(CHCMe_3)(THF)_2X_3$ in ether, cis- and trans-Me_3CCH=CHPh and the yellow (R = Ph) or white (R = Me or CMe_3) imido complexes form quantitatively (eq 1). When PhN=CHPh is added to $M(CHCMe_3)(THF)_2X_3$ the reaction is complete in 1 hour. However, when PhN=$CHCMe_3$ is used, the reaction takes 18-20 hours, and when Me_3CN=$CHCMe_3$ is used, no reaction is observed after 24 h at 25°C. These results can all be explained by steric considerations in an intermediate containing an MC_2N ring (eq 2). The cis,mer configuration for $M(NR)(THF)_2X_3$ is proposed



(1)

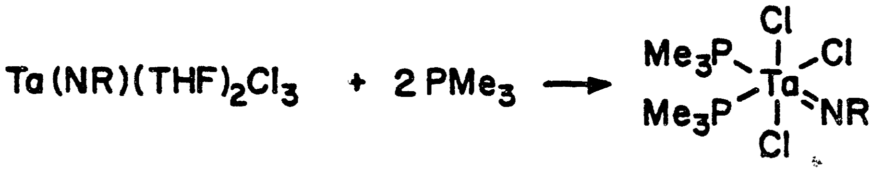
M = Nb, Ta; X = Cl, Br; R = Ph, CMe_3, Me



(2)

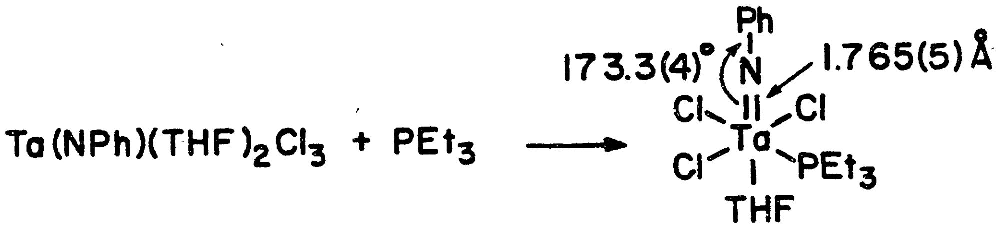
on the basis of the presence of two types of THF ligands in the ^1H NMR spectra. When THF is added to the sample the signals for coordinated THF are broadened due to exchange of the free THF with the coordinated THF.

The reaction between $Ta(NR)(THF)_2X_3$ and PMe_3 gives light yellow $Ta(NR)(PMe_3)_2Cl_3$ (eq 3). The cis,mer configuration is proposed since



(3)

the PMe$_3$ ligands are inequivalent (-11.65 and -40.0 ppm in the $^{31}P\{^1H\}$ NMR spectrum at -30°C) and one of them (we propose the PMe$_3$ ligand trans to the imido ligand at -40.0 ppm) exchanges faster with added PMe$_3$ at temperatures above ca. -30°. When one equivalent of PEt$_3$ is added to Ta(NR)(THF)$_2$Cl$_3$ one THF is displaced to give Ta(NPh)(THF)(PEt)$_3$Cl$_3$ (eq 4). A single



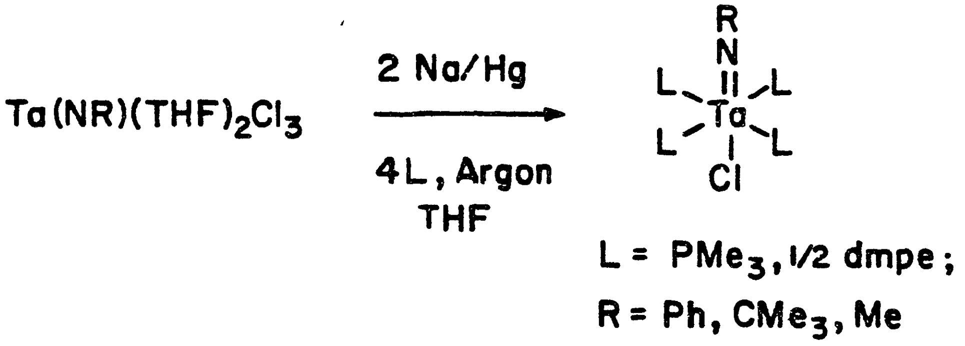
(4)

crystal x-ray study by Churchill[49] shows the complex to be an octahedral species containing a THF molecule trans to the imido function. The three meridional chlorides have Ta-Cl distances of 2.366(2)Å to 2.389(2)Å. The Ta-P and Ta-O distances are 2.667(2)Å and 2.378(4)Å, respectively. As expected, the nearly linear Ta-N-C system (173.3(4)°) has a Ta=N bond length of 1.765(5)Å. This distance compares favorably with 1.77(2)Å for the Ta=N bond in $Ta(NMe_2)_3(NBu^t)$[50] and is generally thought to represent a metal-nitrogen bond order between two and three.

Addition of $MgNp_2$(dioxane) to $Ta(NPh)(THF)_2Cl_3$ yields white $Ta(NPh)Np_3(THF)$. By ^1H NMR it appears that $Ta(NPh)Np_3(THF)$ is a trigonal bipyramid with the three neopentyl groups in equatorial positions. $Ta(NPh)(CH_2CMe_3)_3(THF)$ is thermally stable and does not decompose readily to an alkylidene complex,[15] even in the presence of PMe_3.

—$Ta(NPh)(THF)_2Cl_3$ reacts cleanly with 1 equivalent of benzaldehyde to give diphenylimine in high yield. The initial metal containing product is probably the oxo analog of the imido complex, but no product could be readily identified.

Preparation and Reactions of $Ta(NR)L_4Cl$ (R = Ph, CMe_3, CH_3; L = PMe_3 or 1/2 dmpe. $Ta(NR)(THF)_2Cl_3$ can be reduced with two equivalents of sodium amalgam in THF to give $Ta(NR)L_4Cl$ complexes in high yield (eq 5). The phosphine ligands in $Ta(NR)(PMe_3)_4Cl$ are labile, probably for steric reasons. Therefore $Ta(NR)(PMe_3)_4Cl$ did not analyze well. $Ta(NR)(dmpe)_2Cl$ did, however. The structure shown in equation 5 is based on the facts that

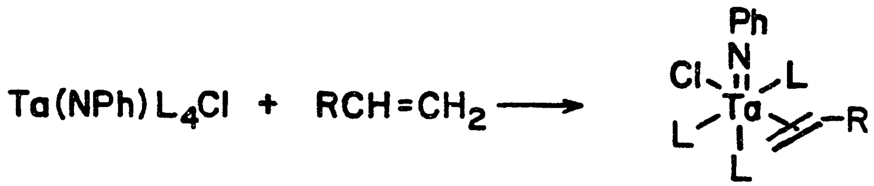


L = PMe_3, 1/2 dmpe;
R = Ph, CMe_3, Me

(5)

down to -80° the phosphorus nuclei are all equivalent by $^{31}P\{^1H\}$ NMR, and the methyl group ($R = CH_3$) is a quintet in the ^1H NMR spectrum ($J_{HP} = 3.5$ Hz).

Although the Ta(V) imido complexes did not react with olefins, $Ta(NPh)(PMe_3)_4Cl$ reacts readily with ethylene or styrene to displace one PMe_3 ligand and give imido-olefin complexes (eq 6). As expected, Ta(NPh)-



(6)

$(dmpe)_2Cl$ does not react with ethylene or styrene. We proposed the structure for $Ta(NPh)L_3$(olefin) shown in equation 6 based on the following information: a triplet and doublet are found in a 1:2 ratio ($J_{PP} = 14.6$ Hz) in the $^{31}P\{^1H\}$ NMR spectrum, only one ethylene carbon is observed in the $^{13}C\{^1H\}$ NMR spectrum, and the unique phosphine exchanges readily with free phosphine on the NMR time scale. We believe the unique phosphine would be more labile if it were trans to the imido group as shown, rather than trans to the olefin.

NMR and IR Studies of Tantalum Imido Complexes. One of the most powerful tools for the study of diamagnetic organoimido complexes is nuclear magnetic resonance spectroscopy. The ^1H NMR of methylimido complexes shows a downfield shift of the methyl group from the free amine (NMe_3; 2.12δ). The methylimido group in $Ta(NMe)(PMe_3)_4Cl$ is observed at 2.96δ while the methylimido group in $Ta(NMe)(THF)_2Cl_3$ is found at 4.62δ.

No ^{15}N NMR studies on imido ligands have been reported.[41] We decided to make ^{15}N-labelled imido complexes since our high yield method could be employed in a small scale reaction and since ^{15}N-labelled aniline, used to prepare $Ph^{15}N{=}CHPh$, is readily available. The ^{15}N chemical shifts for four compounds, referenced to liquid NH_3, are listed in Table I. It is interesting to compare these data with the ^{13}C chemical shifts for the α-carbon atoms in the analogous neopentylidene complexes. In each case the chemical shift of the nitrogen or carbon atom bound to the more reduced metal is found at higher field.

Table I. ^{15}N and ^{13}C Chemical Shift Data for Some Phenylimido and Neopentylidene Complexes of Tantalum[a]

Compound	Solvent	^{15}N (ppm)	Compound	C_α (ppm)
$Ta(NPh)(THF)_2Cl_3$	THF	369	$Ta(CHCMe_3)(THF)_2Cl_3$	254
$Ta(NPh)(PEt_3)_2Cl_3$	THF	353	$Ta(CHCMe_3)(PEt_3)_2Cl_3$	254
$Ta(NPh)(dmpe)_2Cl$	C_6H_5Cl	303	$Ta(CHCMe_3)(dmpe)_2Cl$	217
$Ta(NPh)(PMe_3)_4Cl$	THF	304	$Ta(CHCMe_3)(PMe_3)_4Cl$	208

[a] Aniline-^{15}N (ppm 56.5) used as external reference and shifts corrected to liquid $^{15}NH_3$. For $Ph^{15}N{=}CHPh$ in $CHCl_3$ the ^{15}N chemical shift is 326 ppm.

Nugent has pointed out that the ^{13}C chemical shifts for t-butylimido compounds can provide some insight into the nature of the metal-nitrogen bond.[41] The difference in chemical shift between the α and β carbon resonances of the t-butyl group can be considered a qualitative measure of the electron density on the imido nitrogen atom.[41] For example, $OsO_3(NBu^t)$, an electrophilic imido species,[43] has a Δ-value of 55, while the nucleophilic main group phosphinimine, Ph_3PNBu^t, displays a Δ-value of 16. Tantalum and niobium complexes, $M(NMe_2)_3(NBu^t)$, have Δ-values of 32 and 35, respectively.[41] The Δ-values for a series of t-butyl imido complexes we have prepared are listed in Table II. Although we know that the reactions of analogous alkylidene complexes depend markedly on what halides and other ligands (THF or PR_3) are present,[19] the difference of only 1 ppm between the Δ-values for $Ta(NCMe_3)(THF)_2Br_3$, $Ta(NCMe_3)(THF)_2Cl_3$, and $Ta(NCMe_3)(PMe_3)_2Cl_3$ suggests that Δ-values are not a sensitive measure of the influence of ligands upon the reactivity of the metal-nitrogen bond. However, the Δ-values do respond in the direction they should to a lowering of the oxidation state.

Table II. ^{13}C Chemical Shift Data for Some t-Butylimido Complexes[a]

Complex	C_α (ppm)	C_β (ppm)	Δ
$Ta(NCMe_3)(THF)_2Br_3$	67.0	32.0	35
$Ta(NCMe_3)(THF)_2Cl_3$	66.3	32.0	34
$Ta(NCMe_3)(PMe_3)_2Cl_3$	66.2	32.2	34
$Ta(NCMe_3)(PMe_3)_4Cl$	63.4	35.6	28
$Ta(NCMe_3)(dmpe)_2Cl$	62.6	35.6	27[b]

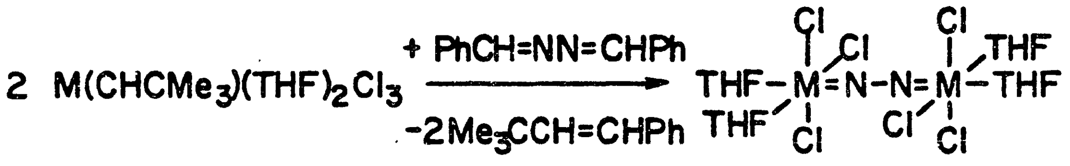
[a] Solvent = tol-d_8, T = 238K unless otherwise noted. [b] T = 305K.

Few careful ^{15}N infra-red studies on organoimido complexes have been reported.[41] Locating the "M=N" vibrational modes can be troublesome since they are prone to couple with, or be obscured by, other metal-ligand modes and especially with modes of the organic substituent on the imido nitrogen atom. The IR spectra of several ^{15}N-labelled phenylimido complexes are identical to those of the ^{14}N phenylimido complexes, except a peak at ~1350 cm^{-1} in the spectra of the ^{15}N complexes is shifted 20-25 cm^{-1} to lower energy in the spectra of the ^{15}N complexes (Table III). The fairly high energy absorptions support the contention that these bands probably represent some combination of the Ta=N stretching mode coupled to the N-C stretching mode.[41]

Table III. IR Data for Phenylimido Complexes

Complex	$\nu_{Ta^{14}NR}(cm^{-1})$	$\nu_{Ta^{15}NR}(cm^{-1})$	Δ
$Ta(NPh)(THF)_2Cl_3$	1360	1335	25
$Ta(NPh)(PMe_3)_2Cl_3$	1345	1325	20
$Ta(NPh)(PMe_3)_4Cl$	1340	1318	22
$Ta(NPh)(dmpe)_2Cl$	1350	1328	22
$Ta(NPh)(C_2H_4)(PMe_3)_3Cl$	1355	1332	23

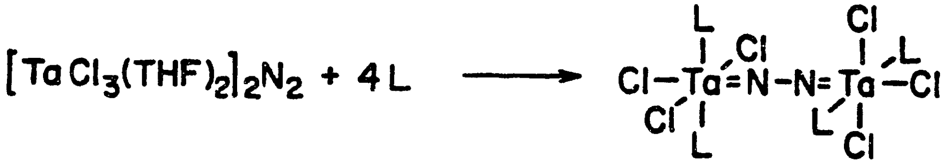
Preparation of μ-Dinitrogen Complexes. Preparation of $\{MCl_3L_2\}_2(\mu\text{-}N_2)$ (M = Ta, Nb; L = THF, tertiary phosphine). We wanted to extend the reaction of imines with alkylidene complexes to diimines, such as benzalazine, to see if dimeric compounds containing a $\mu\text{-}N_2$ bridge could be prepared. When PhCH=NN=CHPh is added to an ether solution containing 2 equivalents of $M(CHCMe_3)(THF)_2Cl_3$, cis and trans-$Me_3CCH{=}CHPh$ and the orange (M = Ta) or light plum-colored (M = Nb) dinitrogen complexes are formed in high yield (95%, M = Ta; 70%, M = Nb). The tantalum complex is an orange powder that precipitates from ether as it forms. It has extremely low solubility and is only sparingly soluble in CH_2Cl_2. The niobium complex behaves similarly. We propose the structure shown in equation 7 by analogy with the alkyl imido analogue shown in equation 1.



(7)

M = Ta or Nb

The THF ligands are displaced from $[TaCl_3(THF)_2]N_2$ by several phosphines to give bis-phosphine complexes (eq 8). Since the bis-phosphine complexes all display only one type of phosphorus atom in the $^{31}P\{^1H\}$ NMR spectra, they are formulated as shown in equation 8.



(8)

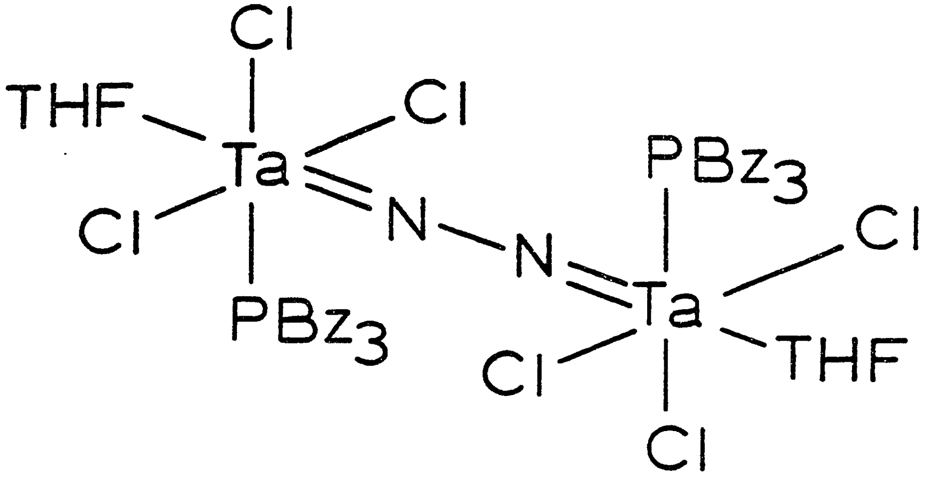
L = PMe_2Ph, PEt_2Ph, PEt_3, PPr_3

When PBz_3 (Bz = CH_2Ph) is added to $[TaCl_3(THF)_2]_2N_2$, however, a monophosphine adduct, $[TaCl_3(THF)(PBz_3)]_2N_2$, is obtained. A single x-ray diffraction study on $[TaCl_3(THF)(PBz_3)]_2N_2$ has been performed by M. Churchill.[51] As is shown in figure 1 the bimolecular tantalum (V) complex lies on a crystallographic center of symmetry. The three chloride ligands are arranged in a meridional configuration with the Ta-Cl distances ranging from 2.375(1)Å to 2.385(2)Å. The octahedral coordination geometry about each tantalum center is completed by a tribenzylphosphine ligand (Ta-P = 2.689(1)Å), a THF ligand (Ta-O = 2.038(4)Å), and one nitrogen atom of the μ-dinitrogen bridge. The Ta=N distance (1.796(5)Å) compares favorably with that in $Ta(NPh)Cl_3(THF)(PEt_3)$ (vide supra). The rather long N-N distance (1.282(6)Å) and essentially linear Ta=N-N arrangement (178.9(4)°) suggest that the valence bond description, Ta=N-N=Ta, has some validity.

Preparation of $[MX_3L]_2(\mu-N_2)$ (M = Ta, Nb; X = CH_2CMe_3, $OCMe_3$; L = THF, PMe_3). The chloride ligands in $[MCl_3(THF)_2]_2N_2$ can be cleanly substituted by $Mg(CH_2CMe_3)_2$(dioxane) to yield the yellow (M = Ta) or orange (M = Nb) dinitrogen complexes shown in equation 9. The neopentyl groups are equi-

Figure 1. The Crystal Structure of $[TaCl_3(THF)(PBz_3)]_2N_2$

STRUCTURE OF $\{TaCl_3(THF)(PBz_3)\}_2(\mu\text{-}N_2)$



	$\{(\eta^5\text{-}C_5Me_5)_2Zr(N_2)\}_2(\mu\text{-}N_2)$
Ta — N : 1.796(5) Å	Zr — N : 2.08 Å
N — N : 1.282(6) Å	N — N : 1.18 Å
∠ Ta—N—N : 178.9(4)°	∠ Zr—N—N : 177.0°

$$[MCl_3(THF)_2]_2N_2 + 3\,MgNp_3(diox) \longrightarrow [MNp_3(THF)]_2N_2$$

$$M = Ta \text{ or } Nb$$

valent by NMR so we propose that they occupy the equatorial positions of a trigonal bipyramidal arrangement of ligands about each metal with the THF trans to the bridging N_2. Thus $[MNp_3(THF)]_2N_2$ has the same basic geometry as $Ta(NPh)Np_3(THF)$ (vide supra). An analogous reaction employing $KOCMe_3$ gives pale yellow $[Ta(OCMe_3)_3(THF)]_2N_2$ in good yield. The NMR shows the geometry to be similar to $[MNp_3(THF)]_2N_2$, as expected. The ligated THF can be displaced from yellow $[TaNp_3(THF)]_2N_2$ with excess PMe_3 at ca. 25°C to give the monophosphine adduct, $[TaNp_3(PMe_3)]_2N_2$, in quantitative yield.

We have not labelled any of the μ-N_2 complexes with ^{15}N for IR and ^{15}N NMR studies. We will show in the next chapter that μ-N_2 complexes can be prepared directly from N_2, and by ^{15}N labelling that a characteristic IR mode for Ta=N-N=Ta complexes is found at ~845 cm^{-1}. In the IR spectrum of $[TaCl_3(PEt_3)_2]_2N_2$ there is a medium strength peak at 855 cm^{-1} which we assign to the Ta_2N_2 stretching mode. In other complexes we report here the 850 cm^{-1} region is obscured by peaks due to other ligands.

Reactions of $\{MX_3L_2\}_2N_2$ with Acetone and HCl (M = Ta, Nb; X = Cl, CH_2CMe_3, $OCMe_3$; L = THF, tertiary phosphine). As discussed earlier, the tantalum alkylimido complexes react with ketones in a nucleophilic manner to yield organic imines and Ta=O species. One measure of how valid the Ta=N-N=Ta description is whether our μ-N_2 complexes also will react with carbonyl compounds. Acetone is a fairly good choice for these studies since the cleavage product, dimethylketazine ($Me_2C=NN=CMe_2$), can be readily identified by GLC (Carbowax 20M column). Several of the μ-N_2 complexes were treated with ten equivalents of acetone. In all cases dimethylketazine is formed (Table IV). A side product which is formed in greater than 100% yield in the poorest reactions is mesityl oxide (4-methyl-3-penten-2-one). This condensation product of acetone is also formed when acetone reacts with other tantalum compounds such as $TaCl_5$, $TaCl_3(PMe_3)_3$, and $Ta(C_2H_4)(PMe_3)_2Cl_3$. $[TaCl_3(THF)_2]_2N_2$ is too insoluble to react readily with acetone, but some dimethylketazine is still observed. These results lend some credence to the proposal that the μ-N_2 is behaving as an imido ligand.

Table IV. Reactions of μ-N_2 Complexes with Acetone or HCl[a]

Complex	$N_2H_4 \cdot 2HCl$[b]	$(Me_2C=N\}_2$	$Me_2C=CHCOMe$
$[TaCl_3(THF)_2]_2N_2$	80	<20	>100
$[TaCl_3(PR_3)_2]_2N_2$	85	50	34
$[Ta(OBu^t)_3(THF)]_2N_2$	90	52	66
$[TaNp_3(THF)]_2N_2$	86	60	31

[a] Expressed as mol percent vs. metal. [b] ±10% accuracy.

DISCUSSION

The number of known organoimido complexes of niobium and tantalum is not large. The three types are $M(NR)(NR'R'')_3$,[50,52] $[Cl_3M{=}N(Me)C]_2$ and related species,[53,54] and $M(CH_2CMe_3)_3[N(Me)C{=}CHCMe_3]$.[55] The approach we have used is potentially the most general method of preparing niobium and tantalum imido complexes, since it should be successful for a number of different organic groups on the imido ligand, and once $M(NR)(THF)_2Cl_3$ is prepared, the chlorides may be replaced by the desired anionic ligand. Since the starting complexes, $M(CHCMe_3)(THF)_2Cl_3$, can be prepared in high yield from MCl_5 and $Zn(CH_2CMe_3)_2$, the overall yield of an imido complex is high.

It is not surprising that the organoimido complexes should react with the carbonyl function to give imines and metal oxides. Nugent found that $M(NCMe_3)(NR_2)_3$ complexes did also.[50] It is reasonable that a more electronegative element should be able to form a stronger bond to an electropositive metal than the element immediately to the left of it.

The ^{15}N-labelling studies provide some new information about metalloimido complexes as the ^{15}N NMR spectra have resonances ranging from 300δ to 370δ depending upon the ligand substitution and oxidation state of the metal. The range of known ^{15}N chemical shifts is from 0δ to ~800δ.[56] Although the bands in the IR spectra are probably not representative of a pure metal-nitrogen mode, the ^{15}N-labelling confirmed that the peaks at ~1350 cm^{-1} are associated with the metal-organoimido functionality.

It was interesting to find that our method can be used to prepare μ-dinitrogen complexes, the first characterizable ones of niobium or tantalum to be reported in the literature.[57] Even more interesting is the fact that they appear to be structurally unique among the hundreds of μ-dinitrogen complexes which are known.[58] The N-N bond in $[TaCl_3(THF)(PBz_3)]_2N_2$ is the longest by approximately 0.08Å in any simple μ-N_2 complex[60] whose structure has been determined accurately.[62] As to whether the N-N bond is a "true" single bond or not is moot since there is no equivalent system which contains a metal with which to compare it. For example, the closest organic system is benzalazine,[64] where the sp^2 hybridized N-N bond is 1.38Å long. But in the imido-like dinitrogen complex each nitrogen should be viewed as being sp hybridized because the Ta=N-N=Ta system is nearly linear. The N-N bond would be shorter than 1.38Å either because of the rehybridization (and π-electron donation from N to Ta,[41] or conjugation throughout the Ta=N-N=Ta system.

The reaction of the μ-N_2 complexes with acetone to give dimethylketazine tends to confirm the implications of the structural results -- the Ta=N bond reacts as it does in an organoimido complex. Not surprising, then, is the fact that these μ-N_2 complexes react with HCl to give hydrazine. These μ-N_2 complexes appear to contain the most "activated" dinitrogen to date (in a simple M_2N_2 system[60]) in the sense that the dinitrogen most closely approaches a μ-N_2^{4-} ligand.

It is interesting to compare our tantalum μ-N_2 complexes with $[Cp''_2Zr(N_2)]_2(\mu$-$N_2)$[65] ($Cp'' = \eta^5$-C_5Me_5) and $[Cp''_2Ti(N_2)]_2(\mu$-$N_2)$.[66] The μ-N_2 ligands do not have exceptionally long N-N bonds (1.182(5) and 1.155(14)-1.165(14Å, respectively), yet they do react with HCl to give high yields of hydrazine. What is unknown at this stage is whether the titanium and zirconium complexes also react with acetone to give dimethylketazine. Irrespective of whether they do or not, it is still puzzling why the μ-N_2 ligands in the Ti and Zr species are not more like μ-N_2^{4-} ligands structurally. Perhaps they are not because terminal imido[41] (or oxo[67]) complexes of the Group IV metals may not be as favorable as those containing bridging imido or oxo ligands, for electronic reasons, rather than simply because the coordination number of a Group VI metal complex is often low. Niobium and tantalum, on the other hand, form strong bonds to O, NR, or CHR.

Addendum

As discussed earlier, the reaction of PhCH=NN=CHPh with 2 equivalents of $Ta(CHCMe_3)(THF)_2Cl_3$ cleaves both C-N double bonds and produces $[TaCl_3(THF)_2]_2N_2$. We attempted to cleave only one of the C-N bonds by slowly adding $Ta(CHCMe_3)(THF)_2Cl_3$, dissolved in ether, to an excess of PhCH=NN=CHPh in ether. The product, $Ta(NN{=}CHPh)(THF)_2Cl_3$, precipitates from solution, as an orange-red solid, as it forms. This "half-azine" complex is insoluble in most hydrocarbons but slightly soluble in chloroform and benzene. The ^{1}H NMR shows phenyl and THF resonances. The IR has a medium strength broad peak ~1580 cm^{-1} (phenyl and C=N stretch), a strong sharp peak ~1210 cm^{-1} (Ta=N stretch), and a broad peak ~825 cm^{-1} (Ta-O stretch).

The reaction of $Ta(=NN{=}CHPh)(THF)_2Cl_3$ with $Nb(CHCMe_3)(THF)_2Cl_3$ gives a nearly quantitative yield of cis/trans-$Me_3CCH{=}CHPh$ and an insoluble flesh-orange colored solid. The IR spectrum looks good for the mixed-metal μ-dinitrogen dimer, $[TaCl_3(THF)_2]N_2[NbCl_3(THF)_2]$. (VI-19, 20, 21)

CHAPTER 2 EXPERIMENTAL

$M(CHCMe_3)(THF)_2X_3$[18] (M = Ta, Nb; X = Cl, Br) and PMe_3[68] were prepared by published methods. PEt_3 was a gift from S. Pedersen and dmpe from G. Rupprecht. PMe_2Ph, PEt_2Ph, and $P(CH_2C_6H_5)_3$ were purchased (Strem) and used as received. Imines were prepared by condensation of the appropriate aldehyde and amine and purified by standard methods. We believe the extreme lability of PMe_3 in $Ta(NR)(PMe_3)_4Cl$ prevented acceptable C and H analyses.

Preparations

$Ta(NPh)(THF)_2Cl_3$

$Ta(CHCMe_3)(THF)_2Cl_3$ (10.0 g, 20.0 mmol) was dissolved in ether (40 mL) and the solution was cooled to -30°C. PhNCHPh (3.62 g, 20.0 mmol) was added and the reaction allowed to warm to room temperature. After 30 min yellow crystals began forming and after 90 min 8.4 g (81% yield) of product was isolated by filtration. Cis and trans $Me_3CCH{=}CHPh$ were identified by GC and NMR (^1H and ^{13}C).

Anal. Calcd. for $TaC_{14}H_{21}NO_2Cl_3$: C, 32.17; H, 4.05. Found: C, 31.91; H, 3.99. ^1H NMR (C_6D_6): 7.30-6.64 (m, 5, $NC_6\underline{H}_5$), 4.19 (br m, 4, $\overline{OC\underline{H}_2CH_2CH_2C\underline{H}_2}$, 3.95 (br m, 4, $\overline{OC\underline{H}_2CH_2CH_2C\underline{H}_2}$), 1.35 (br m, 4, $\overline{OCH_2C\underline{H}_2C\underline{H}_2CH_2}$), 1.11 (br m, 4, $\overline{OCH_2C\underline{H}_2C\underline{H}_2CH_2}$).

$Ta(^{15}NPh)(THF)_2Cl_3$ was prepared using $Ph^{15}N{=}CHPh$ (^{15}N NMR data given in text).

$Ta(NMe)(THF)_2Cl_3$

$Ta(NMe)(THF)_2Cl_3$ was prepared as in the first preparation using MeN=CHPh.

Anal. Calcd. for $TaC_9H_{19}NO_2Cl_3$; C, 23.47; H, 4.16. Found: C, 23.09, H, 4.18. ^1H NMR (C_6D_6): 4.62 (s, 3, $NC\underline{H}_3$), 4.04 (br m, 4, $\overline{OC\underline{H}_2CH_2CH_2C\underline{H}_2}$), 3.87 (br m, 4, $\overline{OC\underline{H}_2CH_2CH_2C\underline{H}_2}$), 1.34 (br m, 4, $\overline{OCH_2C\underline{H}_2C\underline{H}_2CH_2}$), 1.17 (br m, 4, $\overline{OCH_2C\underline{H}_2C\underline{H}_2CH_2}$).

$Ta(NCMe_3)(THF)_2Cl_3$

$Ta(NCMe_3)(THF)_2Cl_3$ was prepared using Me_3CN=CHPh except after 2 hr the ether was removed in vacuo leaving a sticky yellow solid. The product was taken up in a minimal amount of ether, and the solution was filtered and cooled to -30°C. After 24 hr beige crystals (80% yield) were isolated by filtration.

Anal. Calcd. for $TaC_{12}H_{25}NO_2Cl_3$: C, 28.67; H, 5.01. Found: C, 28.81; H, 5.26. ^1H NMR ($CDCl_3$): 4.30 (br m, 4, $\overline{OC\underline{H}_2CH_2CH_2C\underline{H}_2}$), 4.18 (br m, 4, $\overline{OC\underline{H}_2CH_2CH_2C\underline{H}_2}$), 2.00 (br m, 4, $\overline{OCH_2C\underline{H}_2C\underline{H}_2CH_2}$), 1.88 (br m, 4, $\overline{OCH_2C\underline{H}_2C\underline{H}_2CH_2}$), 1.23 (s, 9, $NC\underline{Me}_3$). $^{13}C\{^1H\}$ NMR (tol-d_8, -35°C): 78.04 (t, J_{CH} = 154, $\overline{O\underline{C}H_2CH_2CH_2\underline{C}H_2}$), 72.02 (t, J_{CH} = 151, $\overline{O\underline{C}H_2CH_2CH_2\underline{C}H_2}$), 66.30 (s, $N\underline{C}Me_3$), 31.97 (q, J_{CH} = 124, $NC\underline{Me}_3$), 25.60 (t, J_{CH} = 133, $\overline{OCH_2\underline{C}H_2\underline{C}H_2CH_2}$).

$Nb(NPh)(THF)_2Cl_3$

$Nb(CHCMe_3)(THF)_2Cl_3$ (1.0 g, 2.42 mmol) was dissolved in a 1:1 mixture of ether and THF (5 ml). Diphenylimine (0.44 g, 2.42 mmol) was added to the deep purple solution. After 2 hr the solvent was removed in vacuo. The remaining red-brown oil was dissolved in THF. Pentane was added and the solution was cooled to -40°C to give 0.4 g (40% yield) of red crystals.

^1H NMR (tol-d_8, -30°C): 7.48 (d, 2, J_{HH} = 7.3, o-phenyl), 6.98 (t, 2, J_{HH} = 7.7, m-phenyl), 6.77 (t, 1, J_{HH} = 7.3, p-phenyl), 3.81 (br, 4, $\overline{\mathrm{OC\underline{H}_2CH_2CH_2C\underline{H}_2}}$), 3.25 (br, 4, $\overline{\mathrm{OC\underline{H}_2CH_2CH_2C\underline{H}_2}}$), 1.35 (br, 4, $\overline{\mathrm{OCH_2C\underline{H}_2C\underline{H}_2CH_2}}$), 0.89 (br, 4, $\overline{\mathrm{OCH_2C\underline{H}_2C\underline{H}_2CH_2}}$).

$Ta(NPh)(PEt_3)(THF)Cl_3$

$Ta(NPh)(THF)_2Cl_3$ (1.0 g, 1.91 mmol) was dissolved in THF (30 ml) and PEt_3 (0.23 g, 1.91 mmol) was added. After 1 hr the light orange solution was concentrated in vacuo and cooled to -30°C to give 500 mg of yellow crystals. These were dissolved in toluene (5 ml). Cooling to -30°C produced 150 mg of fluffy yellow crystals which were removed by filtration. The filtrate was cooled slowly to -30°C and left three days at this temperature to give crystals suitable for x-ray diffraction.

^1H NMR ($CDCl_3$): 7.37-6.87 (m, 5, NC_6H_5), 4.41 (br, m, 4, $\overline{\mathrm{OC\underline{H}_2CH_2C\underline{H}_2CH_2}}$ 2.02 (br, m, 4, $\overline{\mathrm{OCH_2C\underline{H}_2C\underline{H}_2CH_2}}$), 1.94 (m, 6, $PC\underline{H}_2CH_3$), 1.13 (m, 9, $PCH_2C\underline{H}_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 19.1 (s).

$Ta(NPh)(PMe_3)_2Cl_3$

$Ta(NPh)(THF)_2Cl_3$ (0.52 g, 1.0 mmol) in ether (10 ml) was treated with two equivalents of PMe_3. The yellow slurry immediately became a homogeneous orange solution. After 30 min the ether was removed in vacuo leaving a yellow crystalline solid.

^{1}H NMR (tol-d_8, -30°C): 7.17-6.64 (m, 5, NC_6H_6), 1.08 (d, 9, $^{2}J_{HP}$ = 6.7, PMe_3), 0.97 (d, 9, $^{2}J_{HP}$ = 9.2, PMe_3). $^{31}P\{^{1}H\}$ NMR (tol-d_8): -12.8 (br s), -40.8 (br s).

$Ta(^{15}NPh)(PMe_3)_2Cl_3$ was prepared from $Ta(^{15}NPh)(THF)_2Cl_3$ in a similar manner.

$Ta(NPh)(PEt_3)_2Cl_3$ was prepared in a manner analogous to that for $Ta(NPh)(PMe_3)_2Cl_3$.

^{1}H NMR (tol-d_8, -30°C): 7.40-6.69 (m, 6, NC_6H_5), 1.63 (m, 12, $P\underline{CH_2}CH_3$), 0.87 (m, 18, $PCH_2\underline{CH_3}$). $^{31}P\{^{1}H\}$ NMR (tol-d_8): 14.9 (s); 15.5 (s) at -30°C.

$Ta(NCMe_3)(PMe_3)_2Cl_3$

$Ta(NCMe_3)(PMe_3)_2Cl_3$ was prepared in a manner analogous to that for $Ta(NPh)(PMe_3)_2Cl_3$. It is a light yellow pentane-soluble oil.

$^{31}P\{^{1}H\}$ NMR (tol-d_8): -12.2 (s), -44.4 (br s); -12.5 (s), -43.2 (s) at -30°C. $^{13}C\{^{1}H\}$ NMR (tol-d_8, -35°C): 66.20 ($N\underline{C}Me_3$), 32.23 ($NC\underline{Me_3}$), 15.28 (br s, PMe_3), 12.78 (d, J_{CP} = 11.7, PMe_3).

$Ta(NPh)(PMe_3)_4Cl$

$Ta(NPh)(THF)_2Cl_3$ (3.4 g, 6.4 mmol) was dissolved in THF (75 ml) and five equivalents of PMe_3 were added. Na/Hg amalgam (0.41% wt, 72 g, 12.8 mmol) was added under Ar. The reaction immediately turned green. The mixture was stirred vigorously for 60 min. The solution was decanted and the THF was removed in vacuo. Ether (100 ml) was added to the residue and the NaCl was removed by filtration. Concentrating the ether solution in vacuo and cooling to -30°C induced crystallization (90% yield). Ta(^{15}NPh)(PMe$_3$)$_4$Cl was prepared in a similar manner from Ta(^{15}NPh)(THF)$_2$Cl$_3$.

^{1}H NMR (C$_6$D$_6$): 7.16-6.65 (m, 5, NC$_6$H$_5$), 1.48 (t, 36, $^2J_{HP}$ = 2.4, PMe$_3$). ^{31}P{^{1}H} NMR (toluene, -50°C): -13.3 (s).

Ta(NCH$_3$)(PMe$_3$)$_4$Cl

Ta(NCH$_3$)(THF)$_2$Cl$_3$ (1.0 g, 2.1 mmol) was dissolved in THF (20 ml) and five equivalents of PMe$_3$ were added. The yellow solution turned bright red when sodium amalgam (0.41% wt, 24 g, 4.3 mmol) was added under argon. The slurry was stirred vigorously for 60 min. The solution was decanted and the THF removed in vacuo. Ether (30 ml) was added and after filtration the volume of the filtrate was reduced to 10 ml. Cooling to -30°C produced beautiful red crystals in 90% yield.

^{1}H NMR (C$_6$D$_6$): 2.96 (quint, 3, $^4J_{HP}$ = 3.5, NC$\underline{H}_3$), 1.45 (t, 36, $^2J_{HP}$ = 2.4, PMe$_3$). ^{31}P{^{1}H} NMR (tol-d$_8$, -50°C): -13.2 (br s). ^{13}C{^{1}H} NMR (tol-d$_8$, -20°C): 48.0 (NCH$_3$), 22.2 (PMe$_3$). IR (Nujol, cm^{-1}): 1340 (Ta=N-CH$_3$).

Ta(NCMe$_3$)(PMe$_3$)$_4$Cl

Ta(NCMe$_3$)(PMe$_3$)$_4$Cl was prepared in a manner analogous to that used to prepare Ta(NCH$_3$)(PMe$_3$)$_4$Cl.

^{1}H NMR (C$_6$D$_6$): 1.50 (br m, 36, PMe$_3$), 1.11 (s, 9, NCMe$_3$). ^{31}P{^{1}H} NMR (tol-d$_8$): -16.4 (br s); -15.6 (s) at -35°C. ^{13}C{^{1}H} NMR (tol-d$_8$,

-35°C): 63.35 ($N\underline{C}Me_3$), 35.57 ($NC\underline{Me}_3$), 24.34 (PMe_3).

$\underline{Ta(NCMe_3)(dmpe)_2Cl}$

Dmpe (0.18 g) and sodium amalgam (0.41% wt, 6.8 g, 1.2 mmol) were added to $Ta(NCMe_3)(THF)_2Cl_3$ (0.3 g, 0.6 mmol) in ether (25 ml). After 12 hr the reaction mixture was filtered through a Celite pad. The solvent was removed in vacuo from the orange filtrate to give 320 mg (90% yield) of pure product.

Anal. Calcd. for $TaC_{16}H_{41}NP_4Cl$: C, 32.69; H, 7.03. Found: C, 32.28; C, 7.10. ^1H NMR (C_6D_6): 1.53 (s, 24, $\underline{Me}_2PCH_2CH_2P\underline{Me}_2$), 1.21 (m, 8, $Me_2PC\underline{H}_2C\underline{H}_2PMe_2$), 0.97 (s, 9, $NC\underline{Me}_3$). $^{31}P\{^1H\}$ NMR (tol-d_8): 29.4 (s). $^{13}C\{^1H\}$ NMR (tol-d_8): 62.60 (s, $N\underline{C}Me_3$), 35.60 (q, J_{CH} = 124, $NC\underline{Me}_3$), 34.04 (t, J_{CP} = 8.1, J_{CH} = 132, $Me_2P\underline{C}H_2\underline{C}H_2PMe_2$), 20.78 (q, J_{CP} = 4.4, J_{CH} = 128, $\underline{Me}_2PCH_2CH_2P\underline{Me}_2$), 19.31 (q, J_{CP} = 5.6, J_{CH} = 128, $\underline{Me}_2PCH_2CH_2P\underline{Me}_2$).

$\underline{Ta(NPh)(dmpe)_2Cl}$

$Ta(NPh)(THF)_2Cl_3$(1.05 g, 2.0 mmol) was dissolved in THF (40 ml) and dmpe (0.60 g) added. Much precipitate forms which is believed to be polymeric $Ta(NPh)(dmpe)Cl_3$. Sodium amalgam (0.41% wt, 23 g, 4.1 mmol) was added and the slurry slowly turned green. After stirring for 18 hr the reaction mixture was filtered through a Celite pad to give a green-red filtrate that yielded light green crystals upon concentrating it in vacuo and cooling to -30°C; yield 0.95 g (70%). The ^{15}N-labelled species was prepared analogously.

$^{31}P\{^1H\}$ NMR (C_6D_6): 28.6 (s).

$Ta(NPh)(C_2H_4)(PMe_3)_3Cl_2$

An ether solution (5 ml) of $Ta(NPh)(PMe_3)_4Cl$ (0.5 g, 0.82 mmol) was stirred under 40 psi of ethylene. After 1 hr the yellow product was filtered off and recrystallized from a mixture of toluene and ether.

^1H NMR (tol-d_8): 6.94-6.49 (m, 5, NC_6H_5), 1.77 (m, 2, C_2H_4), 1.58 (m, 2, C_2H_4), 1.31 (t, 18, J_{HP} = 3.1, PMe_3), 1.19 (d, 9, J_{HP} = 4.8, PMe_3). $^{31}P\{^1H\}$ NMR (tol-d_8, -40°C): -16.2 (d, J_{PP} = 14.6), -27.2 (t, J_{PP} = 14.6). $^{13}C\{^1H\}$ NMR (C_6D_6): 128.4-119.7 (m, $N\underline{C}_6H_5$), 39.0 (s, $\underline{C}_2H_4$), 17.7 (t, J_{CP} = 10.4, PMe_3). IR (cm^{-1}, Nujol): 1355 ($Ta{=}N{-}C_6H_5$).

$Ta(^{15}NPh)(C_2H_4)(PMe_3)_3Cl$ was prepared analogously from $Ta(^{15}NPh)(PMe_3)_4Cl$.

$Ta(NPh)(CH_2CMe_3)_3(THF)$

$Ta(NPh)(THF)_2Cl_3$ (2.09 g, 4.0 mmol) was dissolved in THF (20 ml) and 3.06 g (12.0 mmol) $Mg(CH_2CMe_3)_2$(dioxane) was added. After 24 hr the THF was removed in vacuo. The resulting yellowish solid was extracted into toluene. The mixture was filtered and the toluene was removed from the filtrate in vacuo to give a crystalline white solid. The crude product was recrystallized from ether to give 1.78 g (80%) of pure compound.

Anal. Calcd. for $TaC_{25}H_{46}NO$: C, 53.85; H, 8.32. Found: C, 53.68; H, 8.45. ^1H NMR (C_6D_6): 7.65-6.87 (m, 5, NC_6H_5), 3.66 (br, 4, $\overline{OC\underline{H}_2CH_2CH_2C\underline{H}_2}$), 1.22 (s, 27, $CH_2C\underline{Me}_3$), 1.10 (br, 4, $\overline{OCH_2C\underline{H}_2C\underline{H}_2CH_2}$), 0.74 (s, 6, $C\underline{H}_2CMe_3$).

$[TaCl_3(THF)_2]_2N_2$

$Ta(CHCMe_3)(THF)_2Cl_3$ (1.0 g, 2.0 mmol) was dissolved in ether (10 ml) and the purple solution cooled to -30°C. n-Nonane (300 µl, 1.68 mmol) was added as an internal standard. PhCH=N-N=CHPh (0.21 g, 1.0 mmol) was added with stirring. The solution turned orange and the orange product began depositing from solution. GC analysis after 2 hr showed > 90 mol % of the expected cis and trans $Me_3CCH{=}CHC_6H_5$ present; yield, 0.85 g (95%). The orange product is insoluble in ether and hydrocarbons, very slightly soluble in chloroform, tetrahydrofuran and chlorobenzene, and slightly soluble in dichloromethane.

^1H NMR (CD_2Cl_2): 4.48 (br m, 8, $\overline{\mathrm{OC\underline{H}_2CH_2CH_2C\underline{H}_2}}$), 2.03 (br m, 8, $\overline{\mathrm{OCH_2C\underline{H}_2C\underline{H}_2CH_2}}$).

$[TaCl_3(PR_3)_2]_2N_2$

Four equivalents of phosphine (PMe_2Ph, PEt_2Ph, $P(n\text{-}Pr)_3$) were added to $[TaCl_3(THF)_2]_2N_2$ (0.5 g, 0.56 mmol) in dichloromethane to give red-purple (PMe_2Ph or PEt_2Ph) or green (PEt_3, $P(n\text{-}Pr)_3$) solutions. After 1 hr the solvent was removed in vacuo to yield red-purple or green microcrystals. Attempts at crystallization to produce x-ray quality crystals failed. Attempted analyses gave low C and H and high N values, probably due to loss of phosphine during combustion.

$^{31}P\{^1H\}$ NMR of PEt_2Ph complex ($CDCl_3$): 21.1 (s). $^{31}P\{^1H\}$ NMR of PMe_2Ph complex (CH_2Cl_2): -0.5 (br s), -21.5 (br s). $^{31}P\{^1H\}$ NMR of $P(n\text{-}Pr)_3$ complex (toluene): 8.3 (s). $^{31}P\{^1H\}$ NMR of PEt_3 complex (CH_2Cl_2): 14.8 (s). IR of PEt_3 complex (cm^{-1}, Nujol): 855 (Ta_2N_2).

$[TaCl_3(THF)(PBz_3)]_2N_2$

Tribenzylphosphine (0.70 g, 2.25 mmol) was added to $[TaCl_3(THF)_2]_2N_2$ (1.0 g, 1.12 mmol) in 40 ml of dichloromethane and the mixture was stirred for 2 hr. The dichloromethane was removed in vacuo and the resulting red solid extracted with a minimal amount of CH_2Cl_2/toluene. The mixture was filtered and the filtrate was cooled to -30°C to give crystals suitable for x-ray analysis.

$^{31}P\{^1H\}$ NMR (CH_2Cl_2): 9.3 (br s).

$[Ta(CH_2CMe_3)_3(THF)]_2N_2$

$Mg(CH_2CMe_3)_2$(dioxane) (0.80 g, 3.13 mmol) was added to $[TaCl_3(THF)_2]_2N_2$ (0.93 g, 1.04 mmol) in ether (5 ml) at -30°C. The reaction mixture was warmed to 25°C and filtered after three hours. The ether was removed from the filtrate in vacuo and the resulting yellow solid was extracted with pentane. The filtrate was cooled to -30°C to give 0.69 g (70% yield) of bright yellow crystals.

Anal. Calcd. for $Ta_2C_{38}H_{82}N_2O_2$: C, 47.50; H, 8.60; N, 2.92. Found: C, 46.89; H, 8.54; N, 3.32.

^1H NMR (C_6D_6): 3.70 (m, 4, $\overline{OC\underline{H}_2CH_2CH_2C\underline{H}_2}$), 1.35 (s, 27, $CH_2C\underline{Me}_3$), 1.30 (m, 4, $\overline{OCH_2C\underline{H}_2C\underline{H}_2CH_2}$), 0.89 (s, 6, $C\underline{H}_2CMe_3$).

$[Ta(OCMe_3)_3(THF)]_2N_2$

$[TaCl_3(THF)_2]_2N_2$ (2.0 g, 2.24 mmol) was slurried in THF (40 ml) and $KOCMe_3$ (1.51 g, 13.47 mmol) added while stirring. The slurry immediately began lightening as KCl deposited from solution. After stirring 18 hr the THF was removed in vacuo, yielding an oily yellow solid which was extracted with pentane. The filtrate was concentrated in vacuo until crystals began forming. The deep yellow solution was then cooled to -30°C. The extreme solubility of the compound prevented a high yield crystallization but 0.14 g of pure product for elemental analysis and NMR studies was obtained. The pentane was removed from the mother liquor to give 1.47 g of essentially pure product; total yield, 1.61 g (80%).

Anal. Calcd. for $Ta_2C_{32}H_{70}N_2O_8$: C, 39.51; H, 7.27; N, 2.88. Found: C, 39.83; H, 7.32; N, 2.48. ^1H NMR (C_6D_6): 3.51 (m, 4, $\overline{\mathrm{OC\underline{H}_2CH_2CH_2C\underline{H}_2}}$), 1.52 (s, 27, $\mathrm{OC\underline{Me}_3}$), 1.39 (m, 4, $\overline{\mathrm{OCH_2C\underline{H}_2C\underline{H}_2CH_2}}$).

$[NbCl_3(THF)_2]_2N_2$

$Nb(CHCMe_3)(THF)_2Cl_3$ (1.0 g, 2.42 mmol) was dissolved in ether (7 ml) and benzalazine (0.25 g, 1.21 mmol) was added. After 3 hr 0.60 g (70% yield) of pink-violet product was isolated by filtration. GLC analysis of the filtrate shows 95 mol % of cis and trans $Me_3CCH{=}CHPh$.

$[Nb(CH_2CMe_3)_3(THF)]_2N_2$

$[NbCl_3(THF)_2]_2N_2$ (0.71 g, 1.0 mmol) was slurried in ether (35 ml) and $Mg(CH_2CMe_3)_2$(dioxane) (0.76 g, 3.0 mmol) was added slowly with stirring. The reaction mixture turned orange. After 18 hr the solution was filtered and the ether removed in vacuo to yield orange crystals. The product was extracted into pentane, from which it crystallized at -30°C; yield (0.50 g (60%).

^{1}H NMR (C_6D_6): 3.67 (m, 4, $\overline{\mathrm{OC\underline{H}_2CH_2CH_2C\underline{H}_2}}$), 1.39 (s, 27, $\mathrm{CH_2C\underline{Me}_3}$), 1.34 (m, 4, $\overline{\mathrm{OCH_2C\underline{H}_2C\underline{H}_2CH_2}}$ and s, 6, $\mathrm{C\underline{H}_2CMe_3}$).

Hydrazine Determinations[69]

The dinitrogen complex (0.10-0.15 mmol) was dissolved in ether/THF and 25 equivalents of HCl in ether were added. The reaction was stirred overnight and the solvent removed in vacuo leaving a beige/white residue which was extracted with H_2O, filtered through Celite (removes organometallic product), and diluted with water to one liter in a volumetric flask. Aliquots of the above solution were treated with an H_2O/HCl solution of p-dimethylaminobenzaldehyde and the absorbance measured at 358 nm in 1 mm path length cells after 15 min.

CHAPTER 3

MONOMERIC TANTALUM(III) COMPLEXES AND THEIR REACTIONS WITH REDUCIBLE SUBSTRATES

INTRODUCTION

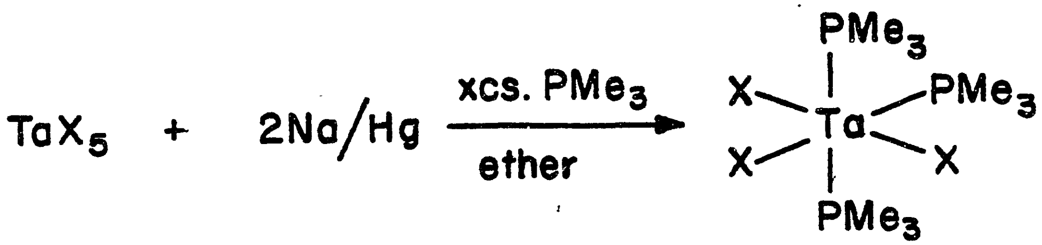
The chemistry of niobium(III) and tantalum(III) complexes remains a relatively unexplored area of transition metal chemistry. The preparation of $Nb_2X_6(SC_4H_8)_3$[70] and $Ta_2X_6(SC_4H_8)_3$[71] (X = Cl, Br, I), dimeric Nb(III) and Ta(III) complexes, by the two-electron reduction of the metal pentahalide with sodium amalgam in the presence of excess tetrahydrothiophene, represents the first example of discrete niobium and tantalum(III) halide complexes to be confirmed in the literature. Recently,[72] a trimethylphosphine adduct, $Ta_2Cl_6(PMe_3)_4$, has been prepared and characterized. No mononuclear Ta(III) halide species has yet been reported. Wreford has found that the sodium amalgam reduction of $TaCl_5$ in the presence of 1,2-bis(dimethylphosphino)ethane (dmpe) yields only paramagnetic $TaCl_2(dmpe)_2$ or $TaCl_4(dmpe)$ but no Ta(III) complexes were isolated.[13]

In this chapter we discuss how mononuclear Ta(III) species can be prepared via the sodium amalgam reduction of Ta(V) halide and halo/alkyl complexes in the presence of trimethylphosphine. $TaCl_3(PMe_3)_3$, a novel octahedral halo/phosphine complex (discovered by J. Fellmann[74]) is prepared and some simple reactions explored. Turner and Fellmann[74] found that the reduction of $Ta(R)Cl_3(PMe_3)_2$ (R = $CHCMe_3$, C_2H_4) under Ar yielded mononuclear Ta(III) species that react rapidly with dinitrogen to form binuclear species containing a reduced dinitrogen bridge. Any chemistry described within which is not attributed to other workers was performed by the author.

RESULTS

Preparation and Reactions of $TaX_3(PMe_3)_3$ (X = Cl, Br)

When $TaCl_5$, in the presence of PMe_3, is reduced by two electrons using sodium amalgam, a bright red complex which analyzes as $TaCl_3(PMe_3)_3$ is isolated in 80% yield (eq 1). Fellmann has established this complex to be a



(1)

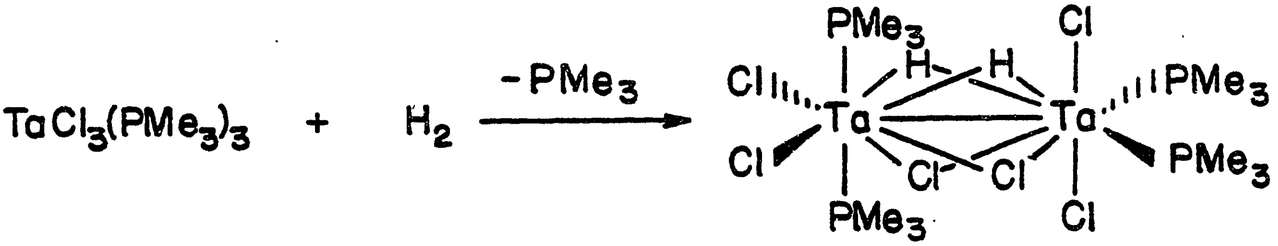
monomer by cryoscopic molecular weight determination in benzene.[74] This d^2 complex is best formulated as an octahedron containing meridional ligands as two types of PMe_3 resonances are observed in the high field ^1H NMR. The unusual chemical shifts of -6.21 ppm and 9.57 ppm (2:1) and the lack of "virtual" coupling by the trans phosphines is a result of the d^2 metal center being weakly paramagnetic. No signal is observed in the $^{31}P\{^1H\}$ NMR spectrum.

No EPR signal is observed at room temperature. At 77 K an eight line pattern (g_{av} = 1.92) with a peak separation of ~240 G (at 9.162 GHz) is observed. The first three lines exhibit hyperfine splitting of ~30 G, possibly due to phosphorous coupling.

Fellmann has shown that $TaCl_3(PMe_3)_3$ can also be prepared from $Ta_2Cl_6(THT)_3$ and PMe_3 in a sealed tube at 60°C.[74] In solution $TaCl_3(PMe_3)_3$ readily decomposes by loss of phosphine (only slow decomposition in solid state at -30°C) to yield the known dimer, $[TaCl_3(PMe_3)_2]_2$. The $^{31}P\{^1H\}$ NMR spectrum has two sharp singlets at -32 δ and -54 δ (1:1). The crystal structure, performed by A. Sattelberger, confirmed the supposition that $[TaCl_3(PMe_3)_2]_2$ is a bioctahedron containing two PMe_3 ligands in axial positions on one metal and two phosphines in equatorial positions on the other metal center.[72]

$TaCl_3(PMe_3)_3$ can be further characterized by its reaction with ethylene. Fellmann demonstrated that $Ta(C_2H_4)(PMe_3)_2Cl_3$, a previously characterized complex, is obtained in 95% yield by heating a benzene solution of $TaCl_3(PMe_3)_3$ under C_2H_4.[74] Me_3SiN_3 (TMSA) reacts rapidly with $TaCl_3(PMe_3)_3$ giving off dinitrogen and yielding an imido complex, $Ta(NSiMe_3)(PMe_3)_2Cl_3$, in good yield. The $^{31}P\{^1H\}$ NMR spectrum shows 2 slightly broadened singlets establishing a cis, mer configuration by analogy to $Ta(NPh)(PMe_3)_2Cl_3$ (cf. Chapter 2).

$TaCl_3(PMe_3)_3$ reacts readily with H_2 (30 psi) to yield the green bridging dihydride, $[TaCl_3(PMe_3)_2]_2H_2$, in quantitative yield (eq 2). The low energy metal hydride stretch (1260 cm^{-1}) in the IR spectrum was the basis for the bridging formulation for the hydride ligands. The deuteride, $[TaCl_3(PMe_3)_2]_2D_2$, did not have any peak at ~1260 cm^{-1} but a new absorbance at ~890 cm^{-1} was observed as expected. Although $[TaCl_3(PMe_3)_2]_2H_2$ has been structurally characterized the authors noted that the hydride stretch was unobservable from 2915 cm^{-1} to 1420 cm^{-1}.[72] The $^{31}P\{^1H\}$ NMR spectrum of $[TaCl_3(PMe_3)_2]_2H_2$ is very useful as two AX doublets (each of area one; $J_{PP'}$ = 7.32 Hz) centered about a



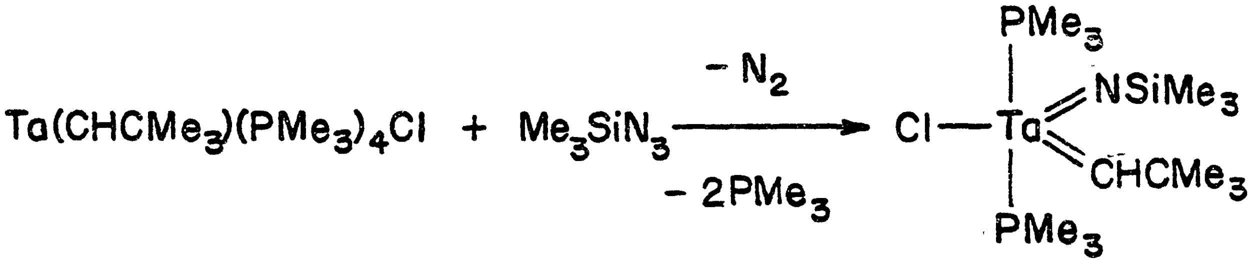
(2)

singlet (area two) is observed. The spectrum remains unchanged to -60°C and the spectrum of the deuteride shows the exact same pattern. The 250 MHz ^1H NMR spectrum of $[TaCl_3(PMe_3)_2]_2H_2$ shows a complex thirteen line multiplet centered at 8.41 δ assigned to the two equivalent bridging hydride ligands. The phosphine methyl resonances at 1.70, 1.38, and 1.25 δ are found in a 1:2:1 ratio as expected. As previously reported[72] $[TaCl_3(PMe_3)_2]_2H_2$ does not react with carbon monoxide under mild conditions (40 psi, 65°C).

Reactions of $Ta(CHCMe_3)(PMe_3)_4Cl$

H. Turner has demonstrated that the reduction of $Ta(CHCMe_3)(PMe_3)_2Cl_3$ by sodium amalgam in the presence of PMe_3 gives the novel Ta(III) alkylidene complex, $Ta(CHCMe_3)(PMe_3)_4Cl$, in 80% yield. The characterization of this molecule can be found in reference 75.

Azidotrimethylsilane reacts rapidly with $Ta(CHCMe_3)(PMe_3)_4Cl$ to release dinitrogen and form an imido-alkylidene complex, $Ta(CHCMe_3)(NSiMe_3)(PMe_3)_2Cl$ (eq 3).[76]



$$Ta(CHCMe_3)(PMe_3)_4Cl + Me_3SiN_3 \xrightarrow[-\,2PMe_3]{-\,N_2} Cl{-}Ta(PMe_3)_2(=NSiMe_3)(=CHCMe_3) \quad (3)$$

A vigorous reaction ensues as the Ta(III) complex is rapidly oxidized to Ta(V) and subsequently, best yields are obtained by conducting the reaction at 0°C or lower. The phosphinimine, $Me_3SiN{=}PMe_3$, can be formed as a side product so excess Me_3SiN_3 is used to keep the yield of $Ta(CHCMe_3)(NSiMe_3)(PMe_3)_2Cl$

high (80%). Sublimation under high vacuum (< 1 μm) at 100°C provides pure tantalum imido-alkylidene. The compound is best formulated as a trigonal bipyramid with axial phosphines, similar to bisneopentylidene complexes.[77] Unfortunately, $Ta(CHCMe_3)(NSiMe_3)(PMe_3)_2Cl$ reacts slowly with ethylene (40 psi, 50°C, 2 hr) to give a quantitative yield of the two expected organic products of rearrangement of an intermediate metallacyclobutane complex. 4,4-dimethyl-2-pentene (20%) as well as the ethylene dimerization product, 1-butene, are observed. No 3,3-dimethyl-1-butene, the expected product from olefin metathesis is seen. $Ta(CHCMe_3)(NSiMe_3)(PMe_3)_2Cl$ does react with cis-2-pentene in the presence of $PdCl_2$(1,5-COD) to give a low yield (20%) of the expected metathesis cleavage products (12%, cis/trans-4,4-dimethyl-2-pentene; 8% trans-2,2-dimethyl-3-hexene). It reacts with 1 equiv of acetone to give a 90% yield of 2,4,4-trimethyl-2-pentene and with 1 equiv of benzaldehyde to give a 90% yield of cis/trans-3,3-dimethyl-1-phenyl-1-butene.[15] A white insoluble complex which shows a Ta=O stretch at ~835 cm^{-1} in the IR spectrum is the inorganic product in the above reactions.

$LiCH_2CMe_3$ reacts with $Ta(CHCMe_3)(NSiMe_3)(PMe_3)_2Cl$ to give pentane soluble $Ta(CHCMe_3)(CH_2CMe_3)(NSiMe_3)(PMe_3)_2$. ^1H NMR shows the geometry to be trigonal bipyramidal with trans phosphines. It reacts sluggishly with ethylene to yield only rearrangement products and 1-butene.

Turner has found that when $Ta(CHCMe_3)(PMe_3)_4Cl$ is stirred under a nitrogen atmosphere a binuclear μ-dinitrogen complex, $[Ta(CHCMe_3)(PMe_3)_2Cl]_2(\mu\text{-}N_2)$, precipitates as a yellow powder.[48] This μ-dinitrogen reacts with HCl in ether to give a quantitative yield of $N_2H_4 \cdot 2HCl$ by visible spectroscopy (for method see Experimental, Chapter 2). Acetone rapidly cleaves the μ-dinitrogen ligand as dimethylketazine, $Me_2C=NN=CMe_2$. As discussed in Chapter 2, tantalum μ-dinitrogen complexes of the type $[TaCl_3(THF)_2]_2N_2$ react similarly.

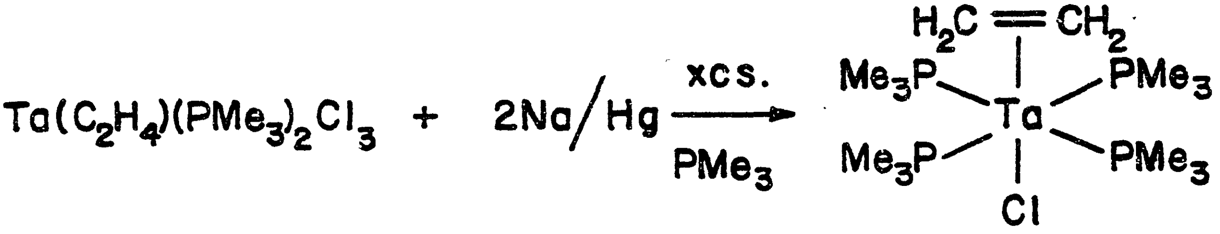
Stirring a pentane solution of $Ta(CHCMe_3)(PMe_3)_4Cl$ under $^{15}N_2$ for 24 hr gives $[Ta(CHCMe_3)(PMe_3)_2Cl]_2(\mu\text{-}^{15}N_2)$ in ~50% yield. The IR spectrum of the ^{15}N-labelled complex differs from that of the ^{14}N complex in only one respect; a medium-strength sharp peak at 847 cm^{-1} in the IR spectrum of the ^{14}N complex shifts to 820 cm^{-1}. We do not know if this is a N-N stretching mode, a M-N stretching mode, or a combination, i.e., M_2N_2 mode.

The ^{15}N NMR of $[Ta(CHCMe_3)(PMe_3)_2Cl]_2{}^{15}N_2$ consists of a sharp singlet at 414 ppm (referenced to liquid NH_3).[56] This chemical shift should be compared with chemical shifts of 350-370 ppm for organoimido complexes such as $Ta(^{15}NPh)(THF)_2Cl_3$ (Chapter 2), and, equally important, with the rather different chemical shift of 679 ppm for the bridging dinitrogen in $[Zr(\eta^5\text{-}C_5Me_5)_2\text{-}(^{15}N_2)]_2{}^{15}N_2$.[56,78]

The crystal structure of $[Ta(CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2N_2$ has been reported by Churchill.[79] The structure shows the dinitrogen to be quite activated with a N-N distance of 1.298(12)Å and tantalum-nitrogen bond lengths of 1.837(8)Å and 1.842(8)Å in an essentially linear arrangement. The N-N distance is approximately 0.01Å longer than that found in $[TaCl_3(THF)(PBz_3)]_2N_2$ (N-N = 1.282(6)Å; cf. Chapter 2) and represents the longest N-N distance in a simple bridging dinitrogen complex.[62] $[Zr(\eta^5\text{-}C_5Me_5)_2(N_2)]_2N_2$ has a N-N bond length of 1.182(5)Å.[65] We propose that the μ-N_2 ligand has been reduced by four electrons and may be formally regarded as a N_2^{4-} ligand bridging two Ta(V) centers. The crystal structure and chemical data demonstrate that Ta=N-N=Ta is a valid valence bond description for these unique molecules.

Preparation and Reactions of $Ta(C_2H_4)L_4Cl$ (L = PMe_3, 1/2 dmpe)

J. Fellmann first found that when $Ta(C_2H_4)(PMe_3)_2Cl_3$ is reduced with Na/Hg in the presence of excess PMe_3 under Ar a Ta(III) olefin complex, $Ta(C_2H_4)(PMe_3)_4Cl$, is isolated[74] (eq 4). This complex is an extremely air and dinitrogen sensitive molecule and great care must be exercised in its preparation and handling. The ^1H NMR exhibits equivalent ethylene protons at 2.25 δ equally coupled to four phosphorous nuclei (quintet, $^3J_{HP}$ = 3.66 Hz). The ethylene carbon atoms are equivalent and are found at 33.2 δ in the ^{13}C NMR spectrum. No signal is observed in the $^{31}P\{^1H\}$ NMR spectrum. On the basis of our spectroscopy, it is difficult to ascertain whether the ethylene ligand is rotating about the plane of phosphines or is rigidly bound in a metallacyclopropane-like manner.[80]



(4)

The sodium amalgam reduction of $Ta(C_2H_4)(PMe_3)_2Cl_3$ under dinitrogen does not give $Ta(C_2H_4)(PMe_3)_4Cl$. Instead orange microcrystals of $[Ta(C_2H_4)(PMe_3)_3Cl]_2N_2$ are isolated from solution. $[Ta(C_2H_4)(PMe_3)_3Cl]_2N_2$ is thought to be a dimer containing a bridging N_2^{4-} ligand by analogy to the previously described $[Ta(CHCMe_3)(PMe_3)_2Cl]_2N_2$. The presence of coordinated dinitrogen is demonstrated by the reaction of $[Ta(C_2H_4)(PMe_3)_3Cl]_2N_2$ with HCl in ether to give a quantitative yield of $N_2H_4\cdot 2HCl$. The bridging dinitrogen can be cleaved with excess acetone to yield dimethylketazine. $[Ta(C_2H_4)(PMe_3)_3Cl]_2N_2$ can be cleanly alkylated with $LiCH_2CMe_3$ to yield $[Ta(C_2H_4)(CH_2CMe_3)(PMe_3)_2]_2N_2$ and one equivalent of free phosphine.

The ^{15}N-labelled complex, $[Ta(C_2H_4)(PMe_3)_3Cl]_2{}^{15}N_2$ is prepared be reacting $Ta(C_2H_4)(PMe_3)_4Cl$ with $^{15}N_2$. One equivalent of PMe_3 is displaced and the labelled complex isolated in 65% yield. The IR of the ^{14}N complex has a peak at 825 cm^{-1} that shifts to 793 cm^{-1} in $[Ta(C_2H_4)(PMe_3)_3Cl]_2{}^{15}N_2$. As previously discussed for $[Ta(CHCMe_3)(PMe_3)_2Cl]_2N_2$ we believe this mode is associated with the M_2N_2 bridge. The ^{15}N NMR in THF shows a slightly broadened (due to unresolved phosphorous coupling) singlet at 374 ppm.

A low valent tantalum olefin complex, $Ta(C_2H_4)(dmpe)_2Cl$, which does not react with dinitrogen, can be prepared by reducing $Ta(C_2H_4)(THF)_2Cl_3$ in the presence of two equivalents of dmpe with sodium amalgam. We believe it does not react with dinitrogen because the bidentate dmpe ligands do not dissociate readily in solution. The ethylene protons are found at an unusual chemical shift of -0.7 ppm (quintet, $^3J_{HP}$ = 2.4 Hz) in the ^1H NMR spectrum and the ethylene carbon atoms are equivalent in the ^{13}C NMR spectrum. The $^{31}P\{^1H\}$ NMR spectrum exhibits a sharp singlet.

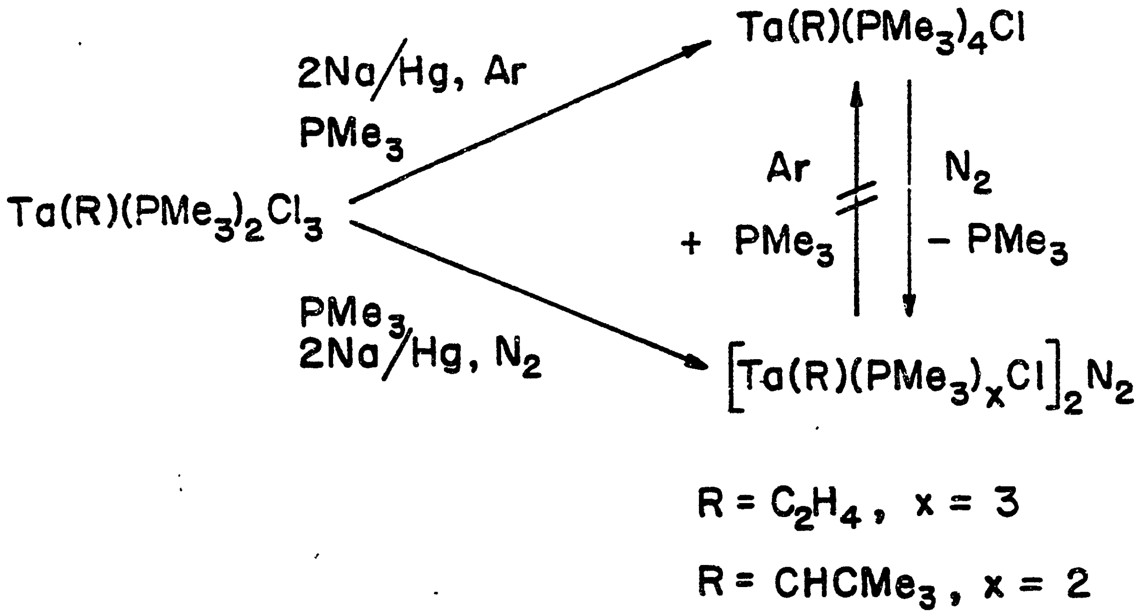
DISCUSSION

We have shown in this chapter that monomeric Ta(III) complexes can indeed be prepared by reducing Ta(V) species with sodium amalgam in the presence of trimethylphosphine. This fairly small Lewis base stabilizes and allows for the isolation of these monomeric molecules. Fortunately, the trimethylphosphine ligand is labile enough to facilitate reactions with the Ta(III) metal centers. The reaction chemistry of these Ta(III) complexes is dominated by reduction of substrate with subsequent oxidation of the tantalum species. It should be noted that $Me_3P{=}O$ does not react with $Ta(CHCMe_3)(PMe_3)_4Cl$ at ca. 25°C possibly because it cannot get into the coordination sphere of the metal or because the P-O bond is at least as strong as any Ta-O bond which might form. Propylene oxide reacts rapidly with $Ta(CHCMe_3)(PMe_3)_4Cl$ and $TaCl_3(PMe_3)_3$ but no clean products could be isolated.

Azidotrimethylsilane (TMSA) reacts with the Ta(III) species to oxidize the metal to formally Ta(V) yielding trimethylsilylimido complexes. However, when TMSA reacts with higher valent tantalum species such as $Ta(R)\ L_2Cl_3$ ($R = C_2H_4$, $CHCMe_3$; L = THF, PMe_3) simple substitution occurs and azido complexes, $Ta(R)(N_3)L_2Cl_2$, are formed. These reactions lend justification to formulating our reduced complexes as Ta(III).

The reduction of dinitrogen to formally N_2^{4-} by $Ta(R)(PMe_3)_4Cl$ ($R = CHCMe_3$, C_2H_4) demonstrates the reducing power of this class of molecules. Scheme I summarizes the reactions of reduced tantalum species and dinitrogen. The dinitrogen ligand cannot be displaced from the binuclear tantalum complexes by heating in the presence of trimethylphosphine under Ar.

Scheme I.


Ta(R)(PMe3)2Cl3
2Na/Hg, Ar
PMe3
Ta(R)(PMe3)4Cl
Ar
+ PMe3
N2
− PMe3
PMe3
2Na/Hg, N2
[Ta(R)(PMe3)xCl]2N2
R = C2H4, x = 3
R = CHCMe3, x = 2

Addendum

As mentioned in the text of this chapter $TaCl_3(PMe_3)_3$ does not reduce dinitrogen and form complexes of the type $[TaCl_3(PMe_3)_2]_2N_2$ although such complexes can be prepared via other routes (cf. Chapter 2). $TaCl_3(PMe_3)_3$ does not form a dinitrogen complex even under N_2 at 10 atm and 60°C in toluene. Instead $[TaCl_3(PMe_3)_2]_2$ and $[TaCl_3(PMe_3)_2H]_2$ (the source of hydrogen is currently unknown but could be solvent or possibly water) are observed by $^{31}P\{^1H\}$ NMR (VI-41, VII-26). The same products are observed when $TaCl_5(PMe_3)_2$ is reduced with 2Na/Hg in the dry box in toluene (V-74).

$TaCl_5(PEt_3)_2$ was reduced by sodium amalgam in toluene under Ar (V-75, VII-22), under N_2 (V-75, VI-6), in the presence of 0.5 equivalents N_2(VI-5), and in vacuo (VI-7). Under no conditions were tractable products obtained. The product obtained from the reduction of $TaCl_5(PEt_3)_2$ under Ar did not react with N_2 at 7 atm pressure and 50°C in toluene (VII-22). Reduction in the presence of PEt_2Ph gave similar results (VI-42).

We believe that dinitrogen does not react with $TaCl_3(PMe_3)_3$ because the first step requires loss of phosphine and $[TaCl_3(PMe_3)_2]_2$ would immediately be formed. The crystal structure shows that this dimer contains a metal-metal bond and bridging chlorides.[72] Dinitrogen would not be expected to "break-up" this kind of molecule even under our forcing conditions.

CHAPTER 3 EXPERIMENTAL

$Ta(C_2H_4)(PMe_3)_2Cl_3$,[19b] $Ta(CHCMe_3)(PMe_3)_4Cl$,[75] and $[Ta(R)(PMe_3)_xCl]_2N_2$[75] were prepared by published methods. $Ta(C_2H_4)(THF)_2Cl_3$ was prepared by stirring a concentrated ether solution of $Ta(CHCMe_3)(THF)_2Cl_3$[18] under C_2H_4 (30 psi) and isolating royal blue crystals by filtration. The preparation of $Ta(CHCMe_3)(PMe_3)_4Cl$ and $Ta(C_2H_4)(PMe_3)_4Cl$ is best accomplished using solvents that have been subjected to successive freeze-pump-thaw cycles. $^{15}N_2$ was purchased from Merck & Co. and transferred via Toepler pump on a high-vacuum line.

PREPARATIONS

$TaCl_3(PMe_3)_3$

50 mL of ether containing PMe_3 (5 mL, 52.6 mmol, excess) and 0.41% Na/Hg (112 g, 20 mmol) was cooled to -30°. Solid $TaCl_5$ (3.5 g, 10 mmol) was added. The reaction mixture was warmed to RT and in 60 min the color of the solution changed from green to red. The NaCl was filtered through Celite and the ether removed in vacuo leaving red crystals. The crude product was extracted with 25 mL of ether and filtered. Pentane (~2 mL) and PMe_3 (~0.1 mL) were added to the filtrate. Cooling the solution to -30° for 12 h gave 2.76 g of irregular deep red crystals. Concentrating and cooling the mother liquor to -30° gave an additional 1.26 g of pure product (78% yield). An analytically pure sample was obtained after repeated crystallizations from concentrated ether solutions containing free PMe_3.[74]

^1H NMR (C_6D_6, 250 MHz, ppm): -6.21 (s, 18, PMe_3(A)), 9.57 (s, 9, PMe_3(B)).

$TaBr_3(PMe_3)_3$

$TaBr_3(PMe_3)_3$ was prepared in a manner analogous to that for $TaCl_3(PMe_3)_3$. It is a red-purple crystalline solid.

^1H NMR (C_6D_6, 250 MHz, ppm): -11.52 (s, 18, PMe_3(A)), 14.79 (s, 9, PMe_3(B)).

$[TaCl_3(PMe_3)_2H]_2$

$TaCl_3(PMe_3)_3$ (0.52 g, 1.0 mmol) was dissolved in ether (5 mL) and the red solution pressurized with H_2 (35 psi). In 60 min a green solid began depositing from solution. After stirring 12 h the product was isolated by filtration (0.44 g, 85% yield). Crystals of $[TaCl_3(PMe_3)_2H]_2$ can be obtained from concentrated toluene/ether solutions.

^1H NMR (d_8-toluene, 250 MHz, ppm): 8.41 (m, 2, H_b), 1.70 (d, 9, J_{PH} = 9.8, P_{ax}-CH_3), 1.38 (d, 18, J_{PH} = 9.39, P_{eq}-CH_3), 1.25 (d, 9, J_{PH} = 9.0, P'_{ax}-CH_3). $^{31}P\{^1H\}$ NMR (d_8-toluene, 101 MHz, ppm): 13.3 (d, 1, $J_{PP'}$ = 7.32, P_{ax}), -4.8 (s, 2, P_{eq}), -20.2 (d, 1, $J_{PP'}$ = 7.32, P'_{ax}). IR (Nujol, cm^{-1}): 1260 (Ta-H-Ta).

$[TaCl_3(PMe_3)_2D]_2$

The deuteride was prepared in an analogous manner to that for $[TaCl_3(PMe_3)_2H]_2$ using D_2.

^1H NMR (d_8-toluene, 250 MHz, ppm): 1.70 (d, 9, J_{PH} = 9.8, P_{ax}-CH_3), 1.38 (d, 18, J_{PH} = 9.4, P_{eq}-CH_3), 1.25 (d, 9, J_{PH} = 8.6, P'_{ax}-CH_3). $^{31}P\{^1H\}$ NMR (d_8-toluene, 36 MHz, ppm) 13.4 (d, 1, $J_{PP'}$ = 7.32, P_{ax}), -4.5 (s, 2, P_{eq}), -19.8 (d, 1, $J_{PP'}$ = 7.32, P'_{ax}). IR (Nujol, cm^{-1}): 890 (Ta-H-Ta).

$Ta(NSiMe_3)(PMe_3)_2Cl_3$

$TaCl_3(PMe_3)_3$ (0.52 g, 1.0 mmol) was dissolved in ether (5 mL) and the red-purple solution cooled to -30°. TMSA (135 µl, 1.0 mmol) was added and the reaction turned orange-brown. After stirring 60 min the reaction was filtered and the solvent removed in vacuo yielding a light orange oil. Very soluble crystals of $Ta(NSiMe_3)(PMe_3)_2Cl_3$ can be obtained from concentrated ether solutions with a small amount of pentane added.

^1H NMR (C_6D_6, 60 MHz, ppm): 1.20 (d, 18, J_{HP} = 7, PMe_3), 0.18 (s, 9, $NSiMe_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 36.2 MHz, ppm): -45.4 (br s), -11.5 (br s).

$Ta(CHCMe_3)(NSiMe_3)(PMe_3)_2Cl$

$Ta(CHCMe_3)(PMe_3)_4Cl$ (0.5 g, 0.85 mmol) was dissolved in ether (10 mL) and after cooling to 0°C the Me_3SiN_3 (150 µl, 1.14 mmol , ~30% excess) was added. Dinitrogen was evolved immediately. The ice bath was removed and the orange reaction stirred for 4 hr. The ether was removed in vacuo leaving an orange solid. The product is best purified by sublimation (100°C, 0.1 µ).

^1H NMR (C_6D_6, 250 MHz, ppm): 7.98 (s, 1, $C\underline{H}CMe_3$), 1.25 (s, 9, $CHC\underline{Me}_3$), 1.16 (t, 18, J_{HP} = 3.3, PMe_3), 0.21 (s, 9, $NSi\underline{Me}_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 22.5 MHz, ppm), 275.8 (d, J_{CH} = 99, $\underline{C}HCMe_3$), 43.8 (s, $CH\underline{C}Me_3$), 34.9 (q, J_{CH} = 125, $CHC\underline{Me}_3$), 15.7 (t, J_{CH} = 126, PMe_3), 4.6 (q, J_{CH} = 126, $NSi\underline{Me}_3$).

$Ta(CHCMe_3)(CH_2CMe_3)(NSiMe_3)(PMe_3)_2$

$LiCH_2CMe_3$ (0.15 g, 1.9 mmol) was added to $Ta(CHCMe_3)(NSiMe_3)(PMe_3)_2Cl$ (1.0 g, 1.9 mmol) in ether (10 mL) at -20°. After 1 hr the LiCl was removed by filtration and the ether removed in vacuo yielding an orange-brown solid which was taken up in pentane (~5 mL), treated with activated charcoal, and cooled to -30°. After 24 hr 0.65 g (61% yield) of beautiful orange crystals were isolated. The product is very hydrocarbon soluble and must be quickly isolated from solution on a cold frit.

^1H NMR (C_6D_6, 250 MHz, ppm): 6.87 (t, 1, J_{HP} = 2.2, $C\underline{H}CMe_3$), 1.28 (s, 9, $CH_2C\underline{Me}_3$), 1.23 (s, 9, $CHC\underline{Me}_3$), 1.22 (t, 18, J_{HP} = 3.1, PMe_3), 0.54 (t, 2, J_{HP} = 16.5, $C\underline{H}_2CMe_3$), 0.25 (s, 9, $NSiMe_3$).

$[Ta(CHCMe_3)(PMe_3)_2Cl]_2{}^{15}N_2$

$^{15}N_2$ (1.82 mmol) was added to $Ta(CHCMe_3)(PMe_3)_4Cl$ (1.0 g, 1.70 mmol) in pentane (20 mL) via Toepler pump and stirred for 12 h. The labelled dinitrogen complex was isolated by filtration and recrystallized from ether. Yield, 0.37 g (48%). ^{15}N NMR (thf, 9.04 MHz, ppm): 414 (s). IR (Nujol, cm^{-1}): 820 ($Ta_2{}^{15}N_2$).

$Ta(C_2H_4)(PMe_3)_4Cl$

Since this complex is extremely dinitrogen sensitive all solvents were subjected to three freeze-pump-thaw cycles prior to use. $Ta(C_2H_4)(THF)_2Cl_3$ (2.29 g, 5.0 mmol) and PMe_3 (3 mL, 32 mmol) were stirred in thf (75 mL) under argon. Na/Hg (0.41%, 56.1 g, 10.0 mmol) was added and the blue solution turned green. After stirring 2 hr the thf was removed in vacuo, ether (75 mL) added, and the green slurry filtered through Celite. The solids and Celite were washed with ether (2 x 15 mL). The ether was slowly removed in vacuo yielding a dark violet crystalline product. Yield 2.2 g (80%).

^1H NMR (d_8-tol, 250 MHz, ppm): 2.25 (quint, 4, J_{HP} = 3.66, $C_2\underline{H}_4$), 1.38 (t, 36, J_{HP} = 2.44, $P\underline{Me}_3$). $^{13}C\{^1H\}$ NMR (d_8-tol, 62.8 MHz, ppm): 33.17 (t, J_{CH} = 145.9, J_{CP} = 2, $\underline{C}_2H_4$), 20.42 (q, J_{CH} = 128.2, J_{CP} = 8.6, PMe_3).

$Ta(C_2H_4)(dmpe)_2Cl$

Blue $Ta(C_2H_4)(THF)_2Cl_3$ (1.83 g, 4.0 mmol) and dmpe (1.20 g, 8.0 mmol) were stirred in thf (40 mL) under dinitrogen. Na/Hg (45 g, 8 mmol) was added and after 2 hr the thf was removed in vacuo from the forest green reaction mixture. Ether (50 mL) was added and the mixture filtered through Celite. The green ether solution was concentrated in vacuo, filtered through a fine frit, and cooled to -30°C. After 24 hr 1.63 g (76%) of beautiful large crystals were isolated.

Anal. Calcd. for $TaC_{14}H_{36}P_4Cl$: C, 30.87; H, 6.66. Found: C, 31.06; H, 6.81.

^1H NMR (C_6D_6, 250 MHz, ppm): 1.77 (br m, J_{HP} = 2.94, $Me_2PC\underline{H}_2C\underline{H}_2PMe_2$), 1.36 and 1.17 (br s, $\underline{Me}_2PCH_2CH_2P\underline{Me}_2$), -0.69 (quint, J_{HP} = 2.4, $C_2\underline{H}_4$). $^{13}C\{^1H\}$ NMR (C_6D_6, 62.8 MHz, ppm): 41.81 (t, J_{CH} = 147.4, $\underline{C}_2H_4$), 41.10 (t, J_{CH} = 128.8, J_{CP} = 8.5, ($Me_2P\underline{C}H_2\underline{C}H_2PMe_2$), 24.85 (q, J_{CH} = 128, J_{CP} = 5.8, $\underline{Me}_2PCH_2CH_2P\underline{Me}_2$), 22.73 (q, J_{CH} = 128, J_{CP} = 5.8, $\underline{Me}_2PCH_2CH_2P\underline{Me}_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 36.2 MHz, ppm): 17.5 (s).

$[Ta(C_2H_4)(PMe_3)_3Cl]_2{}^{15}N_2$

$^{15}N_2$ (2 mmol) was added to $Ta(C_2H_4)(PMe_3)_4Cl$ (0.82 g, 1.5 mmol) in ether (10 mL) via Teopler pump and stirred for 3 h. Pentane was added and the labelled dinitrogen complex was isolated by filtration.

^{15}N NMR (thf, 9.04 MHz, ppm): 374 (s). IR (Nujol, cm^{-1}): 793 ($Ta_2{}^{15}N_2$).

$[Ta(C_2H_4)(CH_2CMe_3)(PMe_3)_2]_2N_2$

$LiCH_2CMe_3$ (0.16 g, 2.06 mmol) was added to $[Ta(C_2H_4)(PMe_3)_3Cl]_2N_2$ (1.0 g, 1.03 mmol) in toluene (40 mL) at -30°. After warming to room temperature and stirring 3 hr the toluene was removed in vacuo yielding a dark sticky solid that was extracted with pentane (2 x 25 mL), filtered, concentrated, and cooled to -30°. 0.25 g of orange crystals were isolated by filtration.

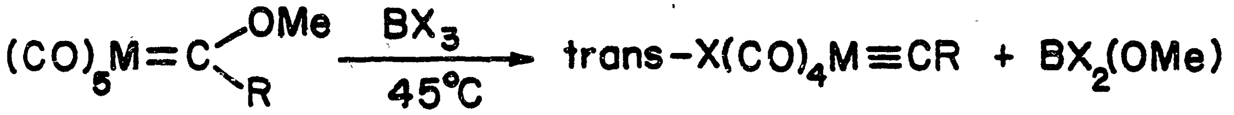
^1H NMR (C_6D_6, 250 MHz, ppm): 1.38 (d, 9, J_{HP} = 4.3, PMe_3), 1.17 (d, 9, J_{HP} = 4.3, PMe_3), 0.79 (m, 2, $C\underline{H}_2CMe_3$), 0.72 (s, 9, $CH_2C\underline{Me}_3$), 0.06 (br m, 4, C_2H_4). $^{13}C\{^1H\}$ NMR (C_6D_6, 22.5 MHz, ppm): 60.5 ($\underline{C}H_2CMe_3$), 37.5 (C_2H_4), 35.9 ($CH_2C\underline{Me}_3$), 33.9 ($CH_2\underline{C}Me_3$), 14.9 (t, J_{CP} = 9.7, PMe_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 36.2 MHz, ppm): -9.6 (s).

CHAPTER 4

THE REACTION CHEMISTRY OF $[W(CCMe_3)Cl_4][NEt_4]$ WITH WATER, AMINES, AND PHOSPHINES

INTRODUCTION

The preparation of $CH_3CCo_3(CO)_9$ in 1958[81] marked the beginning of the chemistry of a novel class of organometallic compounds, metal carbynes. The chemistry of alkylidynetricobalt nonacarbonyl complexes has been developed largely by Seyferth and co-workers.[82] In 1973 Wilkinson reported the first examples of dinuclear carbyne-bridged complexes, $[M(\mu\text{-}CSiMe_3)(CH_2SiMe_3)_2]_2$ (M = Nb, Ta).[83] These unique molecules were obtained by the interaction of MCl_5 with Me_3SiCH_2MgCl. In 1976 Wilkinson, et al,[84] as well as Cotton, et al,[85] prepared another example of this class of molecules, $[W(\mu\text{-}CSiMe_3)(CH_2SiMe_3)_2]_2$. This complex is obtained via the reaction of WCl_4 and Me_3SiCH_2MgCl in tetrahydrofuran. The compound is formally W(V) and metal-metal bonding is invoked to account for its diamagnetism.[86] The first mononuclear carbyne complexes were reported by Fischer and co-workers in 1973.[87] An attempt to replace the methoxy group of $(CO)_5M{=}C(OMe)R$ with a chlorine atom from boron trichloride was unsuccessful but metal carbyne complexes were formed in ca. 50% yield (eq 1). Recently Wilkinson reported



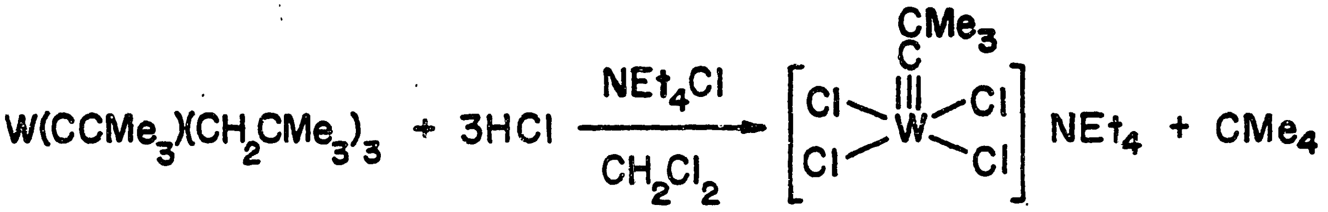
$$(CO)_5M{=}C(OMe)(R) \xrightarrow[45^{\circ}C]{BX_3} trans\text{-}X(CO)_4M{\equiv}CR + BX_2(OMe) \qquad (1)$$

M = Cr, Mo, W, R = Me, Ph, X = Cl, Br, I

that a W(IV) ethylidyne complex, trans-$W(CMe)Me(PMe_3)_4$, is formed when $WMe_6(PMe_3)$ is photolytically decomposed in neat PMe_3.[88]

Schrock and co-workers have found that tantalum alkylidene complexes can be decomposed to alkylidyne complexes by either simple deprotonation[89] or α-hydrogen abstraction.[89] Sharp and Schrock found that a methylidyne complex, $W(CH)Cl(PMe_3)_4$, can be obtained in 60% yield by the interaction of $WCl_2(PMe_3)_4$ and $2AlMe_3$ in the presence of tmeda.[90]

Clark and Schrock in 1978 reported the preparation of $[W(CCMe_3)(CH_2CMe_3)_3]_2$, a dimeric W(VI) alkylidyne complex, from WCl_6 and $LiCH_2CMe_3$.[91] Although this complex could only be isolated in 20% yield it represents a novel class of Group VI alkylidyne complexes, that is, those in their highest possible oxidation state (+6). Very recently Sancho[40] has found that $[W(CCMe_3)(CH_2CMe_3)_3]_2$ can be isolated in 60% yield by the addition of $W(OMe)_3Cl_3$[92] to Me_3CCH_2MgCl. Sancho found that $[W(CCMe_3)(CH_2CMe_3)_3]_2$ reacts cleanly with HCl in the presence of NEt_4Cl to yield anionic $[W(CCMe_3)Cl_4]NEt_4$ (eq 2). This



$$W(CCMe_3)(CH_2CMe_3)_3 + 3HCl \xrightarrow[CH_2Cl_2]{NEt_4Cl} [W(CCMe_3)Cl_4]NEt_4 + CMe_4 \quad (2)$$

unique molecule undergoes clean substitution chemistry with alcoxide, amide, and carbanionic ligands. In fact Sancho has prepared $W(CCMe_3)(OBu^t)_3$ from $[W(CCMe_3)Cl_4]NEt_4$ and $KOBu^t$ and found it to be an active catalyst for the metathesis of acetylenes.[93]

Herein we discuss the preparation of mixed alcoxy-halo tungsten neopentylidyne complexes and the reaction of $W(CCMe_3)(OBu^t)_3$ with alcohols.

The main thrust of the chapter involves the reaction chemistry of $[W(CCMe_3)Cl_4]NEt_4$. We have prepared simple phosphine substituted complexes as well as oxo- and imido-alkylidene species. A secondary-amido species is found to transfer its proton to the alkylidyne α-carbon and kinetic data has been obtained. Mononuclear tungsten phosphido complexes have been obtained via metallation of primary and secondary phosphines. The crystal structure of $W(CCMe_3)(PHPh)(PEt_3)_2Cl_2$ has been determined by M. Churchill and co-workers.

RESULTS

Reactions of $W(CCMe_3)(OBu^t)_3$

Sancho has shown that $W(CCMe_3)(OBu^t)_3$ can be prepared in 90% yield from $[W(CCMe_3)Cl_4]NEt_4$ and $3KOBu^t$.[93] The mono- or bis-alcoxy species cannot be prepared by using stoichiometric amounts of $KOBu^t$ or $LiOBu^t$.[40] $W(CCMe_3)(OBu^t)_3$ does not react with 1 equivalent of HCl to protonate the carbyne carbon or cleave the tert-butoxide, instead only starting material is isolated. The HCl may in fact cleave the alcoxide giving $W(CCMe_3)(OBu^t)_2Cl$ which, in a fast back reaction with the tert-butanol produced, gives starting material and HCl. The mono-alcoxy anion, $[W(CCMe_3)(OBu^t)Cl_3]NEt_4$, can be prepared by an equilibration reaction as shown in equation 3. The

$$2\left[W(CCMe_3)Cl_4\right]NEt_4 + W(CCMe_3)(OBu^t)_3 \xrightarrow[CH_2Cl_2]{+NEt_4Cl} 3\left[W(CCMe_3)(OBu^t)Cl_3\right]NEt_4 \qquad (3)$$

blue anion and yellow $W(CCMe_3)(OBu^t)_3$ react to yield the mono-tert-butoxide complex, quantitatively. Neutral $W(CCMe_3)(OBu^t)Cl_2(PEt_3)$ can easily be prepared from $[W(CCMe_3)(OBu^t)Cl_3]NEt_4$ and PEt_3 in CH_2Cl_2 (eq 4). This should

$$\left[W(CCMe_3)(OBu^t)Cl_3\right]NEt_4 \xrightarrow[-\ NEt_4Cl]{+\ PEt_3} W(CCMe_3)(OBu^t)Cl_2(PEt_3) \qquad (4)$$

be compared with the reaction of $[W(CCMe_3)Cl_4]NEt_4$ and PEt_3 where the product, $[W(CCMe_3)Cl_4(PEt_3)]NEt_4$, remains anionic (vide infra). The tert-butoxide ligand in $W(CCMe_3)(OBu^t)Cl_2(PEt_3)$ probably donates enough electron density to the metal or is too sterically demanding so the NEt_4Cl is released.

Unfortunately the above equilibration technique was not successful for the preparation of $[W(CCMe_3)(OBu^t)_2Cl_2]NEt_4$ (eq 5). The reaction does not

$$\left[W(CCMe_3)Cl_4\right]NEt_4 + 2W(CCMe_3)(OBu^t)_3 + 2NEt_4Cl \not\longrightarrow 3\left[W(CCMe_3)(OBu^t)_2Cl_2\right]NEt_4 \qquad (5)$$

go to completion after 2 days in CH_2Cl_2. Starting materials, as well as $[W(CCMe_3)(OBu^t)Cl_3]NEt_4$, can be observed by $^{13}C\{^1H\}$ NMR.

Since Sancho has shown that $W(CCMe_3)(OBu^t)_3$ is an active acetylene metathesis catalyst[93] we thought a complex such as $W(CHCMe_3)(OBu^t)_4$ would probably be active for the metathesis of olefins. No synthetic route to such a molecule yet exists. Although not observed spectroscopically, a small concentration of an alkylidene complex, presumably $W(CHCMe_3)(OBu^t)_4$, is formed in the reaction of $W(CCMe_3)(OBu^t)_3$ with t-BuOH (eq 6). This

$$W(CCMe_3)(OBu^t)_3 \quad + \quad \text{xcs. t-BuOH} \rightleftharpoons W(CHCMe_3)(OBu^t)_4 \qquad (6)$$

was confirmed by the reaction of cis-2-pentene with $W(CCMe_3)(OBu^t)_3$ in the presence of t-BuOH. Cleavage and productive metathesis products of cis-2-pentene were observed by GC. It should be noted that $W(CCMe_3)(OBu^t)_3$ does <u>not</u> react with cis-2-pentene unless t-BuOH is present. As can be observed in Table I, the yield of metathesis products is not substantial, possibly

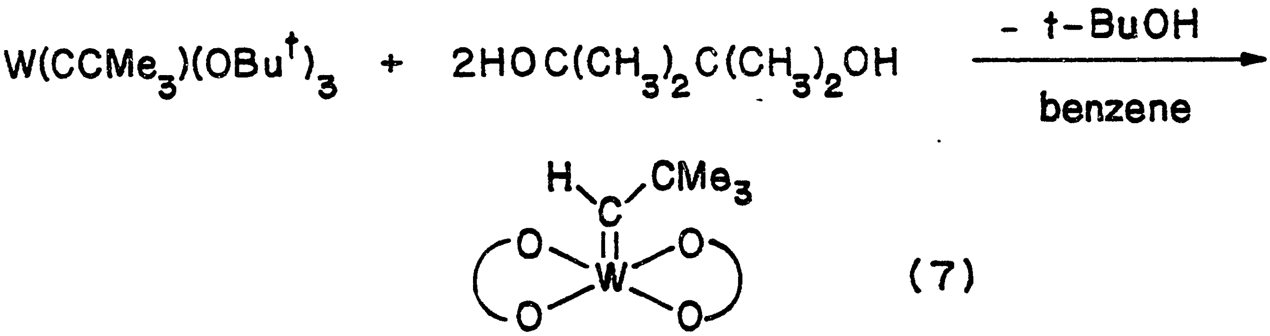
Table I. Metathesis of cis-2-pentene by $W(CCMe_3)(OBu^t)_3$/ 4-t-BuOH[a]

Time, hr	t-$Me_3CCH=CHMe$	t-$Me_3CCH=CHCH_2Me$	3-hexenes	2-butenes
12	20	11	103	120
36	29	16	317	181
60[b]	37	20	327	230

[a] The numbers are expressed as mole percent vs. the metal. [b] No further activity beyond this point possibly due to destruction of the alkylidene complex by t-BuOH or air oxidation.

the result of the equilibrium in equation 6 lying far to the left. When only 1 mole equivalent of t-BuOH is added the yield of metathesis products is substantially lower since K_{eq} is probably much smaller.

We had hoped to isolate a tetra-alcoxy alkylidene complex by using a chelating diol. When pinacol is added to $W(CCMe_3)(OBu^t)_3$ in benzene t-butanol is observed in the benzene azeotrope (eq 7). However, workup of



(7)

the reaction did not give any readily identifiable products. Furthermore, no metathesis products were observed when pinacol (up to 6 equivalents) was added to $W(CCMe_3)(OBu^t)_3$ in the presence of cis-2-pentene. Reaction of $W(CCMe_3)(OBu^t)_3$ with the triol, $(HOCH_2)_3CCH_3$, was also tried and again t-BuOH was observed but no tractable material was obtained. Sancho has been unable to obtain clean products from alcohol exchange reactions of $W(CCMe_3)(OBu^t)_3$ with, for example, phenol.

Reactions of $[W(CCMe_3)Cl_4]NEt_4$ with PEt_3

Wengrovius has shown that $[W(CCMe_3)Cl_4]NEt_4$ reacts with excess PMe_3 to yield $W(CCMe_3)Cl_3(PMe_3)_3$.[93] However, PEt_3 is much larger than PMe_3 and gives the mono-phosphine anion, $[W(CCMe_3)Cl_4(PEt)_3]NEt_4$ when an excess is added to $[W(CCMe_3)Cl_4]NEt_4$. This pale blue complex has a sharp singlet at 34 ppm (J_{PW} = 260 Hz) in the $^{31}P\{^1H\}$ NMR spectrum and exchanges with added PEt_3 on the NMR time scale. $[W(CCMe_3)Cl_4(PEt_3)]NEt_4$ reacts with $ZnCl_2$(dioxane) in CH_2Cl_2 to yield a neutral tungsten species, $W(CCMe_3)Cl_3(PEt_3)$, and $[ZnCl_3]^-NEt_4^+$. This violet tungsten compound is more conveniently prepared by reacting $[W(CCMe_3)Cl_4]NEt_4$ and $ZnCl_2(PEt_3)$ in CH_2Cl_2 (eq 8).

$$\left[W(CCMe_3)Cl_4\right]NEt_4 + ZnCl_2(PEt_3) \xrightarrow[-\,ZnCl_3^-\,NEt_4^+]{CH_2Cl_2} W(CCMe_3)Cl_3(PEt_3) \qquad (8)$$

$W(CCMe_3)Cl_3(PEt_3)$ and added PEt_3 exchange on the NMR time scale. Mostly $W(CCMe_3)Cl_3(PEt_3)_2$ is observed by $^{31}P\{^1H\}$ NMR at ca. 30°C but only $W(CCMe_3)Cl_3(PEt_3)$ can be isolated from solution. $W(CCMe_3)Cl_3(PEt_3)$ does not catalyze the metathesis of acetylenes at ca. 25°C. No $Me_3CC{\equiv}CCH_2CH_3$, the cleavage product expected from metathesis of $PhC{\equiv}CCH_2CH_3$, was observed. $W(CCMe_3)Cl_3(PEt_3)$ does not react with $[HPEt_3]Cl$ in CH_2Cl_2 after 24 hr.

Reactions of $[W(CCMe_3)Cl_4]NEt_4$ with $LiOH/H_2O$

In the presence of PEt_3 $[W(CCMe_3)Cl_4]NEt_4$ undergoes an interesting reaction with LiOH or H_2O/NEt_3. Tungsten oxo-alkylidene complexes are formed in quantitative yield (eq 9). This unique class of molecules was fortuitously discovered by Wengrovius.[19a,34] When $W(O)(OBu^t)_4$ and $Ta(CHCMe_3)(PEt_3)_2Cl_3$ are allowed to react in pentane, $Ta(OBu^t)_4Cl$ and $W(O)(CHCMe_3)(PEt_3)_2Cl_2$

added to $[W(CCMe_3)Cl_4]NEt_4$. This pale blue complex has a sharp singlet at 34 ppm (J_{PW} = 260 Hz) in the $^{31}P\{^1H\}$ NMR spectrum and exchanges with added PEt_3 on the NMR time scale. $[W(CCMe_3)Cl_4(PEt_3)]NEt_4$ reacts with $ZnCl_2$(dioxane) in CH_2Cl_2 to yield a neutral tungsten species, $W(CCMe_3)Cl_3(PEt_3)$, and $[ZnCl_3]^-NEt_4{}^+$. This violet tungsten compound is more conveniently prepared by reacting $[W(CCMe_3)Cl_4]NEt_4$ and $ZnCl_2(PEt_3)$ in CH_2Cl_2 (eq 8).

$$\left[W(CCMe_3)Cl_4\right]NEt_4 + ZnCl_2(PEt_3) \xrightarrow[-\ ZnCl_3^-\ NEt_4^+]{CH_2Cl_2} W(CCMe_3)Cl_3(PEt_3) \quad (8)$$

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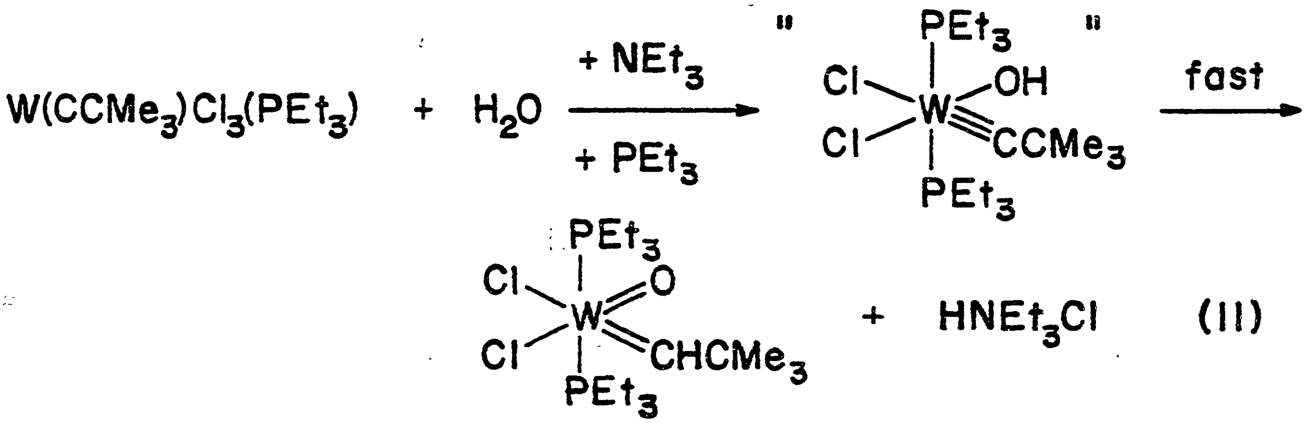
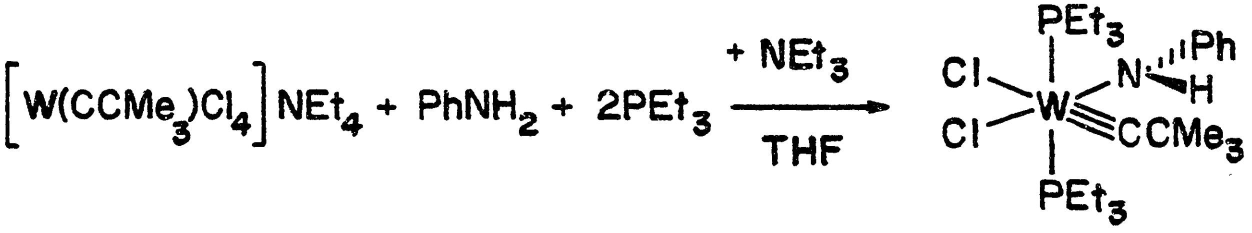


(11)

too fast (goes to completion at -30°C in ~5 min with H_2O) to isolate or observe the proposed intermediate but an analogous reaction with amines provides direct evidence for its formation (vide infra). Unfortunately without added phosphine no tractable product could be obtained from the reaction of $[W(CCMe_3)Cl_4]NEt_4$ and H_2O/NEt_3.

Reaction of $[W(CCMe_3)Cl_4]NEt_4$ with Primary Amines

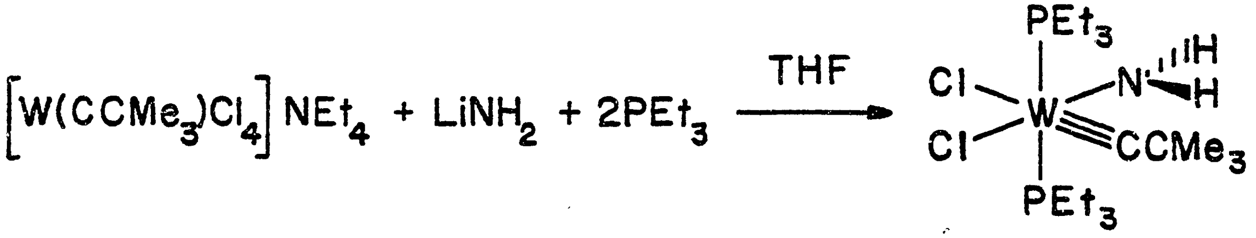
We hoped to prepare tungsten imido-alkylidene complexes, a class of molecules discovered by Pedersen,[35] from the reaction of $[W(CCMe_3)Cl_4]NEt_4$ and primary amines in the presence of NEt_3. When $[W(CCMe_3)Cl_4]NEt_4$ reacts with aniline in thf a tungsten amido-alkylidyne complex is isolated from solution as red-orange crystals (eq 12). In contrast to the hydroxy system



(12)

(vide supra) the amido proton does not transfer to the alkylidyne carbon even if the reaction stirs 24 hr at ca. 35°C. The 250 MHz ^{1}H NMR is straightforward and shows the amide proton as a broad peak at 13.2 ppm. The alkylidyne α-carbon is observed at 300.5 ppm as a triplet equally coupled to the two trans phosphines (J_{CP} = 10.7 Hz) in the $^{13}C\{^1H\}$ NMR spectrum. The ipso-phenyl carbon is found at 153.5 ppm. The $^{31}P\{^1H\}$ NMR spectrum consists of a sharp singlet at 16 ppm (J_{PW} = 276 Hz). The complex does not exchange with added PEt_3 on the NMR time scale. $W(CCMe_3)(NHPh)(PMe_2Ph)_2Cl_2$, prepared by using PMe_2Ph instead of PEt_3, shows inequivalent phosphine methyl groups in the ^{1}H NMR spectrum. The inequivalency of the methyl groups provides good evidence for the cis-arrangement of amido and alkylidyne ligands. The crystal structure of a phosphido derivative showed the phosphide and alkylidyne ligands to be cis with trans triethylphosphine ligands (vide infra). $W(CCMe_3)(NHPh)(PEt_3)Cl_2$, an orange oil, can be prepared from $W(CCMe_3)Cl_3(PEt_3)$ and LiN(H)Ph (or $PhNH_2$ in the presence of NEt_3). Since this compound is an oil it is not readily purified. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 40 ppm (J_{PW} = 308 Hz) and a small amount of the bis-phosphine complex, $W(CCMe_3)(NHPh)(PEt_3)_2Cl_2$, at 16 ppm. The $^{13}C\{^1H\}$ NMR spectrum of $W(CCMe_3)(NHPh)(PEt_3)Cl_2$ shows the alkylidyne α-carbon at 304.6 ppm as a doublet (J_{CP} = 12.2 Hz).

A bis-protio amido species, $W(CCMe_3)(NH_2)(PEt_3)_2Cl_2$, can be prepared as outlined in equation 13. The $LiNH_2$ is not very soluble, even in thf, so

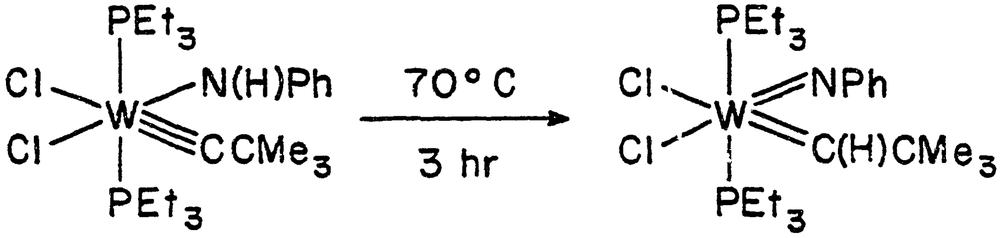


(13)

the reaction is slow (~8 hr). The amido protons are inequivalent and are found at 9.4 ppm and 10.8 ppm in the 250 MHz ^1H NMR spectrum. The inequivalency of the amido protons suggests that the amido ligand is not freely rotating about the W-N bond and lies in the basal plane defined by the alkylidyne α-carbon and chloride ligands. The amido ligand can either be planar or rapidly inverting so we observe the average (a planar NH_2 moiety) on the NMR time scale.

Thermal Transformation of "W($CCMe_3$)(NHPh)" to "W($CHCMe_3$)(NPh)": Kinetics of Amido-alkylidyne to Imido-alkylidene

W($CCMe_3$)(NHPh)(PEt_3)$_2$$Cl_2$ is a stable molecule in the solid state or solution at ca. 25°C. However, if a sample is heated in an NMR tube a new compound can be cleanly observed by ^1H NMR. This new complex is the imido-alkylidene, W($CHCMe_3$)(NPh)(PEt_3)$_2$$Cl_2$ (eq 14). The reaction is very clean



(14)

(by ^1H or $^{31}P\{^1H\}$ NMR) and the product is formed quantitatively. The $^{31}P\{^1H\}$ NMR chemical shifts are only separated by ~1.3 ppm and the ^{31}P coupling to ^{183}W is equivalent (J_{PW} = 276 Hz) for the two molecules. By 250 MHz ^1H NMR we can observe both species in solution. The amido proton is observed at 13.2 ppm and the alkylidene proton is a triplet($^3J_{HP}$ = 4 Hz) at 12.0 ppm. The tert-butyl groups are distinctive (Δ = 0.03 ppm) but the PEt_3 resonances overlap. The ortho-protons on the phenyl ring are observed at 7.9 ppm ($W{=}NC_6H_5$) and 7.5 ppm ($W{-}N(H)C_6H_5$).

In order to further investigate the transformation of red-orange amido-alkylidyne to yellow imido-alkylidene we elected to perform some simple kinetic measurements. We chose ^{1}H NMR to monitor the reaction (Figure 1). Data were obtained by integration of the ortho-phenyl resonances in starting material versus the ortho-phenyl resonances in product. Plotting ln $^{C_o}/_C$ (where C_o = concentration of starting material and C = concentration of product) versus time (minutes) gave straight lines with slope equal to the rate constant. The slope was determined by a linear least-squares fit of the data and correlation coefficients were always >0.99.

The reaction was found to be first order in metal complex and concentration independent through 3 half-lives. In d_8-toluene solution the rate constants (k) are 2.8 x 10^{-2} min^{-1} and 3.0 x 10^{-2} min^{-1} for solutions 0.03 M and 0.30 M in tungsten complex, respectively. These rate constants are within experimental error (rate constants derived from multiple runs gave values within ±5-10%) and represent a half life of ~25 min. Rate constants along with thermodynamic parameters derived from an Arrhenius plot (Figure 2) are given in Table II. No solvent effect was observed as similar rates (±5%) were observed in d_8-toluene, d-chloroform, and d_5-bromobenzene. A large value for the preexponential factor (log A = 20 ± 2) generally represents a "loose" or disordered transition state.[94] Whitesides and co-workers have observed similar values for log A in the decomposition of L_2PtR_2 (L =

Figure 1. 250-MHz ^{1}H NMR spectra of amido-alkylidyne to imido-alkylidene transformation at 340K.

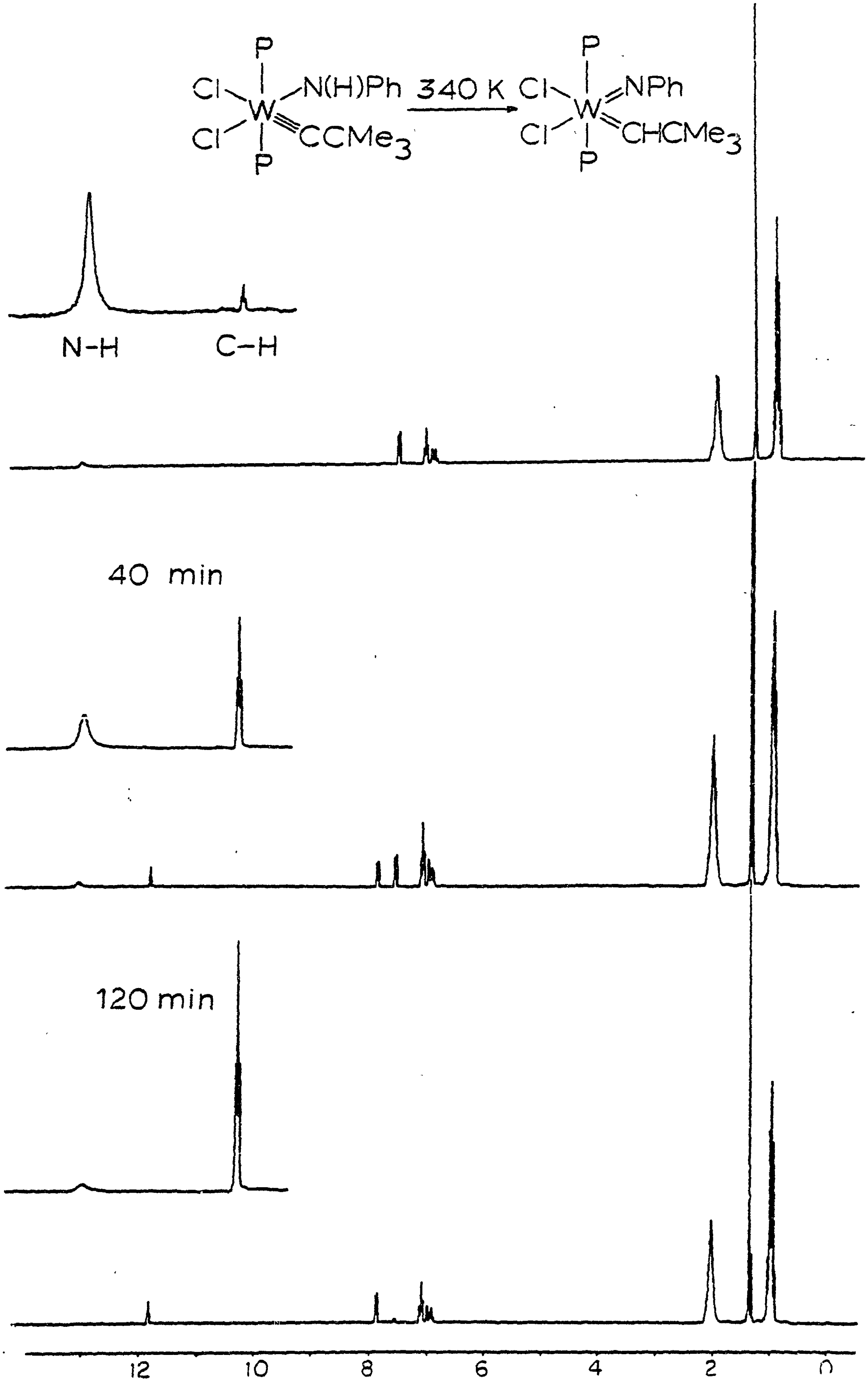

P
Cl
Cl
W
N(H)Ph
CCMe3
P
340 K
P
Cl
Cl
W
NPh
CHCMe3
P
N-H
C-H
40 min
120 min
12
10
8
6
4
2
0

Figure 2. Arrhenius plot of -ln k vs. 1/T for the decomposition of $W(CCMe_3)(NHPh)(PEt_3)_2Cl_2$ at six temperatures (see Table II).

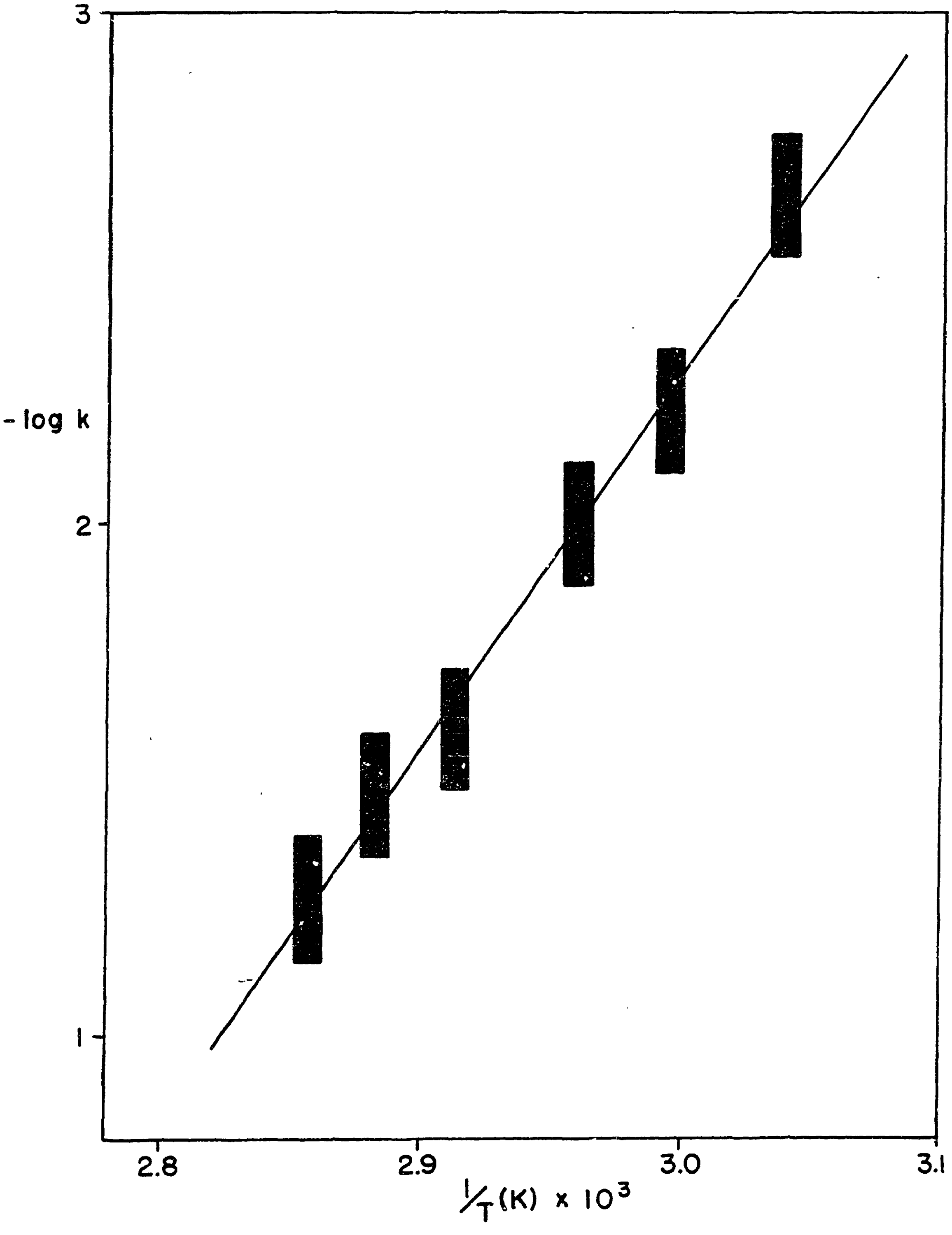

3
2
1
- log k
2.8
2.9
3.0
3.1
1/T(K) x 10^3

TABLE II. Kinetic and Thermodynamic Parameters for Decomposition of $W(CCMe_3)(NHPh)(PEt_3)_2Cl_2$ in d_8-toluene.[a]

T, K	$^1/_T \times 10^3$	$k \times 10^3$, min^{-1}	-log k	$t_{1/2}$, min
350	2.857	55.5	1.26	12
347	2.882	33.7	1.47	21
346	2.890	30.2	1.52	23
343	2.915	25.6	1.59	27
338	2.959	9.9	2.00	70
334	2.994	6.0	2.22	116
329	3.039	2.3	2.64	301

log A = 20 ± 2

E_a = 34 ± 3 kcal mol^{-1}

$\Delta G^{\ddagger}$ = 22 ± 4 kcal mol^{-1}

$\Delta H^{\ddagger}$ (70°C) = 33 ± 3 kcal mol^{-1}

$\Delta S^{\ddagger}$ (70°C) = 31 ± 9 eu

[a] The error in k has been experimentally determined to be ±10%. The difference between the largest and smallest slopes in the Arrhenius plot represents the error in log A. The errors in the thermodynamic values can hence be calculated. Temperature measurements are ±0.5 degrees.

PEt_3, R = alkyl) under certain conditions.[95] They noted an inverse first-order dependence of the rate of decomposition on added phosphine concentrations. However in our system added phosphine has no effect upon the rate of reaction (Table III). This indicates that dissociation of phosphine is not involved in the rate-limiting step. If 10 mole equivalents of NEt_3 (1.5 M) is added to a 0.15 M d_8-toluene solution of $W(CCMe_3)(NHPh)(PEt_3)_2Cl_2$ the rate of reaction increases ten-fold. When a strong base, such as a phosphorane, is added to $W(CCMe_3)(NHPh)(PEt_3)_2Cl_2$ the amide is deprotonated

TABLE III. Rate Dependence Upon Added [PEt_3] at 338 K.[a]

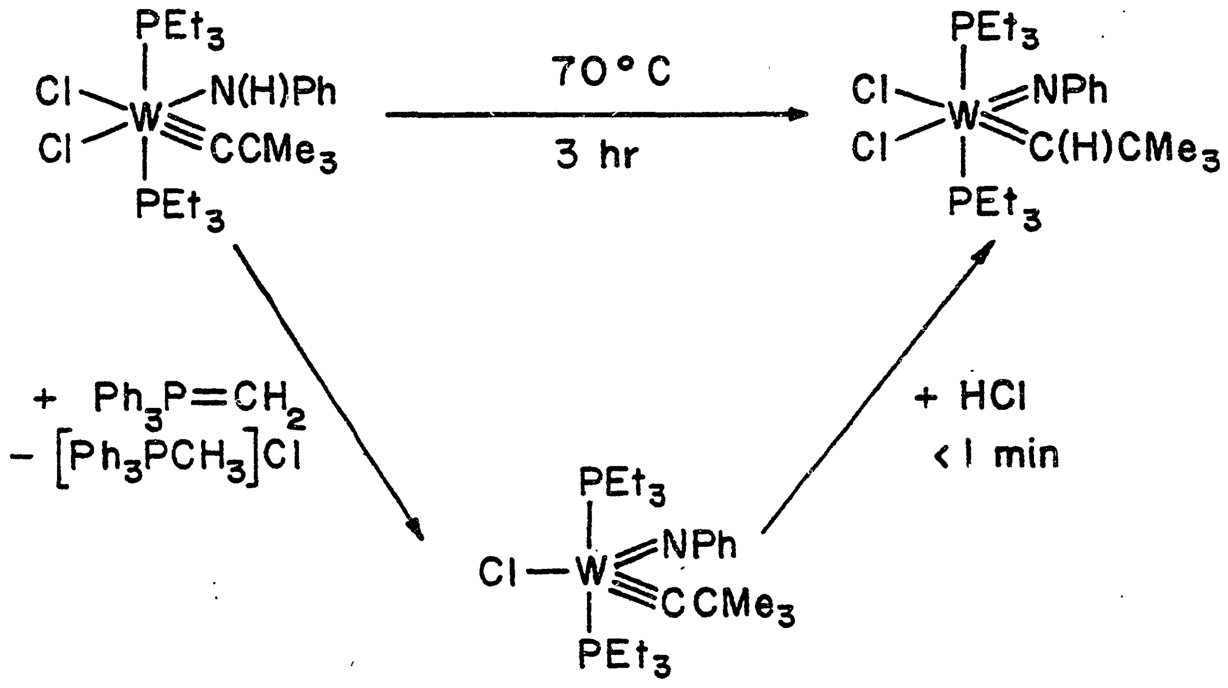
[PEt_3], M	k x 10^3, min^{-1}
0	9.9
0.77 (5 equiv)	9.6
1.54 (10 equiv)	10.3

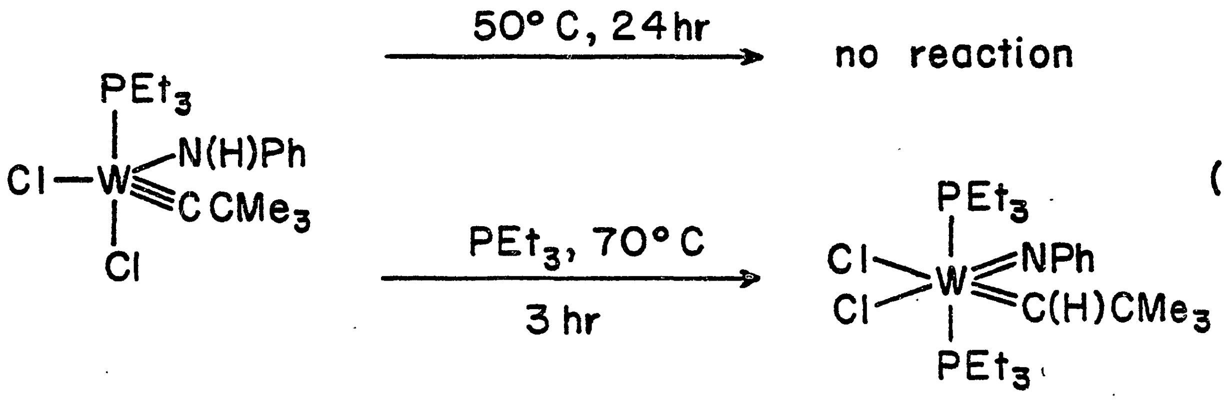
[a] In d_8-toleune solution 0.15 M W complex.

(the complex is actually dehydrohalogenated) and an imido-alkylidyne complex, $W(CCMe_3)(NPh)(PEt_3)_2Cl$ is formed. If 1 mole equivalent of $[HNEt_3]Cl$ or HCl is added to $W(CCMe_3)(NPh)(PEt_3)_2Cl$ in benzene the alkylidyne α-carbon atom is protonated and the imido-alkylidene complex, $W(CHCMe_3)(NPh)(PEt_3)_2Cl_2$, is formed (Scheme I). The protonation with HCl is extremely fast as the reaction is complete in less than 1 min by ^1H NMR. Since $[HNEt_3]Cl$ is not very benzene soluble the protonation is fairly slow using this weak acid ($pK_a \sim 10$) and takes ~3 hr at 55°C to complete.

The mono-phosphine amido complex, $W(CCMe_3)(NHPh)(PEt_3)Cl_2$, does not readily undergo proton transfer to give $W(CHCMe_3)(NPh)(PEt_3)Cl_2$. When a sample of $W(CCMe_3)(NHPh)(PEt_3)Cl_2$ is heated to 50°C in benzene no imido-alkylidene complex is observed after 24 hr. Higher temperatures could not be used since $W(CHCMe_3)(NPh)(PEt_3)Cl_2$ is not stable above ~50°C. However, if 1 mole equivalent of PEt_3 is added the proton transfer is complete within a few hours at 70°C (eq 15).

Scheme I


PEt3
Cl
Cl
W
N(H)Ph
CCMe3
PEt3
70 °C
3 hr
PEt3
Cl
Cl
W
NPh
C(H)CMe3
PEt3
+ Ph3P=CH2
− [Ph3PCH3]Cl
+ HCl
< 1 min
PEt3
Cl—W
NPh
CCMe3
PEt3

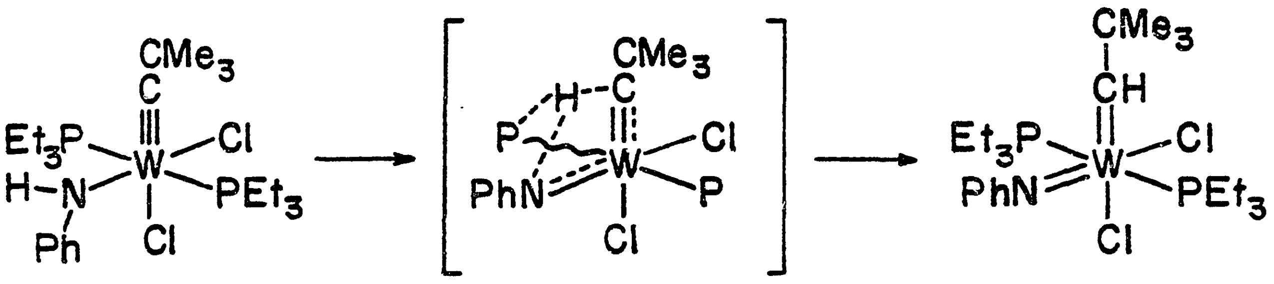

50° C, 24 hr
no reaction
PEt3
Cl—W
N(H)Ph
CCMe3
Cl
PEt3, 70° C
3 hr
PEt3
Cl
Cl
W
NPh
C(H)CMe3
PEt3

(15)

The bis-protio amido complex, $W(CCMe_3)(NH_2)(PEt_3)_2Cl_2$, cleanly decomposes to the protio imido-alkylidene complex, $W(CHCMe_3)(NH)(PEt_3)_2Cl_2$ at about half the rate of $W(CCMe_3)(NHPh)(PEt_3)_2Cl_2$ ($t_{1/2}$ ~ 25 min at 350 K). A 250 MHz ^1H NMR spectrum displaying an approximately 1:1 ratio of amido and imido complexes is shown in figure 3. The alkylidene proton is observed at 12.1 ppm (triplet; $^3J_{HP}$ = 3.7 Hz) and the imido proton is found at 6.1 ppm in the ^1H NMR spectrum. We believe the decrease in rate is related to the acidity of W-N(H)Ph versus $W-NH_2$. The pK_a for $PhNH_2$ is ~27 while the pK_a of NH_3 is ~36.

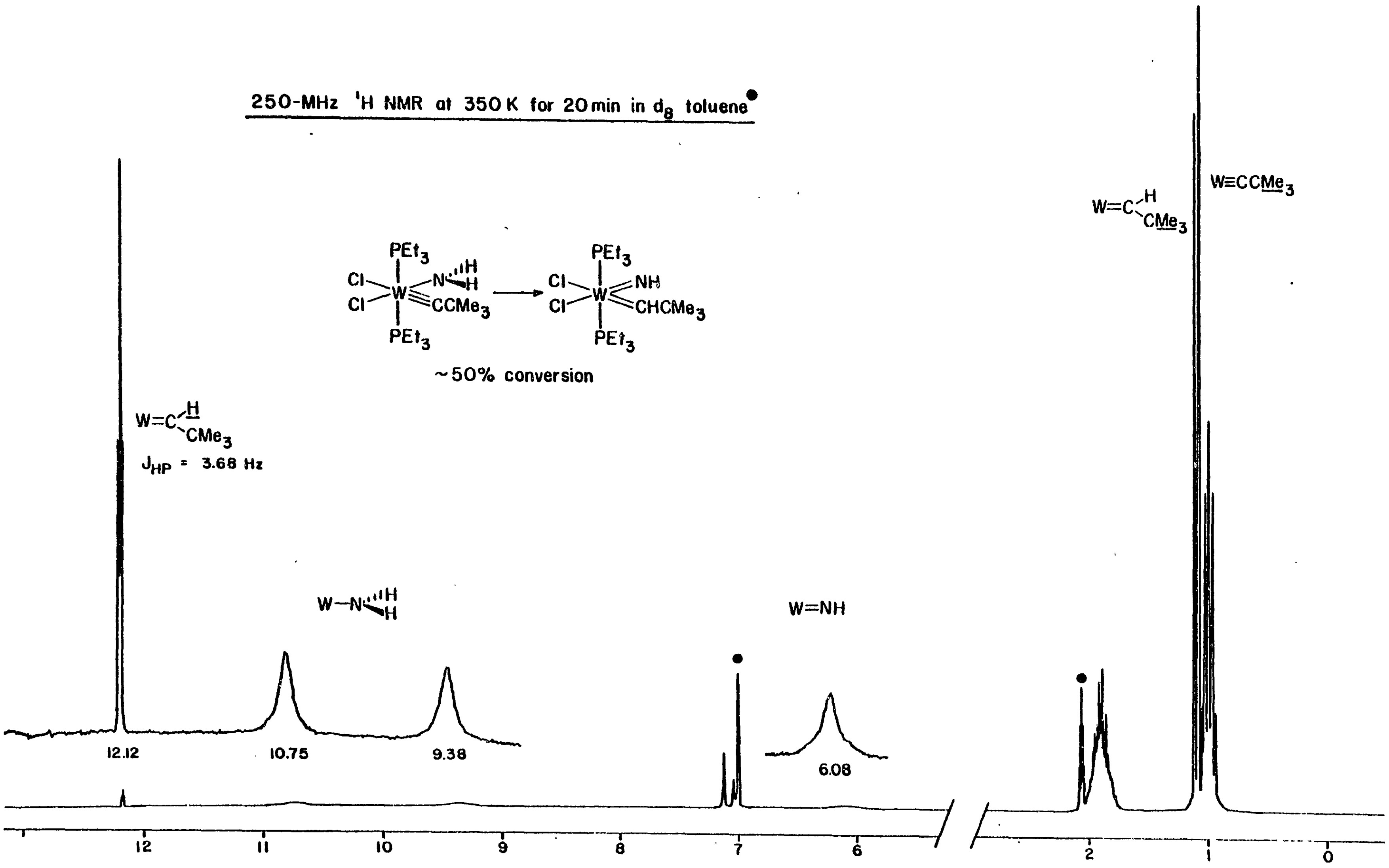
Mechanism of Proton Transfer

Our kinetic work has shown the proton transfer of amido-alkylidyne to imido-alkylidene to be unimolecular and solvent independent. In addition the rate of reaction was found to be independent of added phosphine concentration. One possible mechanism would involve a "phosphine-assisted" proton transfer. Since electrophilic 1,3-shifts are rare in organic systems[96] the "phosphine-assisted" mechanism allows for the transfer to occur via two successive 1,2-shifts. One possible transition state structure could involve a proton-capped octahedron (eq 16). This mechanism could help



(16)

Figure 3. 250-MHz ^{1}H NMR of a ca. 1:1 mixture of $W(CCMe_3)(NH_2)(PEt_3)_2Cl_2$ and $W(CHCMe_3)(NH)(PEt_3)_2Cl_2$ at 350 K.



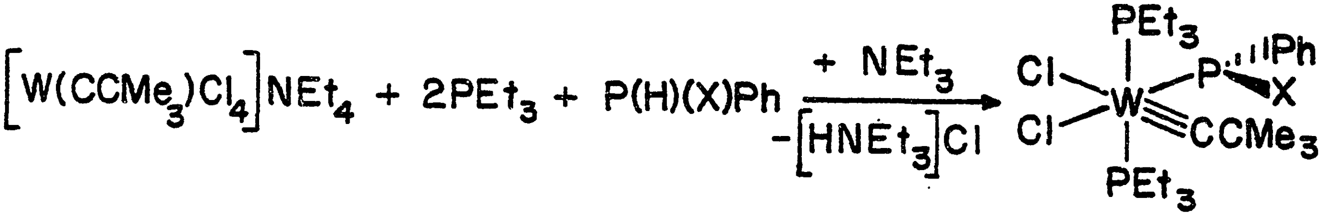
250-MHz ^{1}H NMR at 350 K for 20 min in d_8 toluene ●

account for the rather large preexponential factor as the proton is being averaged over the three sites.

The fact that the mono-phosphine amido complex, $W(CCMe_3)(NHPh)(PEt_3)Cl_2$, does not undergo the proton transfer until an equivalent of phosphine is added (most likely making the bis-phosphine complex) is consistent with this mechanistic proposal. We believe that the most likely structure for $W(CCMe_3)(NHPh)(PEt_3)Cl_2$ is the trigonal bipyramid shown in equation 15. The crystal structure of $W(CHCMe_3)(O)(PEt_3)Cl_2$ shows it to be a trigonal bipyramid with the two π-donor ligands, the oxo and alkylidene, in the equatorial plane and the phosphine in an axial position.[34] If the amido-alkylidyne complex indeed has a similar geometry then the amide and alkylidyne ligands are 120° apart while in the bis-phosphine complex they are 90° apart. Having the amide and alkylidyne ligands in close proximity may be a requirement for the proton transfer.

Preparation of Tungsten Phosphide Complexes of the Type $W(CCMe_3)(P(X)Ph)(PEt_3)_2Cl_2$ (X = H, Me, Ph)

Complexes containing a covalently bonded phosphorous ligand, phosphido complexes, can be conveniently prepared via a metallation reaction involving $[W(CCMe_3)Cl_4]NEt_4$ and P(H)(X)Ph (X = H, Me, Ph) (eq 17). These orange-red



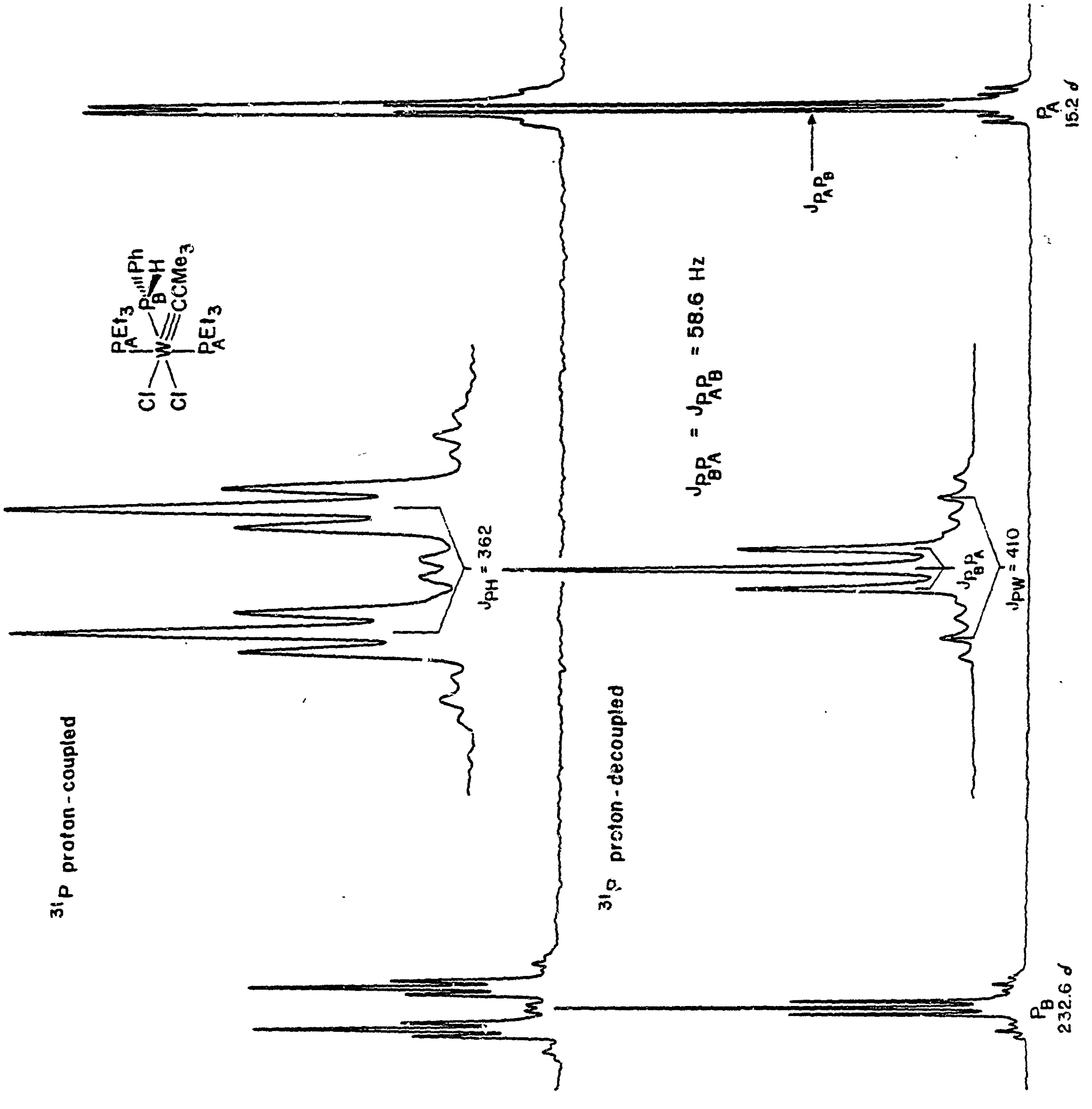
(17)

crystalline alkylidyne species are readily isolated from solution. The $^{31}P\{^1H\}$ NMR spectra are very informative as the typical A_2B meridional phosphine pattern is observed. The phosphide phosphorous is observed as a triplet ($J_{PP'}$ = 59 Hz) at 230-290 ppm while the triethylphosphines are observed as a doublet ($J_{PP'}$ = 59 Hz) at 13-15 ppm. One of the most interesting observations about these molecules is that inequivalent phenyl groups are observed in the $^{13}C\{^1H\}$ NMR spectrum of $W(CCMe_3)(PPh_2)(PEt_3)_2Cl_2$. The ipso-phenyl carbon atoms are found at 150.5 ppm (J_{CP} = 38 Hz) and 147.9 ppm (J_{CP} = 12 Hz). The inequivalency of the phenyl groups indicates that the phosphide ligand is not rotating about the W-P bond on the NMR time scale and that the phosphide is most likely cis to the neopentylidyne. We believe that the lone pair of electrons on phosphorous are sufficiently donating into empty metal orbitals forming a planar phosphide ligand similar to that observed in the bis-protio amide system (vide supra). This would hinder rotation explaining the inequivalent phenyl groups. The different carbon-phosphorous coupling constants in the $^{13}C\{^1H\}$ NMR spectrum may be ascribed to different orientations of the phenyl groups with respect to the equatorial plane.

The proton-coupled ^{31}P NMR spectrum of $W(CCMe_3)(PHPh)(PEt_3)_2Cl_2$ (Figure 4) shows the phosphide phosphorous atom as a doublet (J_{PH} = 362 Hz) of triplets ($J_{PP'}$ = 59 Hz). As expected the P-H proton is observed as a doublet (centered at 10 ppm; J_{HP} = 362 Hz) in the ^1H NMR spectrum. Heating a sample of $W(CCMe_3)(PHPh)(PEt_3)_2Cl_2$ in benzene for 24 hr at 75°C did not induce a proton transfer from phosphorous to carbon as anticipated.

The crystal structure of $W(CCMe_3)(PHPh)(PEt_3)_2Cl_2$ has recently been completed by Churchill and co-workers.[49] The geometry is as shown in

Figure 4. The ^{31}P and $^{31}P\{^{1}H\}$ NMR spectra of $W(CCMe_3)(PHPh)(PEt_3)_2Cl_2$ in C_6D_6 at 36 MHz (300 K).



31P proton-coupled
31P proton-decoupled
Cl, Cl, W, PAEt3, PAEt3, PB, Ph, H, CCMe3
J_PH = 362
J_PBPA
J_PW = 410
J_PBPA = J_PAPB = 58.6 Hz
J_PAPB
PB 232.6 δ
PA 15.2 δ

equation 17. The PEt_3 ligands are bent back from the two π-bonding ligands forming a P-W-P angle of 159.65(4)Å . The most important feature of the structure is the planar phosphide ligand with the phenyl ring lying in the equatorial plane and directed away from the neopentylidyne ligand. The W-P (phosphido) distance is 2.291(1)Å and the W-P-C (ipso) angle is 140.02(17)°.

DISCUSSION

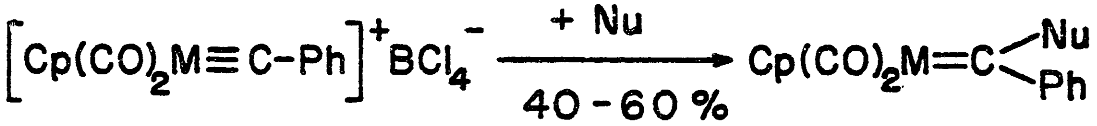
In this chapter we have investigated some simple reaction chemistry of, hitherto, a relatively unexplored area of transition metal chemistry, high-valent tungsten alkylidyne complexes. We have found that $[W(CCMe_3)Cl_4]NEt_4$ undergoes clean substitution (-OR and PEt_3) and metallation reactions (H_2O, H_2NPh, H_2PPh, etc.) to give a variety of novel products.

The preparation of $[W(CCMe_3)(OBu^t)Cl_3]NEt_4$ proved quite useful as McCullough has demonstrated that this complex reacts cleanly with TlC_5H_5 (as well as other Cp^- salts) to yield $(\eta^5\text{-}C_5H_5)W(CCMe_3)(OBu^t)Cl$.[97] The parent complex, $[W(CCMe_3)Cl_4]NEt_4$, does not react with Cp salts under any yet attempted conditions to yield tractable products.[97] The tert-butoxide ligand hence stabilizes the molecule to anionic substitution chemistry. The bis-tert-butoxide could not be prepared by our equilibration technique (eq 5) because the product, $[W(CCMe_3)(OBu^t)_2Cl_2]NEt_4$, would probably not exist as an anion and the NEt_4Cl in solution inhibits the reaction.

It was interesting to observe that we could set-up an equilibrium between $W(CCMe_3)(OBu^t)_3$ and proposed $W(CHCMe_3)(OBu^t)_4$ by the addition of tert-butanol. We believe such an equilibrium is small because the rate of metathesis of cis-2-pentene is modest and related catalysts such as $W(O)(CHCMe_3)(OBu^t)_2$[98] and $W(O)(CH_2CMe_3)_3Br/AlBr_3$[99] are quite active. We had hoped that $W(CCMe_3)(OBu^t)_3$ might react with LiOH or H_2O to give $W(O)(CHCMe_3)(OBu^t)_2$ by analogy to equation 9 but no reaction was observed with LiOH and H_2O was not clean. An attempt at preparing $W(CHCMe_3)(NPh)(OBu^t)_2$ from $W(CCMe_3)(OBu^t)_3$ and LiNHPh was fruitless as only starting material was isolated.

The addition of triethylphosphine to $[W(CCMe_3)Cl_4]NEt_4$ yielded $[W(CCMe_3)Cl_4(PEt_3)]NEt_4$. The fact that chloride ion remained coordinated to the metal is a good indication of the electrophilicity of d^0 tungsten. Although the NEt_4Cl can be removed with $ZnCl_2$(dioxane) to yield $W(CCMe_3)Cl_3(PEt_3)$, a one-step synthesis of the neutral phosphine complex can be accomplished using $ZnCl_2(PEt_3)$. The lack of observed acetylene metathesis products from the reaction of $W(CCMe_3)Cl_3(PEt_3)$ and PhC≡CPh is somewhat surprising in view of the fact that Wengrovius observed metathesis of PhC≡CPh with $W(CCMe_3)Cl_3(OPEt_3)$ (70°C, 1 hr).[93] These results indicate how only slight modifications in the coordination sphere of the metal can allow for acetylene metathesis. Similar observations were seen in olefin metathesis with tantalum and niobium neopentylidene complexes[19] (cf. Chapter 1).

Our observed transformation of tungsten alkylidyne complexes to tungsten alkylidene complexes is not without precedent. Fischer and co-workers have found that nucleophiles readily add to the carbyne carbon of cationic carbyne complexes (eq 18).[100] The non-heteroatom-stabilized carbene complexes



$$\left[Cp(CO)_2M\equiv C\text{-}Ph\right]^+ BCl_4^- \xrightarrow[40-60\%]{+\,Nu} Cp(CO)_2M=C\begin{matrix}Nu\\Ph\end{matrix} \qquad (18)$$

M = Mn, Re ; Nu = CN, NCS, OR, CH_3, H

were only prepared for rhenium. The reaction of $[W(CCMe_3)Cl_4]NEt_4/2PEt_3$ with LiOH or H_2O/NEt_3 is fast at low temperature (-78°C) and the proposed intermediate a tungsten hydroxy-alkylidyne, "$W(CCMe_3)(OH)$", cannot be observed. We believe this hydroxy-alkylidyne is a viable intermediate since the nitrogen analogue, an amido-alkylidyne complex, $W(CCMe_3)(NHPh)(PEt_3)_2Cl_2$, can be isolated and smoothly converted to the imido-alkylidene complex. The greater acidity of the W-OH proton versus that of W-NHPh probably accounts for the much faster transformation in the hydroxy system (organic alcohols are more acidic than the corresponding amines).

There are some simple electronic considerations to be made concerning the aforementioned transformation. One driving force for the proton transfer reaction (other than an acid/base reaction) might be the formation of two multiply bonded ligands. We have seen that d^0 tungsten can be stabilized (especially relative to reduction) by π-bonding ligands. Tungsten oxo-[19a,34] and imido-alkylidene[35] species are generally very stable molecules obtained in high yields. Osborn[99] and Pedersen[35] have found that the oxo and imido ligands help stabilize d^0 tungsten towards alkylating agents (cf. Chapter 5). Clark has found that $W(CCMe_3)(CHCMe_3)(CH_2CMe_3)(PMe_3)_2$, a complex containing both a metal triple and double bond to carbon, is formed when $[W(CCMe_3)(CH_2CMe_3)_3]_2$ is decomposed in neat PMe_3.[91] Symmetry restrictions allow three π-bonds to be formed in any cis-octahedral system.[41] The oxo- and imido-alkylidene species formed probably contain one π-bond involved in alkylidene bonding and two π-bonds in oxo or imido bonding. Oxo and imido ligands are good π-donors and can generally be viewed to form triple bonds (2 π-bonds, 1 σ-bond) to transition metal ions. The formation of three π-bonds (from an alkylidyne complex containing two π-bonds) probably contributes to the driving force for this reaction.

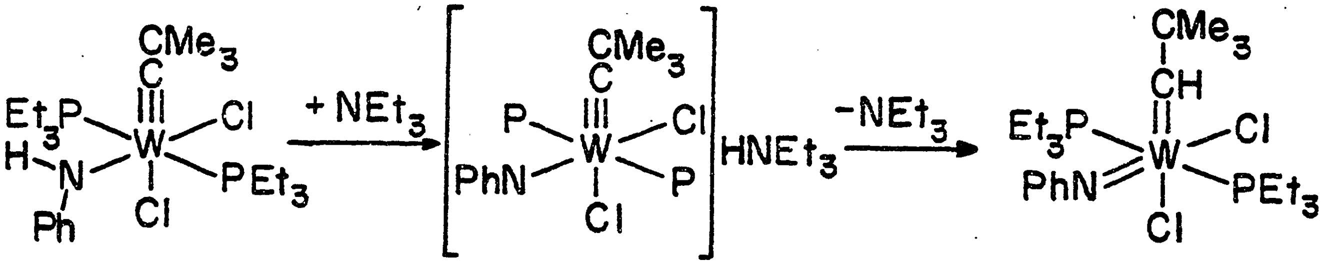
The ease of preparing amido and imido complexes of tungsten containing reactive ligands such as neopentylidyne and neopentylidene is potentially quite useful. Although tungsten alkylidene and alkylidyne complexes are active catalysts for the metathesis of olefins and acetylenes respectively, some difficulties exist. Bimolecular decomposition of reactive intermediates as well as catalyst separation from products are two problems that can be circumvented by covalently attaching the catalysts to solid supports. Pedersen is exploring this area of chemistry via the use of bifunctional reagents such as $(EtO)_3Si(CH_2)_3NHR$ (R = H, alkyl). He has prepared $W(CCMe_3)\{N(R)(CH_2)_3Si(OEt)_3\}(PEt_3)_2Cl_2$ which could be attached to a silica support via a siloxy bond.[35]

The bis-protio amide species, $W(CCMe_3)(NH_2)(PEt_3)_2Cl_2$, provided us with some useful information concerning the geometry of our amido-alkylidyne species. The inequivalency of the amide protons in the ^1H NMR is best explained by a cis-orientation of amide and alkylidyne ligands where the $-NH_2$ ligand is planar and non-rotating on the NMR time scale. The lone pair of electrons on nitrogen are probably donating into empty metal orbitals forming three π-bonds (vide supra) and a planar ligand. $W(CCMe_3)(NH_2)(PEt_3)_2Cl_2$ and $W(CHCMe_3)(NH)(PEt_3)_2Cl_2$ are rare examples of protio amido and imido species.

The mechanism of proton transfer in the "amide to imide" conversion is open to further speculation. We feel comfortable in proposing two successive 1,2-hydrogen shifts but a simple 1,3-shift can by no means be ruled out. The fact that two phosphines are required in the coordination sphere may just indicate the necessity for the amide and alkylidyne to be 90° apart.

This intraligand crowding requirement has been observed in the decomposition of a Ta(V) neopentyl complex.[22] Trigonal bipyramidal $Ta(CH_2CMe_3)_3Cl_2$, in which the neopentyl ligands are in the equatorial plane 120° apart, is stable with respect to α-hydrogen abstraction. However $Ta(CH_2CMe_3)_4Cl$, in which a 90° interaction between neopentyl groups exists, decomposes by α-hydrogen abstraction to yield, in the presence of $LiCH_2CMe_3$, $Ta(CHCMe_3)(CH_2CMe_3)_3$.[22] An example of an octahedral tungsten complex with a proton-capped face has recently been obtained by Wengrovius.[98] The crystal structure of $W(CHCMe_3)(CO)(PMe_3)_2Cl_2$, performed by Churchill and co-workers, has shown that the alkylidene proton (H_α) is located on a P-Cl-C_α face of the distorted octahedral species.[101]

The NEt_3-induced transformation may be occuring by another mechanism. The amine may actually be deprotonating the amide forming an ion pair which, in a fast reaction, the $HNEt_3^+$ protonates the alkylidyne (eq 19). The fact that we can prepare $W(CCMe_3)(NPh)(PEt_3)_2Cl$ and then selectively protonate the alkylidyne α-carbon atom is consistent with this kind of mechanistic proposal. The judicious choice of added base in such a system will be important, as the conjugate acid that may form must be acidic enough to protonate the alkylidyne. The use of the phosphorane, $Ph_3P{=}CH_2$, illustrates



(19)

this point as $[Ph_3PCH_3]Cl$ is a relatively poor acid and $W(CCMe_3)(NPh)(PEt_3)_2Cl$ is isolated in high yield. It is interesting to note that this five-coordinate alkylidyne does not metathesize PhC≡CPh in 24 hr at ca. 25°C. One possible explanation is that if all the orbitals available for π-bonding are taken up by the imido and alkylidyne ligands and coordination of the acetylene is necessary, there may be no orbitals available for such pre-coordination.

Although there are many examples of bridging phosphido groups in bimetallic systems[102] relatively few monomeric phosphide complexes are known. Schumann has prepared lanthanide phosphido complexes using $LiP(Bu^t)_2$[103] and $LnCl_3$ or Cp_2LnCl. $CpNi[P(SiMe_3)_2]_2(PPh_3)$[104] and $[Fe(CO)_4(PPh_2)]PPN$[105] have also been reported. Muetterties and co-workers have reported the structurally characterized $Mo\{P(OCH_3)_3\}_5P(OMe)_2{}^+PF_6{}^-$ which is derived from proton cleavage of the P-O phosphite ester bond.[106] This molecule exhibits rapid OCH_3 exchange among the phosphorous sites which renders all phosphorous nuclei equivalent on the NMR time scale. At -80°C the fluxional process can be frozen out and three resonances are observed in the $^{31}P\{^1H\}$ NMR spectrum. The crystal structure displayed a planar phosphide ($P(OMe)_2$) moiety and the molybdenum-phosphide phosphorous bond length is 2.229(4)Å.

The phosphido complexes prepared in this chapter represent a novel class of monomeric species containing planar phosphide ligands. The crystal structure[49] confirmed our original supposition (NMR evidence) that the phosphorous lone electron pair was donating into low-lying tungsten-based orbitals yielding a planar ligand and that the phosphide and alkylidyne ligands are in a cis orientation.

CHAPTER 4 EXPERIMENTAL

$W(CCMe_3)(OBu^t)_3$ and $[W(CCMe_3)Cl_4]NEt_4$ were prepared by published methods.[93] PMe_2Ph, H_2PPh, $HPPh_2$ and $HP(CH_3)Ph$ were purchased from Strem Chemical Co. and used as received.

PREPARATIONS

$[W(CCMe_3)(OBu^t)Cl_3]NEt_4$ (VII-46)

Solid $W(CCMe_3)(OBu^t)_3$ (0.24 g, 0.50 mmol) was added to $[W(CCMe_3)Cl_4]NEt_4$ (0.53 g, 1.0 mmol) and NEt_4Cl (0.08 g, 0.50 mmol) in CH_2Cl_2 (10 mL). After stirring 24 hr the cherry-red solution was filtered, concentrated in vacuo (~5 mL), ether (~2 mL) added, filtered, and cooled to -30°C. 0.75 g (89% yield) of red-purple crystals were isolated by filtration.

^1H NMR (CH_2Cl_2, 60 MHz, ppm): 3.30 (q, 8, J_{HH} ~ 6 Hz, $N\underline{CH_2}CH_3$), 1.55 (s, 9, $OC\underline{Me_3}$), 1.38 (br m, 12, $NCH_2\underline{CH_3}$), 1.08 (s, 9, $CCMe_3$). $^{13}C\{^1H\}$ NMR (CH_2Cl_2, 22 MHz, ppm): 304.2 ($\underline{C}CMe_3$), 81.3 ($O\underline{C}Me_3$), 52.0 ($N\underline{C}H_2CH_3$), 47.6 ($C\underline{C}Me_3$), 31.8 ($OC\underline{Me_3}$), 30.8 ($CC\underline{Me_3}$), 7.0 ($NCH_2\underline{C}H_3$).

$W(CCMe_3)(OBu^t)(PEt_3)Cl_2$ (VII-51)

$[W(CCMe_3)(OBu^t)Cl_3]NEt_4$ (0.28 g, 0.50 mmol) was dissolved in CH_2Cl_2 (5 mL) and the solution cooled to -30°C. PEt_3 (0.06 g, 0.50 mmol) was added and the red solution immediately turned orange. After 1 hr the reaction was evaporated to dryness, extracted with pentane, filtered, concentrated in vacuo, and cooled to -30°C. A quantitative yield of orange-red crystals were isolated by filtration.

^1H NMR (C_6D_6, 60 MHz, ppm): 2.01 (m, 6, $PC\underline{H}_2CH_3$), 1.82 (s, 9, $OCMe_3$), 1.51 (s, 9, $CCMe_3$), 1.10 (m, 9, $PCH_2C\underline{H}_3$). $^{31}P\{^1H\}$ NMR (C_6H_6, 36 MHz, ppm): 34.1 (s, J_{PW} = 173). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 MHz, ppm): 318.0 ($\underline{C}CMe_3$), 84.3 ($O\underline{C}Me_3$), 51.3 ($C\underline{C}Me_3$), 33.2 ($OC\underline{Me}_3$), 31.9 ($CC\underline{Me}_3$), 18.0 (d, J_{CP} = 26, $P\underline{C}H_2CH_3$), 8.8 ($PCH_2\underline{C}H_3$).

$[W(CCMe_3)(PEt_3)Cl_4]NEt_4$ (VII-60, 62)

PEt_3 (0.47 g, 4.0 mmol) was added to $[W(CCMe_3)Cl_4]NEt_4$ (2.1 g, 4.0 mmol) in thf (10 mL). The solution immediately became homogeneous blue-green. After 3 hr the thf solution was cooled to -30°C. 1.1 g of ether or pentane insoluble light blue crystals were isolated by filtration. The filtrate was concentrated in vacuo and cooled to -30°C for a second crop.

Anal. Calcd. for $WC_{19}H_{44}NPCl_4$: C, 35.48; H, 6.90. Found: C, 34.86; H, 6.66. ^1H NMR ($CDCl_3$, 250 MHz, ppm): 3.36 (q, 8, J_{HH} = 6.1 Hz, $N\underline{C}\underline{H}_2CH_3$), 2.15 (m, 6, $PC\underline{H}_2CH_3$), 1.29 (br t, 12, $NCH_2C\underline{H}_3$), 1.23 (s, 9, $CCMe_3$), 1.14 (m, 9, $PCH_2C\underline{H}_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 36 MHz, ppm): 34.3 (s, J_{PW} = 259). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 22 MHz, ppm): 335.0 (d, $^2J_{CP}$ = 13.2, $\underline{C}CMe_3$), 52.0 ($N\underline{C}H_2CH_3$), 45.4 ($C\underline{C}Me_3$), 34.3 ($CC\underline{Me}_3$), 18.4 (d, J_{CP} = 26, $P\underline{C}H_2CH_3$), 7.28 (br s, $NCH_2\underline{C}H_3$ and $PCH_2\underline{C}H_3$).

$W(CCMe_3)(PEt_3)Cl_3$ (VIII-7)

$ZnCl_2(PEt_3)$ (1.02 g, 4.0 mmol; prepared from $ZnCl_2$(dioxane) and PEt_3) was added with stirring to $[W(CCMe_3)Cl_4]NEt_4$ (2.08 g, 4.0 mmol) in

CH_2Cl_2 (10 mL). The blue solution immediately turned violet and was filtered through Celite and evaporated in vacuo to violet microcrystals (1.72 g, 90% yield). ^1H NMR (C_6D_6, 250 MHz, ppm): 1.54 (m, 6, $PC\underline{H}_2CH_3$), 1.21 (s, 9, $CCMe_3$), 0.74 (dt, 9, $^3J_{HP}$ = 16.2, $^3J_{HH}$ = 7.5, $PCH_2C\underline{H}_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 36 MHz, ppm): 43.4 (J_{PW} = 239).

<u>$W(O)(CHCMe_3)(PEt_3)_2Cl_2$</u> (prep 1: VII-58; prep 2: X-6)

Method 1. PEt_3 (0.12 g, 1.0 mmol) was added to $[W(CCMe_3)Cl_4]NEt_4$ in thf (10 mL). The NEt_4Cl was removed by filtration after 2 hr and the LiOH added. After stirring overnight the cloudy yellow-green solution was evaporated to dryness, extracted with ether, filtered, and the solvent removed in vacuo yielding a yellow-green solid. The ^{31}P (s, 20 ppm; J_{PW} = 320) and ^1H NMR were very clean and confirmed the product as $W(O)(CHCMe_3)(PEt_3)_2Cl_2$.

Method 2. PEt_3 (292 µl, 2.0 mmol) and NEt_3 (140 µl, 1.0 mmol) were added to $[W(CCMe_3)Cl_4]NEt_4$ in thf (15 mL) in a 50 mL Schlenk flask fitted with a 10 mL addition funnel. 1 mL of a 1.0 M H_2O/thf solution was charged to the addition funnel. The green reaction slurry was cooled to -78°C and the H_2O/thf added dropwise. The reaction immediately lightened and the cold bath removed. After 1 hr the cloudy yellow solution was filtered, evaporated to dryness, extracted with ether, filtered, and the solvent removed in vacuo to give a quantitative yield of yellow crystals. The $^{31}P\{^1H\}$ NMR (s, 20 ppm; J_{PW} = 320) shows the material to be pure $W(O)(CHCMe_3)(PEt_3)_2Cl_2$.

$W(O)(CHCMe_3)(PEt_3)Cl_2$ (VIII-10)

$ZnCl_2(PEt_3)$ (0.13 g, 0.50 mmol) was added to $[W(CCMe_3)Cl_4]NEt_4$ (0.26 g, 0.50 mmol) in CH_2Cl_2 (10 mL). After 1 hr the reaction was filtered, evaporated to dryness, dissolved in thf (~ 7 mL) and LiOH (0.01 g, 0.50 mmol) added with stirring. After 6 hr the yellow-green solution was evaporated to dryness, extracted with toluene, filtered, and concentrated in vacuo. The $^{31}P\{^1H\}$ NMR (s, 40.5 ppm, J_{PW} = 361) confirms the product to be $W(O)(CHCMe_3)(PEt_3)Cl_2$. The reaction cannot be allowed to continue for >6 hr because the mono-phosphine complex will decompose in situ to an insoluble blue material and $W(O)(CHCMe_3)(PEt_3)_2$-Cl_2.[98]

$W(CCMe_3)(NHPh)(PEt_3)_2Cl_2$ (IX-39)

PEt_3 (0.95 g, 8.0 mmol) and NEt_3 (560 μl, 4.0 mmol) were added to $[W(CCMe_3)Cl_4]NEt_4$ (2.10 g, 4.0 mmol) in thf (25 mL). The green slurry was cooled to -30°C and $PhNH_2$ (365 μl, 4.0 mmol) added with stirring. The solution turned orange-red as it warmed to RT. After 2 hr the reaction was evaporated to dryness, extracted with ether, filtered, concentrated in vacuo (~10 mL) and cooled to -30°C. 1.90 g of large red-orange crystals were isolated (75% yield). The complex can also be prepared using LiN(H)Ph instead of H_2NPh/NEt_3 (IX-1, 5).

Anal. Calcd. for $WC_{23}H_{45}NP_2Cl_2$: C, 42.35; H, 6.95. Found: C, 42.19; H, 7.08. ^1H NMR (C_6D_6, 250 MHz, ppm): 13.20 (br s, 1, N$\underline{H}$Ph), 7.53 (d, 2, J_{HH} = 8.5, o-phenyl), 7.07 (t, 2, J_{HH} = 7.9, m-phenyl), 6.91 (t, 1, J_{HH} = 7.3, p-phenyl), 1.96 (m, 12, $PC\underline{H}_2CH_3$), 1.32 (s, 9, $CCMe_3$), 0.90 (m, 18,

$PCH_2C\underline{H}_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 36 MHz, ppm): 15.6 (s, J_{PW} = 276). ^{13}C NMR (C_6D_6, 62.8 MHz, ppm): 300.5 (t, $^2J_{CP}$ = 10.7, $\underline{C}CMe_3$), 153.5 (s, ipso-phenyl), 128.9, 125.7, 121.3 (d, J_{CH} = 153-165 , phenyl), 49.6 (s, $\underline{C}CMe_3$), 32.4 (q, J_{CH} = 125, $CC\underline{Me}_3$), 17.4 (tt, J_{CH} = 130, J_{CP} = 12.2, $P\underline{C}H_2CH_3$), 7.7 (q, J_{CH} = 127, $PCH_2\underline{C}H_3$).

$W(CCMe_3)(NHPh)(PMe_2Ph)_2Cl_2$ (IX-20)

PMe_2Ph (0.28 g, 2.0 mmol) was added to $[W(CCMe_3)Cl_4]NEt_4$ (0.52 g, 1.0 mmol) in thf (10 mL) and LiN(H)Ph (0.10 g, 1.0 mmol) added with stirring. The red-orange solution was stirred for 2 hr, filtered, evaporated to dryness, extracted with CH_2Cl_2 (~ 5 mL), filtered, and cooled to -30°C. 0.4 g of red-orange crystals were isolated by filtration (60% yield).

^1H NMR (C_6D_6, 250 MHz, ppm): 13.07 (br s, 1, $N\underline{H}Ph$), 7.41-6.88 (m, 15, phenyl), 1.91 (t, 6, $^2J_{HP}$ = 4.4, P-CH_3(A)), 1.83 (t, 6, $^2J_{HP}$ = 4.4, P-CH_3(B)), 0.93 (s, 9, CMe_3).

$W(CCMe_3)(NHPh)(PEt_3)Cl_2$ (IX-5)

LiNHPh (0.05 g, 0.50 mmol) was added to $W(CCMe_3)(PEt_3)Cl_3$ (0.24 g, 0.5 mmol) at -30°C in ether (10 mL). The reaction immediately turned orange. After stirring for 4 hr the LiCl was removed by filtration and the orange solution evaporated to an orange oil. Attempts at crystallization failed. The $^{31}P\{^1H\}$ NMR spectrum shows mostly $W(CCMe_3)(NHPh)(PEt_3)Cl_2$ at 40.3 ppm (J_{PW} = 308 Hz) but ~20% of the reaction mixture is the bis-phosphine complex, $W(CCMe_3)(NHPh)(PEt_3)_2Cl_2$. The $^{13}C\{^1H\}$ NMR spectrum is not especially clean but the alkylidyne α-carbon is observed as a doublet ($^2J_{CP}$ = 12.2 Hz) at 304.5 ppm. The amido N-H proton is found at 10.5 ppm in the ^{1}H NMR spectrum. The broad peak is coupled (~2 Hz) to phosphorous. A better method of preparation of this compound may be removal of a phosphine from $W(CCMe_3)(NHPh)(PEt_3)_2Cl_2$ with CuCl or C_2Cl_6 or other suitable reagents. The reaction was less clean using $PhNH_2/NEt_3$.

$\underline{W(CCMe_3)(NPh)(PEt_3)_2Cl}$ (IX-56,62)

$Ph_3P=CH_2$ (0.11 g, 0.38 mmol) was added to $W(CCMe_3)(NHPh)(PEt_3)_2Cl_2$ in toluene (~7 mL) at -30°C. The orange solution immediately turned cherry red. After 45 min the $[Ph_3PCH_3]Cl$ was filtered from solution and the purple solution was evaporated to dryness yielding pure product.

^{1}H NMR (C_6D_6, 60 MHz, ppm): 7.6-7.0 (m, 5, phenyl), 2.05 (m, 12, $PC\underline{H}_2CH_3$), 1.65 (s, 9, $CC\underline{Me}_3$), 1.24 (m, 18, $PCH_2C\underline{H}_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 36 MHz, ppm): 32 (s, J_{PW} = 295). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 MHz, ppm): 322.7 (t, $^2J_{CP}$ = 9.9, $\underline{C}CMe_3$), 161.0 (s, ipso-phenyl), 128.5-124.0 (d, J_{CH} ~ 160, phenyl), 52.4 (s, $C\underline{C}Me_3$), 34.2 (q, J_{CH} = 125.2, $CC\underline{Me}_3$), 17.9 (tt, J_{CH} = 128.5, J_{CP} = 13.2, $P\underline{C}H_2CH_3$), 8.8 (q, J_{CH} = 125.2, $PCH_2\underline{C}H_3$).

$\underline{W(CCMe_3)(NH_2)(PEt_3)_2Cl_2}$ (IX-47, 65)

$LiNH_2$ (0.09 g, 3.8 mmol) was added to a thf (40 mL) solution containing PEt_3 (0.90 g, 7.6 mmol) and $[W(CCMe_3)Cl_4]NEt_4$ (2.0 g, 3.8 mmol). No immediate reaction was noted but after 2 hr the reaction began turning orange. The reaction was stirred overnight, filtered through a Celite pad, and evaporated to dryness yielding a sticky orange solid which was extracted with ether/thf (10:1), filtered and cooled to -30°C. 1.0 g of pure orange crystals were isolated by filtration. The filtrate was concentrated in vacuo and cooled to -30°C for a second crop.

Anal. Calcd. for $WC_{17}H_{41}NP_2Cl_2$: C, 35.44; H, 7.17. Found: C, 35.34; H, 7.25. ^1H NMR (C_6D_6, 250 MHz, ppm): 10.84 (br s, 1, NH(A)), 9.37 (br s, 1, NH(B)), 1.95 (m, 12, $P\underline{CH_2}CH_3$), 1.09 (s, 9, $CCMe_3$), 1.02 (m, 18, $PCH_2\underline{CH_3}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 22 MHz, ppm): 298.8 (t, J_{CP} = 11.4, $\underline{C}CMe_3$), 48.2 (s, $C\underline{C}Me_3$), 31.3 (q, J_{CH} = 126, $CC\underline{Me_3}$), 16.4 (tt, J_{CH} = 127, $^2J_{CP}$ = 12.7, $P\underline{C}H_2CH_3$), 6.9 (q, J_{CH} = 126, $PCH_2\underline{C}H_3$).

<u>$W(CCMe_3)(PHPh)(PEt_3)_2Cl_2$</u> (IX-23, 55; X-17)

PEt_3 (0.24 g, 2.0 mmol) and NEt_3 (0.10, 1.0 mmol) were added to $[W(CCMe_3)Cl_4]NEt_4$ (0.52 g, 1.0 mmol) in thf (10 mL). $PhPH_2$ (0.11 g, 1.0 mmol) was added at -30°C and the solution immediately turned red. After 2 hr the reaction was filtered, evaporated to dryness, extracted with ether/thf (10:1), filtered, and cooled to -30°C. 0.44 g of red-orange crystals were isolated by filtration (65% yield).

Anal. Calcd. for $WC_{23}H_{45}P_3Cl_2$: C, 41.28; H, 6.78. Found: C, 41.71; H, 6.82. ^1H NMR (C_6D_6, 250 MHz, ppm): 10.00 (d, 1, J_{HP} = 362, $^2J_{HW}$ = 65, $P(\underline{H})Ph$), 8.56-7.04 (m, 5, phenyl), 2.01 (m, 12, $P\underline{CH_2}CH_3$), 1.30 (s, 9, $CCMe_3$), 0.98 (m, 18, $PCH_2\underline{CH_3}$). $^{31}P\{^1H\}$ NMR (C_6H_6, 36 MHz, ppm): 232.6 (t, $J_{PP'}$ = 58.6, J_{PW} = 410, $\underline{P}(H)Ph$), 15.2 (d, $J_{PP'}$ = 58.6, J_{PW} = 242, PEt_3). ^{31}P (proton coupled) NMR: 232.3 (dt, J_{PH} = 362, $J_{PP'}$ = 58.6, $\underline{P}(H)Ph$), 15.2 (d, $J_{PP'}$ = 58.6). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 MHz, ppm): 288.9

(br s, $\underline{C}CMe_3$), 149.4 (d, J_{CP} = 9.8, ipso-phenyl), 132.8 - 128.4 (d, J_{CH} ~ 160, phenyl), 50.5 (s, $C\underline{C}Me_3$), 32.2 (q, J_{CH} = 126, $CC\underline{Me}_3$), 19.1 (tt, J_{CH} = 129, $^2J_{CP}$ = 12.7, $P\underline{C}H_2CH_3$), 8.1 (q, J_{CH} = 126, $PCH_2\underline{C}H_3$).

$\underline{W(CCMe_3)(PMePh)(PEt_3)_2Cl_2}$ (IX-48)

PEt_3 (292 µl, 2.0 mmol) and NEt_3 (140 µl, 1.0 mmol) were added to $[W(CCMe_3)Cl_4]NEt_4$ (0.52 g, 1.0 mmol) in thf (10 mL) HPMePh (0.12 g, 1.0 mmol) was added and no immediate reaction was noted. After 1 hr the reaction began turning orange. The reaction was stirred overnight, filtered through a Celite pad, evaporated to dryness, extracted with ether/thf, filtered, and cooled to -30°C. The complex was difficult to crystallize but 250 mg of orange-red crystals were isolated by filtration.

^1H NMR ($CDCl_3$, 250 MHz, ppm): 7.82-7.42 (m, 5, phenyl), 2.56 (dt, 3, $^2J_{HP}$ = 18.4, $^4J_{HP}$ = 3.3, $P\underline{Me}Ph$), 2.09 (m, 12, $PC\underline{H}_2CH_3$), 1.13 (m, 18, $PCH_2C\underline{H}_3$), 0.98 (s, 9, $CCMe_3$). $^{31}P\{^1H\}$ NMR (C_6H_6, 36 MHz, ppm): 291.5 (t, $J_{PP'}$ = 58.6, J_{PW} = 420, $\underline{P}MePh$), 13.7 (d, $J_{PP'}$ = 58.6, J_{PW} = 242, PEt_3).

$\underline{W(CCMe_3)(PPh_2)(PEt_3)_2Cl_2}$

PEt_3 (0.24 g, 2.0 mmol) and NEt_3 (140 µl, 1.0 mmol) were added to $[W(CCMe_3)Cl_4]NEt_4$ (0.52 g, 1.0 mmol) and $HPPh_2$ (174 µl, 1.0 mmol) was added. No immediate reaction was noted. After 18 hr the reaction was filtered through Celite and evaporated to dryness to an orange-red crystalline solid. The product was extracted with ether and 450 mg of crystals were isolated by filtration.

$^{31}P\{^1H\}$ NMR (C_6H_6, 36 MHz, ppm): 291.3 (t, $J_{PP'}$ = 58.6, J_{PW} = 430, $\underline{P}Ph_2$), 13.5 (d, $J_{PP'}$ = 58.6, J_{PW} = 239, PEt_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.8 MHz, ppm): 297.3 (quintet, $^2J_{CP}$ = 12.0 $\underline{C}CMe_3$), 150.5 (d, J_{CP} = 37.8, ipso-phenyl), 147.9 (d, J_{CP} = 11.6, ipso-phenyl'), 133.3-127.3 (s, phenyl), 50.4 (s, $C\underline{C}Me_3$), 30.5 (s, $CC\underline{Me}_3$), 19.0 (t, J_{CP} = 13.1, $P\underline{C}H_2CH_3$), 8.0 (s, $PCH_2\underline{C}H_3$).

CHAPTER 5

THE PREPARATION AND REACTIONS OF NOVEL TUNGSTEN(VI) ALKYL COMPLEXES

INTRODUCTION

Transition metal complexes containing σ-alkyl ligands have played a prominent role in the development of mononuclear organometallic chemistry.[6,107] The fascination of σ-alkyl chemistry of transition metals lies not only in the tremendously varied types of structural and bonding forms, but also in the actual and potential practical uses of such materials. Chemists have been intrigued by the role that such complexes may play as models for intermediates in industrially important reactions such as, heterogeneously catalyzed olefin metathesis, petroleum refining, hydrogenation, Fischer-Tropsch synthesis, and olefin polymerization.[45] An increasing number of industrial processes, such as the Wacker acetaldehyde synthesis, hydroformulation, carbonylation of methanol to acetic acid, and 1,4-hexadiene synthesis have been developed employing homogeneous transition metal complexes as catalysts, and in these systems σ-bonded metal alkyl intermediates have been postulated.[6]

For many years it was believed that the σ-alkyl-to-metal bond was inherently weak[108] and that only complexes also containing π-acceptor ligands could be isolated.[109] Many recent studies have shown that the apparent instability is not the result of low bond dissociation energies for these compounds but rather the result of kinetic factors since there are low activation energy pathways for cleavage of the metal-carbon bond;[110] these decomposition pathways have been reviewed.[111] Probably the most common and facile pathway for decomposition of a dialkyl complex involves an initial β-hydrogen abstraction (most often by the metal) which, though sometimes reversible, is accompanied by an irreversible elimination of alkane from the metal center. This pathway is blocked for complexes containing σ-alkyl groups lacking β-hydrogen atoms, however, α- or γ-hydrogen atom abstraction processes may occur. Schrock and co-workers have pioneered the studies involving α-hydrogen abstraction with early transition metal complexes containing σ-alkyls such as CH_2CMe_3, CH_2SiMe_3, and CH_2Ph.[15] γ-Hydrogen abstraction has been observed by Whitesides and co-workers in the thermal decomposition of cis-$Pt(CH_2CMe_3)_2(PEt_3)_2$ to give the 3,3-dimethylplatinacyclobutane complex cis-$Pt[(CH_2)_2CMe_2](PEt_3)_2$ and neopentane.[95a,b]

Herein we describe the synthesis and some reactions of tungsten σ-alkyl complexes prepared via the alkylation of $W(OMe)_3Cl_3$ with zinc reagents. The compounds prepared contain tungsten in the +6 oxidation state. Relatively few σ-alkyl complexes of d^0 tungsten, not containing π-bonding ligands (oxo or imido), are known. $WMeCl_5$ has reportedly been prepared from WCl_6 and the alkylating agents dimethylzinc,[112] tetramethyltin,[112] and dimethylmercury.[113] A better characterized σ-alkyl complex is hexamethyltungsten. WMe_6 was initially prepared via the interaction of three equivalents of methyl-lithium and WCl_6 in diethyl ether at low temperatures.[114] The presence of some oxygen is essential to ensure formation of the product. As stated by the authors the reaction is an exceedingly complex one and the role of oxygen is obscure. Currently the best method for preparing WMe_6 is via the use of $AlMe_3$ as the alkylating agent.[115] A suspension of WCl_6 in isopentane at -70°C is treated with $6AlMe_3$ and after warming to 25°C then cooling to -78°C trimethylamine is added and the relatively insoluble amine adduct, $AlMe_2Cl \cdot NMe_3$, is precipitated out of solution. Filtration and further work-up give pure WMe_6 in ~60% yield.

Recently a tungsten(VI) metallatricycle, $[\overline{W(CH_2C_6H_4CH_2}\text{-o})_3]$, has been prepared via the reaction of $W(O)Cl_4$ with an excess of the di-Grignard reagent, o-$C_6H_4(CH_2MgCl)_2$, in thf.[116] The excess of alkylating agent is crucial as a W(V) complex, $[\{\overline{W(CH_2C_6H_4CH_2}\text{-o})_2\overline{O\}_2Mg}(thf)_4]$, is formed if <3.5 equivalents is used.[117] Compared with WMe_6 the W(VI) metallatricycle is surprisingly thermally robust, being sublimable at 160°C and 10^{-2} torr. The authors attribute this stability to the chelate effect and to the folding of the o-xylidene ligand to allow significant $W(d^0)$-π interaction.

RESULTS

Preparation of $W(OR)_3X_3$ (R = CH_3, CMe_3; X = CH_2CMe_3, CH_2SiMe_3)

The metathetic substitution chemistry of tungsten halides often yields products with the metal in oxidation states other than that of the starting material. For example, Chisholm and co-workers have found that the reaction between WCl_6 and $LiNMe_2$ leads to a mixture of $W(NMe_2)_6$ and $W_2(NMe_2)_6$ while reactions involving WBr_5 and WCl_4 lead to the isolation of only pure $W(NMe_2)_6$ and $W_2(NMe_2)_6$, respectively.[118] Wilkinson and co-workers observed that the interaction of WCl_6 and $6Me_3SiCH_2MgCl$ gives $W_2(CH_2SiMe_3)_6$, a W(III) product.[119] (See Appendix II for full discussion.) Alkoxide ligands, with π-electron donation properties, can help stabilize high oxidation state transition metals, in a similar manner as the oxo and imido ligand.[41,67] The only known W(VI) chloro/alcoxy complex is $W(OMe)_3Cl_3$ prepared in high yield from WCl_6 and Me_3SiOMe[92] (eq 1). The success of this unique reaction can be attributed to the formation of the favorable W-O bond and the alkoxide effect which maintains tungsten in the +6 oxidation state.

$$WCl_6 \quad + \quad 3Me_3SiOMe \longrightarrow W(OMe)_3Cl_3 \; + \; 3Me_3SiCl \qquad (1)$$

Sancho has found $W(OMe)_3Cl_3$ to be a very good starting material for the preparation of $[W(CCMe_3)(CH_2CMe_3)_3]_2$.[40] The tungsten(VI) alkylidyne species is isolated in ca. 60% yield. If WCl_6 is used the alkylidyne complex is isolated in only ca. 20% yield.[91] Sancho has observed that selective alkylation of $W(OMe)_3Cl_3$ with Me_3CCH_2MgCl (<6 equivalents) gives $[W(CCMe_3)(CH_2CMe_3)_3]_2$ in low yield and with $Zn(CH_2CMe_3)_2$ gives intractable red oils.[40] We have recently found that selective alkylation of $W(OMe)_3Cl_3$ can be accomplished using $Zn(CH_2CMe_3)_2$ and NEt_4Cl to precipitate the $ZnCl_2$ as $[ZnCl_3]NEt_4$ (eq 2). Using 1.5 equivalents of $Zn(CH_2CMe_3)_2$ and NEt_4Cl we can prepare $W(OMe)_3(CH_2CMe_3)_3$ virtually quantitatively (by ^1H NMR) and isolate it in 70-75% yield after crystallization or sublimation. The reaction can also be done using $[W(OMe)_3Cl_4]NEt_4$, a colorless crystalline solid, prepared from $W(OMe)_3Cl_3$ and NEt_4Cl. This method has the advantage that the ionic tungsten-alkoxy species has a longer shelf-life. The reaction is generally performed by dissolving

$$W(OMe)_3Cl_3 \; + \; \tfrac{3}{2}Zn(CH_2CMe_3)_2 \xrightarrow[-\,[ZnCl_3]NEt_4]{+\,\frac{3}{2}NEt_4Cl} W(OMe)_3(CH_2CMe_3)_3 \qquad (2)$$

$W(OMe)_3Cl_3$ and NEt_4Cl in CH_2Cl_2 (forming the anion in situ), cooling the colorless solution to -30°C, slow addition of $Zn(CH_2CMe_3)_2$, followed by warming to 25°C and general work-up (see Experimental). Bright yellow $W(OMe)_3(CH_2CMe_3)_3$, like all the other W(VI) alkyls discussed herein is photosensitive even in the solid state, and attempts at elemental analyses have proved futile. The photolyses of our tungsten alcoxy-alkyls will be discussed in a separate section (vide infra).

The tris-trimethylsilylmethyl complex, $W(OMe)_3(CH_2SiMe_3)_3$, can be prepared by a route analogous to that used for $W(OMe)_3(CH_2CMe_3)_3$ (using $Zn(CH_2SiMe_3)_2$). In keeping with the general greater stability of the CH_2SiMe_3 ligand versus CH_2CMe_3[40,120], $W(OMe)_3(CH_2SiMe_3)_3$ can be isolated in pure form from the reaction mixture in 80-85% yield. Both $W(OMe)_3(CH_2CMe_3)_3$ and $W(OMe)_3(CH_2SiMe_3)_3$ have simple ^1H NMR spectra showing equivalent methoxy and alkyl ligands suggesting a fac-geometry. The methoxide ligands can easily be substituted with $LiOBu^t$ to yield canary yellow $W(OBu^t)_3X_3$ ($X = CH_2CMe_3$, CH_2SiMe_3) (eq 3). The fac-geometry is

$$\text{fac-}W(OMe)_3(CH_2CMe_3)_3 + 3LiOBu^t \longrightarrow \text{fac-}W(OBu^t)_3(CH_2CMe_3)_3 \qquad (3)$$

maintained as demonstrated by ^1H NMR. These tris-alkyl complexes are surprisingly thermally stable and can be stored at ca. 25°C for weeks without apparent decomposition. This is particularly surprising since the neopentyl ligands are 90° apart which is a condition in which tantalum neopentyl complexes undergo α-hydrogen abstraction forming neopentylidene complexes.[16,22]

Attempts at preparing mono- and bis-alkyl complexes using stoichiometric amounts of zinc reagent (0.5 and 1.0 equiv) gave either the tris-alkyl product or unidentifiable materials. Attempted cleavage of an alkyl or alcoxide ligand from $W(OMe)_3(CH_2CMe_3)_3$ or $W(OBu^t)_3(CH_2CMe_3)_3$ with stoichiometritic quantities of HCl in ether gave unidentifiable products probably derived from multiple cleavage.

The reaction of $[W(OMe)_3Cl_4]NEt_4$ with 1.5 equiv of $ZnMe_2$ gave poorly soluble products that displayed broad ^1H NMR signals. No clean crystalline product was obtained. A similar reaction with $ZnBz_2$ yielded a product that also was poorly soluble and appeared (by ^1H NMR) to contain NEt_4Cl. No definitive conclusions can be made at this time.

Photolysis of $W(OR)_3X_3$ ($R = CH_3$, CMe_3; $X = CH_2CMe_3$, CH_2SiMe_3)

Although these W(VI) alkyls are thermally stable repeated attempts at elemental analyses gave unacceptably low values for C and H content. We subsequently became aware of the photosensitivity of these molecules. The compounds are mildly sensitive to room light but decompose rapidly under direct sunlight or under unfiltered medium-pressure Hanovia light. Clean decomposition is observed for $W(OBu^t)_3(CH_2CMe_3)_3$ as neopentane is evolved and $W(CCMe_3)(OBu^t)_3$ is formed (eq 4). This known alkylidyne complex (cf. Chapter 4) is an active acetylene metathesis catalyst.[40,93] The optical spectrum of yellow $W(OBu^t)_3(CH_2CMe_3)_3$ (1.30×10^{-3}M) in pen-

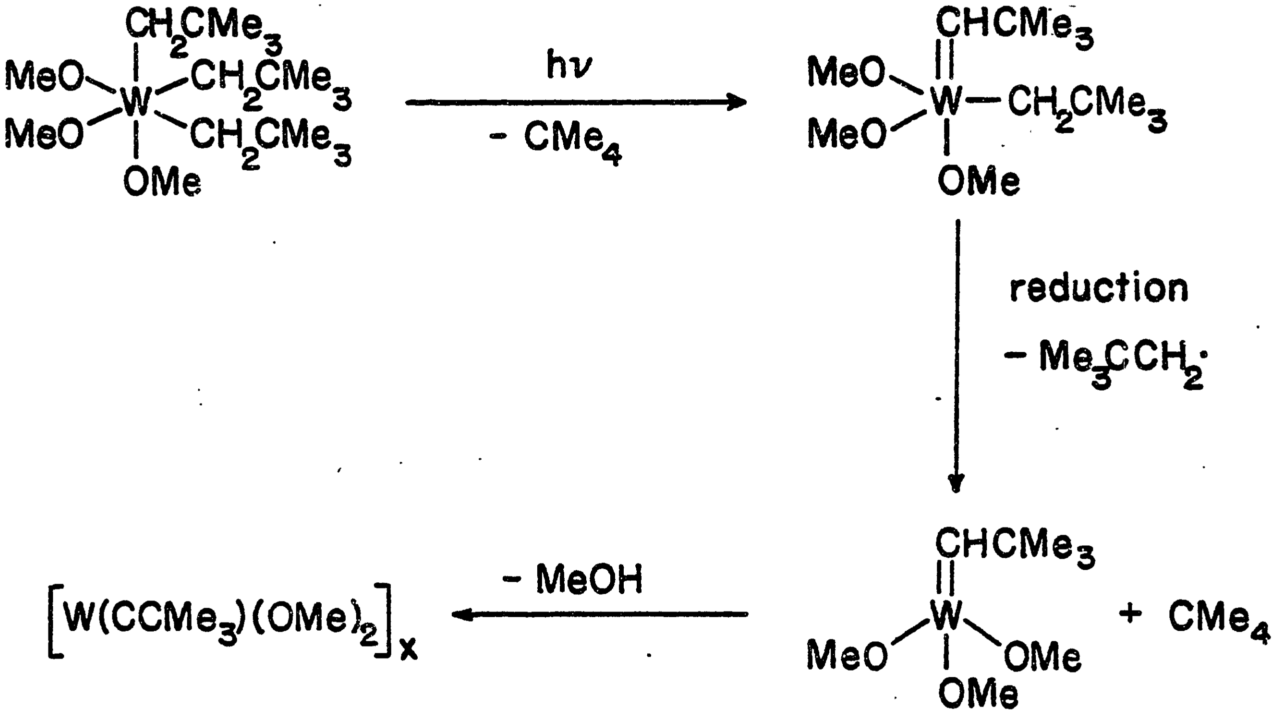
$$W(OBu^t)_3(CH_2CMe_3)_3 \xrightarrow[\text{pentane}]{h\nu} W(CCMe_3)(OBu^t)_3 + 2CMe_4 \qquad (4)$$

tane shows an absorbance at 380 nm (ε = 1540) and a strong peak at <250 nm that tails into the solvent absorbance. The reaction is complete in ~3 hr using the Hanovia lamp. The product, $W(CCMe_3)(OBu^t)_3$, is not photosensitive but the reaction itself is sensitive to conditions and a small amount of paramagnetic impurity is sometimes observed by EPR. Photolysis of $W(OBu^t)_3(CH_2CMe_3)_3$ in CH_2Cl_2 is very messy as insolubles rapidly deposit from solution upon exposure to light. In contact with direct sunlight $W(OBu^t)_3(CH_2CMe_3)_3$ cleanly decomposes in the solid state in vacuo forming the neopentylidyne complex.

The photolysis of $W(OMe)_3(CH_2CMe_3)_3$ is more complex as no diamagnetic products are observed by NMR. Upon photolyzing a sample of $W(OMe)_3(CH_2CMe_3)_3$ with either direct sunlight or Hanovia light the formation of neopentane can be observed by ^1H NMR. The resonances due to starting material disappear rapidly but no resonances attributable to a new organometallic product are observed. An EPR spectrum at this point displayed a strong signal evident of paramagnetic species. Removal of solvent in vacuo yielded a red-brown oil. Addition of PhC≡CPh followed by GC analysis showed the formation of $Me_3CC{\equiv}CPh$, the product expected from metathesis of diphenylacetylene with a neopentylidyne complex. Apparently, $W(OMe)_3(CH_2CMe_3)_3$

photolytically decomposes to a paramagnetic (W(V)) neopentylidyne complex possibly of the nature "$[W(CCMe_3)(OMe)_2]_x$" (x = 1-3). Two successive α-hydrogen abstractions would yield $W(CCMe_3)(OMe)_3$ (W(VI)) so a more complex mechanism must be operating. The formation of "$[W(CCMe_3)(OMe)_2]_x$" could possibly be accounted for by the reaction sequence shown in Scheme I.

Scheme I.



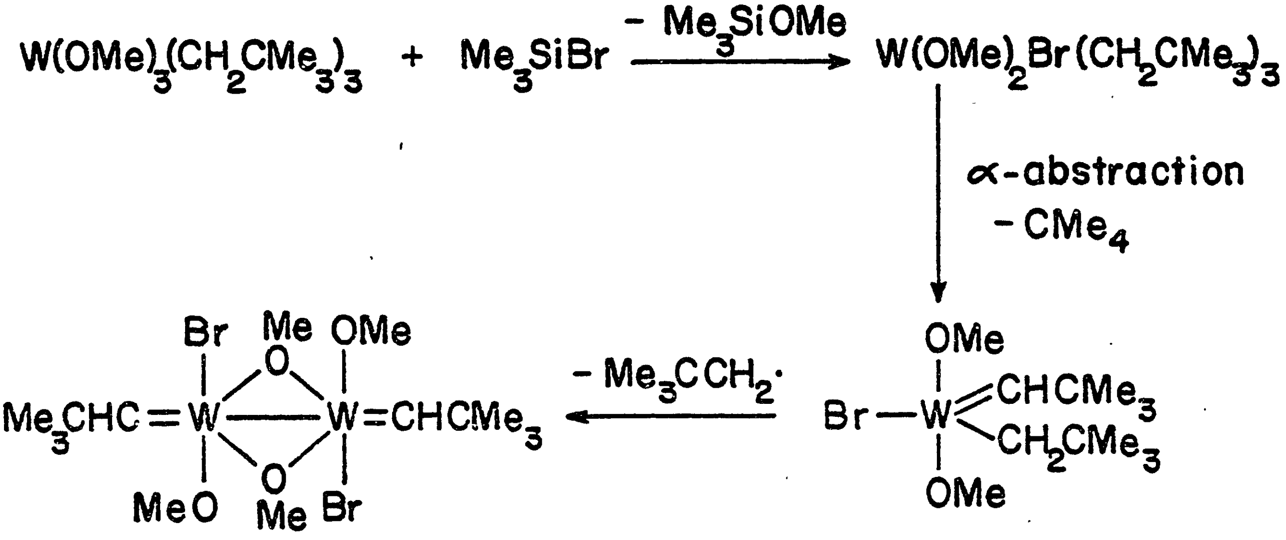
The product is proposed to be formed via an α-hydrogen abstraction, followed by reductive loss of neopentyl radical which scavenges H· forming a second equivalent of neopentane, and subsequent loss of methanol yielding a W(V) neopentylidyne species. Steps 2 and 3 could be exchanged, that is, loss of methanol from "$W(OMe)_3(CHCMe_3)(CH_2CMe_3)$" followed by homolytic cleavage of a neopentyl group from "$W(OMe)_2(CCMe_3)(CH_2CMe_3)$" would yield the proposed product.

$W(OMe)_3(CH_2SiMe_3)_3$ also photolytically decomposes to give a paramagnetic product possibly by a similar mechanism.

Reaction of $W(OMe)_3(CH_2CMe_3)_3$ with Me_3SiBr: Formation of a W(V) Neopentylidene Complex

We wanted to replace an alkoxide ligand with a halide to test whether the subsequent tungsten alkyl complex would be stable with respect to α-hydrogen abstraction and/or reduction. We thought we might be able to replace OMe from $W(OMe)_3(CH_2CMe_3)_3$ with a trimethylsilyl reagent since there is a strong thermodynamic driving force for the formation of the Si-O bond. When Me_3SiBr is added to $W(OMe)_3(CH_2CMe_3)_3$ in ether a white insoluble material deposits from solution but the major product remains in solution and can be isolated as orange crystals. The ^1H NMR spectrum is very clean and displays a single tert-butyl peak, two methoxide peaks, and a small resonance at 11.2 ppm coupled to ^{183}W attributed to the α-hydrogen atom of an alkylidene ligand. The above results are mirrored in the $^{13}C\{^1H\}$ NMR spectrum; the α-carbon atom is found at 312.4 ppm as a doublet (J_{CH} = 125 Hz) in the gated decoupled spectrum. Since only two neopentyl ligands can be accounted for via the above spectroscopy (one via loss of neopentane to form the neopentylidene the second) we thought the third neopentyl group was lost via homolytic cleavage forming a neopentyl radical and a W(V) organometallic fragment. To test this hypothesis we carefully examined the volatiles formed in the above reaction by GC. In addition to the expected Me_3SiOMe we found 160 mole % neopentane and 10 mole % dineopentyl (2,2,5,5-tetramethylhexane; the product derived from coupling of two neopentyl radicals). One equivalent (100 mole %) of neopentane is derived from α-abstraction and the remainder from H· abstraction (possibly from solvent) by the neopentyl radical. The organometallic product, $[W(CHCMe_3)(OMe)_2Br]_2$, is possibly formed via the route in Scheme II. The compound was found to be a dimer by differential vapor pressure

Scheme II.



molecular weight determination and gave a positive $AgNO_3$ halide test. We place one set of OMe ligands in the bridging position because of the inequivalent resonances for the OMe ligands in the ^1H and ^{13}C NMR spectra and the known affinity of methoxide ligands to bridge multi-nuclear centers.

As anticipated, $[W(CHCMe_3)(OMe)_2Br]_2$, is a mildly active catalyst for the metathesis of olefins. As Table I shows, cis-2-pentene is slowly metathesized and rapidly isomerized by this tungsten neopentylidene complex.

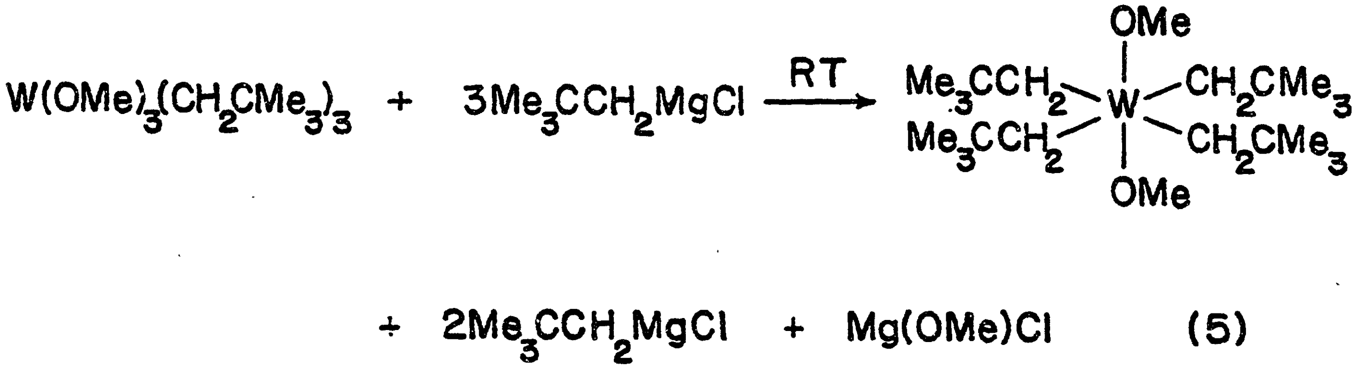
Table I. Metathesis of cis-2-pentene with $[W(CHCMe_3)(OMe)_2Br]_2$[a]

Time (hr)	initial cleavage products[b]	total cis/trans-2-butenes	total cis/trans-3-hexenes	cis/trans ratio of 2-pentenes
2	52	450	370	1.6
4	63	690	500	0.8
6.5	75	910	660	0.7
15	97[c]	1270[c]	930[c]	0.6[c]

[a] 150 mg of complex in chlorobenzene at ca. 25°C. The numbers are expressed as percent yield vs. the metal. [b] Approximately a 2:1 ratio of cis/trans-4,4-dimethyl-2-pentene and trans-2,2-dimethyl-3-hexene. [c] No substantial further activity.

Alkylation Reactions of $W(OMe)_3(CH_2CMe_3)_3$

One might expect that $W(OMe)_3(CH_2CMe_3)_3$ could be an intermediate in the formation of $[W(CCMe_3)(CH_2CMe_3)_3]_2$ from $W(OMe)_3Cl_3$ and $6Me_3CCH_2MgCl$.[40] Alkylation of $W(OMe)_3(CH_2CMe_3)_3$, with appropriate reagents, should then provide $[W(CCMe_3)(CH_2CMe_3)_3]_2$. $W(OMe)_3(CH_2CMe_3)_3$ does not react with a mild alkylating agent, such as $Zn(CH_2CMe_3)_2$ at ca. 25°C. The addition of 3 equivalents of Me_3CCH_2MgCl to $W(OMe)_3(CH_2CMe_3)_3$ at ca. 25°C does not yield the tungsten alkylidyne complex. Inverse addition of starting materials has no effect on the outcome of the reaction. Careful inspection of the pentane soluble fraction of the above reaction shows the major product to be $W(OMe)_2(CH_2CMe_3)_4$ (eq 5). $W(OMe)_2(CH_2CMe_3)_4$ is



(5)

more conveniently prepared using one equivalent of $Mg(CH_2CMe_3)_2$ or $LiCH_2CMe_3$ (vide infra). $W(OMe)_2(CH_2CMe_3)_4$ is a pale yellow liquid at ca. 25°C. The geometry shown in equation 5 is based on the equivalency of the neopentyl groups in the ^1H and $^{13}C\{^1H\}$ NMR spectra.

When the reaction presented in equation 5 is run at 75°C in a glass bomb (ca. 10 psi) in ether $[W(CCMe_3)(CH_2CMe_3)_3]_2$ is the major product. Some $W(OMe)_2(CH_2CMe_3)_4$ is observed in the $^{13}C\{^1H\}$ NMR spectrum of the crude product. Since $[W(CCMe_3)(CH_2CMe_3)_3]_2$ is formed from $W(OMe)_3Cl_3$ and Me_3CCH_2MgCl at 25°C, or below, we conclude that $W(OMe)_3(CH_2CMe_3)_3$ is not an intermediate in the formation of the tungsten(VI) alkylidyne complex by this method. We can form $[W(CCMe_3)(CH_2CMe_3)_3]_2$ by heating $W(OMe)_2(CH_2CMe_3)_4$ in the presence of

Me_3CCH_2MgCl or $Mg(CH_2CMe_3)_2$. The heat is required to force further substitution of $W(OMe)_2(CH_2CMe_3)_4$ which followed by α-hydrogen abstraction would yield $[W(CCMe_3)(CH_2CMe_3)_3]_2$.

Since no further alkylation of $W(OMe)_2(CH_2CMe_3)_4$ will occur with Me_3CCH_2MgCl or $Mg(CH_2CMe_3)_2$ at 25°C we decided to investigate $LiCH_2CMe_3$ as an alkylating agent. $W(OMe)_2(CH_2CMe_3)_4$ reacts rapidly with $LiCH_2CMe_3$ in pentane or ether to yield a product best formulated as $[W(OMe)(CH_2CMe_3)_4]_2$ (eq 6). GC analysis of the volatiles of the above

$$W(OMe)_2(CH_2CMe_3)_4 \quad + \quad LiCH_2CMe_3 \longrightarrow \left[W(OMe)(CH_2CMe_3)_4\right]_2$$

$$+ \; 0.8\,CMe_4 \; + \; 0.05\,Me_3CCH_2CH_2CMe_3 \qquad (6)$$

reaction show 80 mole % neopentane and ca. 5 mole % dineopentyl. Apparently the lithium reagent is reducing the metal to tungsten(V). The yellow crystalline product is only slightly hydrocarbon or ether soluble but is fairly soluble (without apparent reaction) in chloroform and methylene chloride. The compound probably contains methoxy bridges and a metal-metal bond to account for its diamagnetism. $[W(OMe)(CH_2CMe_3)_4]_2$ only slowly reacts with HCl but ca. 7 equivalents of neopentane per dimer were observed in the volatiles by GC analyses (88% yield).

$[W(OMe)(CH_2CMe_3)_4]_2$ will further react with $LiCH_2CMe_3$ in a slightly messy reaction to yield an orange oil whose $^{13}C\{^1H\}$ NMR spectrum contains no methoxide resonances but does contain tert-butyl resonances and a peak at 300 ppm that remains a singlet in the gated-decoupled spectrum. Since the α-carbon atom of $[W(CCMe_3)(CH_2CMe_3)_3]_2$ is found at 316 ppm we conclude that this new product is a W(V) alkylidyne complex, most likely $[W(CCMe_3)(CH_2CMe_3)_2]_2$. This compound was never obtained completely pure but its formulation is probably accurate. The trimethylsilylmethyl analogue, $[W(CSiMe_3)(CH_2SiMe_3)_2]_2$, is known[84,85] (cf. Appendix II).

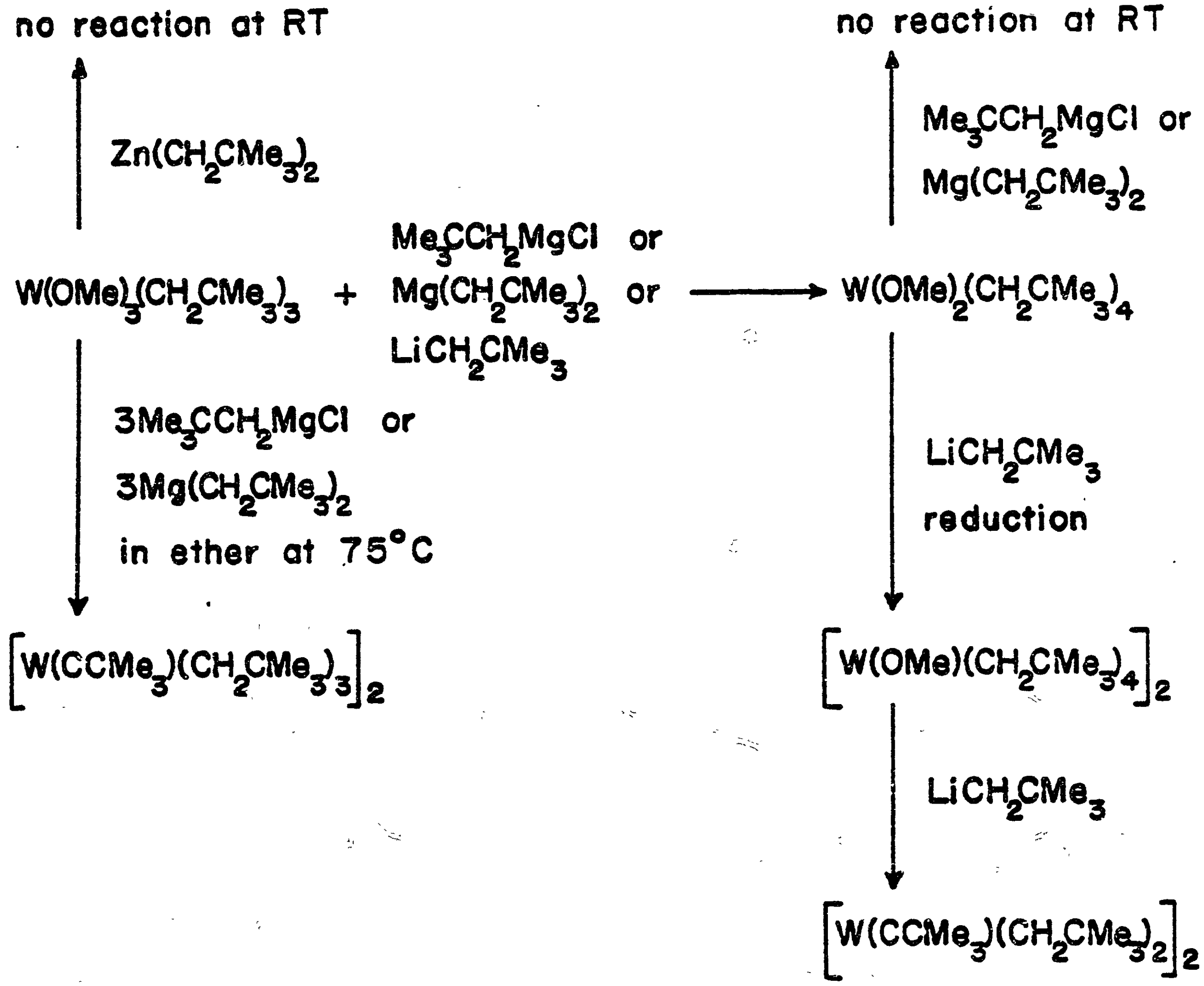
The alkylation reactions of $W(OMe)_3(CH_2SiMe_3)_3$ follow the general trends observed for $W(OMe)_3(CH_2CMe_3)_3$. That is, $W(OMe)_2(CH_2SiMe_3)_4$ can be prepared using Me_3SiCH_2MgCl. However, further alkylation of $W(OMe)_2(CH_2SiMe_3)_4$ provides a product whose $^{13}C\{^1H\}$ NMR spectrum shows ca. 70% of the mixture to be $W(CSiMe_3)(CH_2SiMe_3)_3$ (W(VI)) and the remainder to be reduced material including $[W(CSiMe_3)(CH_2SiMe_3)_2]_2$.[84,85] Apparently, any $W-CH_2SiMe_3$ bonds that may form in the further alkylation of $W(OMe)_2(CH_2SiMe_3)_4$ are not as susceptible to homolytic cleavage and α-abstraction can occur to yield mostly W(VI) product.

The reactions of $W(OMe)_3(CH_2CMe_3)_3$ with various alkylating agents is summarized in Scheme III.

Reduction of $W(OMe)_3(CH_2CMe_3)_3$

We had thought that chemical reduction of $W(OMe)_3(CH_2CMe_3)_3$ with 3 equivalents of sodium amalgam might provide the unknown hexaneopentyl ditungsten (W(III)) dimer (eq 7). The trimethylsilylmethyl analogue, $W_2(CH_2SiMe_3)_6$, is known[85,119] (cf. Appendix II). Performing the above

Scheme III


no reaction at RT
$Zn(CH_2CMe_3)_2$
$W(OMe)_3(CH_2CMe_3)_3$ + Me_3CCH_2MgCl or $Mg(CH_2CMe_3)_2$ or $LiCH_2CMe_3$
$3Me_3CCH_2MgCl$ or $3Mg(CH_2CMe_3)_2$ in ether at 75°C
$[W(CCMe_3)(CH_2CMe_3)_3]_2$
no reaction at RT
Me_3CCH_2MgCl or $Mg(CH_2CMe_3)_2$
$W(OMe)_2(CH_2CMe_3)_4$
$LiCH_2CMe_3$ reduction
$[W(OMe)(CH_2CMe_3)_4]_2$
$LiCH_2CMe_3$
$[W(CCMe_3)(CH_2CMe_3)_2]_2$

$$W(OMe)_3(CH_2CMe_3)_3 \quad + \quad 3Na/Hg \longrightarrow (Me_3CCH_2)_3W{\equiv}W(CH_2CMe_3)_3 \qquad (7)$$

reduction in ether gave beautiful orange crystals in high yield. However, the ^{1}H NMR spectra at 298K were slightly broadened and showed the presence of coordinated ether. To inspect for fluxional behavior the ^{1}H NMR spectrum was obtained at 243K but the resonances (especially for coordinated ether) boradened further. A high temperature spectrum at 323K displayed sharp ether multiplets, a sharp tert-butyl peak, and a broadened set of resonances possibly representing methylene signals. If the above reduction is performed in thf and the orange product recrystallized from ether the ^{1}H NMR spectra display thf and ether resonances. The ^{1}H NMR spectrum at 338K shows sharp coordinated solvent and tert-butyl resonances. A sharp singlet at 4.28 ppm in the 298K spectrum completely disappears in the 338K spectrum. This peak is in the chemical shift range for methoxide resonances. The presence of coordinated ether with this thf adduct is somewhat surprising.

An EPR spectrum of the product reduced in ether displays a single line with a g_{av} = 1.791 at 298K. At 77K the signal displays some anisotropy and splits into two lines. Our NMR data are consistent with a paramagnetic complex since the peaks sharpen at higher temperatures indicative of a lessened magnetic moment. This behavior is predicted by Curie's law. A crystal structure is necessary to firmly identify these paramagnetic products.

DISCUSSION

In this chapter we have demonstrated that W(VI) alkyl complexes can be prepared via the judicious choice of starting materials. The alkoxide ligand, like the oxo and imido ligand, help stabilize d^0 tungsten with respect to reduction by π-electron donation. Osborn and co-workers have found that $W(O)(CH_2CMe_3)_3Cl$ can be prepared via the interaction of $W(O)Cl_4$ and $Mg(CH_2CMe_3)_2$(dioxane).[36] Other reported tungsten oxo-alkyl species include $W(O)(CH_3)Cl_3$ and $W(O)_2(CH_3)Cl$.[121] Pedersen has been able to prepare $W(NPh)(CH_2CMe_3)_3Cl$ and $W(NPh)(CH_2CMe_3)_3(OBu^t)$ from Me_3CCH_2MgCl and $W(NPh)Cl_4$ and $W(NPh)(OBu^t)_4$, respectively.[35] Pedersen discovered that the use of NEt_4Cl allows for the selective alkylation of tungsten imido halide species.[35] That is, $[W(NPh)Cl_5]NEt_4$ (prepared from $W(NPh)Cl_4$ and NEt_4Cl) is cleanly alkylated with $Zn(CH_2SiMe_3)_2$ in CH_2Cl_2 to yield $W(NPh)(CH_2SiMe_3)_2Cl_2$ and $[ZnCl_3]NEt_4$. Attempts at preparing the neopentyl analogue were unsuccessful.

We found the thermal stability of our tungsten(VI) alkyl complexes surprising, particularly for $W(OBu^t)_3(CH_2CMe_3)_3$ a molecule that has six tert-butyl containing ligands in the coordination sphere. The photosensitivity of these tungsten(VI) alkyls is not totally unexpected since Osborn and co-workers have found that $W(OAlBr_3)(CH_2CMe_3)_3Br$ and similar molecules release neopentane and form $W(OAlBr_3)(CHCMe_3)(CH_2CMe_3)Br$ photochemically.[99b] Geoffroy and Wrighton have reviewed the photochemistry of transition metal σ-alkyl complexes.[122] Rausch, Alt, and co-workers have studied the photolysis of $[M(\eta^5\text{-}C_5H_5)_2(CH_3)_2]$ (M = Ti, Zr, Hf).[123] Methane and oligomeric metallocenes containing $\eta^1,\eta^5\text{-}C_5H_4$ bridging ligands were the identified products. Deuteration studies unambiguously ruled out production of free radicals.[123b,124] $[M(\eta^5-C_5H_5)(CH_3)(CO)_3]$ (M = Cr, Mo, W) have been reported to undergo photosubstitution of carbon monoxide.[125] The irradiation of the metallacyclobutane complex $[W(\eta^5-C_5H_5)_2(-CHRCHRCH_2-)]$ (R = H, CH_3) has been reported to give evolution of olefin through an olefin-carbene intermediate.[126] The simple σ-alkyl complexes $V(O)(CH_2SiMe_3)_3$[118] and $M(CH_2Ph)_4$ (M = Ti, Zr)[127] have been shown to be sensitive to light. Although we have no mechanistic evidence one possible mode of photodecomposition of $W(OR)_3(CH_2CMe_3)_3$ (R = CH_3, CMe_3) would involve a ligand-to-metal charge transfer involving lone pairs of electrons on oxygen inducing homolytic metal-carbon bond cleavage and/or α-hydrogen abstraction.

It is interesting to note that replacement of a methoxide ligand in $W(OMe)_3(CH_2CMe_3)_3$ with a bromide ligand via Me_3SiBr induces α-abstraction forming an alkylidene complex. Tantalum alkyl complexes containing alkoxide ligands have been found to be more stable, with respect to α-abstraction, than tantalum halo/alkyl complexes.[74] The reduction of the proposed intermediate "$W(OMe)_2(CHCMe_3)(CH_2CMe_3)Br$" via loss of a neopentyl radical is not unexpected since we know of only one tungsten alkylidene complex, $W(CHCMe_3)(H)Cl_3(PMe_3)_2$,[101] that does not contain a stabilizing π-bonding ligand (such as oxo, imido, alkylidyne, etc.) $W(OBu^t)_3(CH_2CMe_3)_3$ does not react with Me_3SiBr probably for steric reasons.

The successful preparation of $W(OR)_3X_3$ (R = CH_3, CMe_3; X = CH_2CMe_3, CH_2SiMe_3) helps substantiate the theory that alkoxide ligands "stabilize" tungsten especially with respect to reduction.[111b] However, the alkoxide ligands are difficult to substitute with mild alkylating agents. Mg reagents cleanly mono-alkylate $W(OMe)_3(CH_2CMe_3)_3$ yielding $W(OMe)_2(CH_2CMe_3)_4$ but react no further at room temperature. Further alkylation with $Mg(CH_2CMe_3)_2$ or Me_3CCH_2MgCl occurs at 75°C and the tungsten alkylidyne complex, $[W(CCMe_3)(CH_2CMe_3)_3]_2$, is the isolated organometallic product. Alkylation of $W(OMe)_2(CH_2CMe_3)_4$ with the more vigorous reagent $LiCH_2CMe_3$ induces reduction. We do not know if the reduction is occuring via substitution followed by homolytic metal-carbon bond cleavage or by direct electron transfer via the lithium reagent. Reduction of W(VI) by alkylating agents is a common observation.[4e,5,112,114,128] Clark has found that WCl_6 is reduced by three equivalents of $LiCH_2CMe_3$ in ether yielding $WCl_3(ether)_2$.[129] Cotton, Wilkinson and co-workers have reported that WCl_4 and WCl_5 react with $LiCH_3$ in ether at low temperature to give thermally unstable $[W_2Cl_{8-x}(CH_3)_x]^{4-}\cdot[ether]_4$.[130] Lappert has obtained EPR evidence suggesting that the progressive addition of the di-Grignard reagent, $o\text{-}C_6H_4(CH_2MgCl)_2$, to $W(O)Cl_4$ in thf procedes through W(V) mixed oxochloride species (g_{av} = 1.774 and 1.780) before alkylation to yield the W(V) metallacycle, $[\{\overline{W(CH_2C_6H_4C}H_2\text{-}o)_2\overline{O\}_2M}g(thf)_4]$ (g_{av} = 1.948).[117]

CHAPTER 5 EXPERIMENTAL

$W(OMe)_3Cl_3$,[92] $Zn(CH_2CMe_3)_2$,[22] and $Zn(CH_2SiMe_3)_2$[22] were prepared by published methods. NEt_4Cl was dried in vacuo at 120°C for 24 hr prior to use. A 450 W medium-pressure mercury lamp which was surrounded with a water-cooled quartz jacket was used in the photochemical reactions. Elemental analyses proved futile as the tungsten alkyls prepared herein were rapidly decomposed by ambient room light to carbyne species. An example is $W(OBu^t)_3(CH_2CMe_3)_3$; Calcd. for $WC_{27}H_{60}O_3$: C, 52.59; H, 9.81. Found: C, 42.46; H, 8.08. The compound has photolytically decomposed to $W(CCMe_3)(OBu^t)_3$; Calcd. for $WC_{17}H_{36}O_3$: C, 43.23; H, 7.68. The numbers compare quite favorably.

PREPARATIONS

$\underline{W(OMe)_3(CH_2CMe_3)_3}$ (IX-53)

NEt_4Cl (19.45 g, 117.4 mmol) was slowly added to $W(OMe)_3Cl_3$ (30.0 g, 78.3 mmol) in CH_2Cl_2 (400 mL). The yellow solution became colorless. $Zn(CH_2CMe_3)_2$ (24.4 g, 117.4 mmol) in CH_2Cl_2 (~50 mL) was added dropwise at -40°C with the room lights turned off. After the addition was complete the reaction was slowly warmed to 25°C and stirred for 3 hr. The orange reaction mixture was filtered through a Celite pad (removes $ZnCl^-NEt_4^+$), evaporated to dryness, extracted with ether (~250-300 mL), filtered, concentrated in vacuo, and cooled to -30°C to crystallize. Alternatively the ethereal solution can be evaporated to dryness and the dark orange sticky solid placed in a large McCarter sublimer and sublimed at 60-70°C

(<0.5μ vacuum). Sublimation (two crops) yields 27.2 g of pure bright yellow product (72% yield).

^{1}H NMR (C_6D_6, 250 MHz, ppm): 3.83 (s, 9, OMe), 1.36 (s, 6, $\underline{CH_2}CMe_3$), 1.26 (s, 27, $CH_2C\underline{Me_3}$). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 MHz, ppm): 80.81 ($\underline{C}H_2CMe_3$, J_{CW} = 87.9), 61.21 ($O\underline{C}H_3$), 34.30 ($CH_2C\underline{Me_3}$ and $CH_2\underline{C}Me_3$).

$\underline{W(OMe)_3(CH_2SiMe_3)_3}$ (IX-63)

Prepared by the same method used to prepare $W(OMe)_3(CH_2CMe_3)_3$ using $Zn(CH_2CMe_3)_2$. The ether extract was orange and gave light yellow crystals upon cooling. Yield: 80%.

^{1}H NMR (C_6D_6, 250 MHz, ppm): 3.86 (s, 9, OMe), 0.49 (s, 6, $\underline{CH_2}SiMe_3$), 0.29 (s, 27, $CH_2Si\underline{Me_3}$). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 MHz, ppm): 61.04 (q, J_{CH} = 147.1, $O\underline{C}H_3$), 51.07 (t, J_{CH} = 122.0, $\underline{C}H_2SiMe_3$), 1.79 (q, J_{CH} = 121.5, $CH_2Si\underline{Me_3}$).

$\underline{W(OBu^t)_3(CH_2CMe_3)_3}$ (IX-49)

$LiOBu^t$ (0.49 g, 6.12 mmol) was added to $W(OMe)_3(CH_2CMe_3)_3$ (1.0 g, 2.04 mmol) in ether (30 mL) at -30°C. The reaction was warmed to 25°C and after stirring 6 hr the bright yellow slurry was evaporated to dryness, extracted with pentane (40 mL), filtered, and evaporated to pure product in quantitative yield (1.20 g, 95%). The compound can be further purified by sublimation but some decomposition occurs.

^{1}H NMR (C_6D_6, 60 MHz, ppm): 1.55 (s, 33, $\underline{CH_2}CMe_3$ and $OC\underline{Me_3}$), 1.44 (s, 27, $CH_2C\underline{Me_3}$).

$[W(CHCMe_3)(OMe)_2Br]_2$ (VIII-67)

Me_3SiBr (269 μl, 2.04 mmol) was added to $W(OMe)_3(CH_2CMe_3)_3$ (1.0 g, 2.04 mmol) in ether (35 mL) at -30°C. The light orange solution immediately turned red and a white precipitate began depositing from solution. After 5 hr the reaction was filtered (removed 350 mg of fluffy white solid) and the orange solution concentrated in vacuo, filtered, and cooled to -30°C. Two crops of crystals yielded 0.42 g (52% yield).

^1H NMR (C_6D_6, 250 MHz, ppm): 11.12 (s, 1, $^2J_{HW}$ = 12.2, $C\underline{H}CMe_3$), 4.13 (s, 3, OMe), 4.01 (s, 3, OMe), 1.20 (s, 9, $CHC\underline{Me}_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 62.8 MHz, ppm): 312.28 (d, J_{CH} = 125.1, $\underline{C}HCMe_3$), 68.65 (q, J_{CH} = 148.5, $O\underline{C}H_3$), 67.33 (q, J_{CH} = 147.5, $O\underline{C}H_3$), 45.77 (s, $CH\underline{C}Me_3$), 32.17 (q, J_{CH} = 127.2, $CHC\underline{Me}_3$). Molecular weight determination: Calcd., 792. Found, 865.

$W(OMe)_2(CH_2CMe_3)_4$ (X-7)

$Mg(CH_2CMe_3)_2$ (1.52 g, 9.12 mmol) was added to $W(OMe)_3(CH_2CMe_3)_3$ (4.47 g, 9.12 mmol) in pentane (60 mL) at -30°C. The reaction turned orange-red but quickly became almost white upon warming. The $Mg(CH_2CMe_3)$-(OMe) was removed by filtration and the pentane was removed in vacuo yielding 4.60 g of very pale yellow liquid (95% yield).

^1H NMR (C_6D_6, 250 MHz, ppm): 3.80 (s, 6, OMe), 1.79 (s, 8, $C\underline{H}_2CMe_3$), 1.20 (s, 36, $CH_2C\underline{Me}_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 22.5 MHz, ppm): 86.14 (t, J_{CH} = 121.1, J_{CW} = 97.7, $\underline{C}H_2CMe_3$), 57.62 (q, J_{CH} = 141.3, $O\underline{C}H_3$), 34.83 (s, $CH_2\underline{C}Me_3$), 33.27 (q, J_{CH} = 126.3, $CH_2C\underline{Me}_3$).

$\underline{W(OMe)_2(CH_2SiMe_3)_4}$ (X-11)

Me_3SiCH_2MgCl (1.24 mL, 1.50 M soln, 1.86 mmol) was added to $W(OMe)_3(CH_2SiMe_3)_3$ (1.0 g, 1.86 mmol) in ether (15 mL) at -30°C. After warming to 25°C and stirring for 5 hr the dark orange-brown reaction mixture was evaporated to dryness, extracted with pentane (25 mL), filtered, and evaporated to a dark orange oil (1.05 g, 90% yield).

^1H NMR (C_6D_6, 60 MHz, ppm): 3.87 (s, 6, OMe), 1.28 (s, 8, $^2J_{HW}$ = 11, $C\underline{H}_2SiMe_3$), 0.10 (s, 36, $CH_2Si\underline{Me}_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 MHz, ppm): 60.56 ($\underline{C}H_2SiMe_3$), 58.27 ($O\underline{C}H_3$), 1.58 ($CH_2Si\underline{Me}_3$).

$\underline{[W(OMe)(CH_2CMe_3)_4]_2}$ (X -1, 9, 29)

$LiCH_2CMe_3$ (0.29 g, 3.77 mmol) was added to $W(OMe)_2(CH_2CMe_3)_4$ (2.0 g, 3.77 mmol) in pentane (20 mL) at -30°C in the absence of light. After 4 hr the reaction was filtered and evaporated to yellow crystals. The flask was cooled to -30°C, cold pentane added, and 0.5 g of beautiful yellow crystals were isolated by filtration. The filtrate was cooled to -30°C and a second crop (0.6 g) isolated. Total yield 1.10 g (55%).

^1H NMR ($CDCl_3$, 250 MHz, ppm): 4.10 (s, OMe), 1.90 (s, $C\underline{H}_2CMe_3$, $^2J_{HW}$ = 11.7), 1.19 (s, $C\underline{H}_2CMe_3$), 1.09 (s, $CH_2C\underline{Me}_3$), 1.07 (s, $CH_2C\underline{Me}_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.8 MHz, ppm): 83.28 ($\underline{C}H_2CMe_3$), 72.40 ($\underline{C}H_2CMe_3$), 59.09 ($O\underline{C}H_3$), 35.83 ($CH_2\underline{C}Me_3$), 34.45 ($CH_2C\underline{Me}_3$), 34.30 ($CH_2C\underline{Me}_3$), 33.40 ($CH_2\underline{C}Me_3$), 33.19 ($CH_2C\underline{Me}_3$). For more information see N62-29A-X and N22-1A-X for ^{13}C spectra and N250-29A-X and N250-1A-X for ^1H spectra.

APPENDIX I: Organization of Notebooks and Spectra

The experimental data for this research are contained in ten notebooks (I-X). The results are arranged by experiment in chronological order. The NMR references are listed by instrument and nucleus (i.e., field strength) and notebook page number. N60 refers to a ^{1}H NMR experiment on the Varian T-60 while N250 refers to a ^{1}H NMR spectrum obtained on the Bruker WM-250 at 250 MHz. N15 and N22 refer to ^{13}C NMR experiments on the Jeol FX-60Q or FX-90Q, respectively. All ^{31}P NMR data were obtained with the Jeol FX-90Q at 36 MHz and are labelled N36. N60-72A-IX would represent a ^{1}H NMR T-60 experiment from notebook IX page 72. N36-17A-X is a ^{31}P NMR from notebook X page 17. All NMR spectra are grouped in notebooks according to nucleus.

APPENDIX II

THE PREPARATION OF $W(CSiMe_3)(CH_2SiMe_3)_3$: A TUNGSTEN(VI) NEOPENTYLIDYNE COMPLEX

RESULTS AND DISCUSSION

As discussed in Chapter 5 the alkylation of tungsten halide salts rarely yields products with the metal in the same oxidation state as the starting material. Clark has prepared $[W(CCMe_3)(CH_2CMe_3)_3]_2$ in ~20% isolated yield from WCl_6 and $6LiCH_2CMe_3$.[91] It was discovered that each of the first three equivalents of $LiCH_2CMe_3$ reduced the metal. The product was proposed to be formed via alkylation of the reduced metal complex followed by α-hydrogen abstraction/oxidation.[129]

In 1972 Wilkinson and co-workers reported the reaction of WCl_6 and $6Me_3SiCH_2MgCl$.[119] The reduced W(III) metal-metal bonded dimer, $W_2(CH_2SiMe_3)_6$, was the isolated product. No W(VI) product was noted. The crystal structure of this dimer showed it to contain a W-W triple bond.[85] In 1976 Wilkinson and co-workers[84] and Chisolm and co-workers[85] reported that $[W(CSiMe_3)(CH_2SiMe_3)_2]_2$, a W(V) carbyne complex, can be prepared from WCl_4 and $4Me_3SiCH_2MgCl$ in 13-18% isolated yield. Both publications noted that resonances attributable to both $[W(CSiMe_3)(CH_2SiMe_3)_2]_2$ and $W_2(CH_2SiMe_3)_6$ were observed in the ^1H NMR of the crude alkane extractions from the reaction between WCl_6 and $6Me_3SiCH_2MgCl$ (vide supra). Therefore both a W(III) and W(V) product were observed in this reaction. $W_2(CH_2SiMe_3)_6$ is, however, readily isolated because it crystallizes easily and is stable during column chromatography employing cellulose. The crystal structure of $[W(CSiMe_3)(CH_2SiMe_3)_2]_2$, performed by Cotton and co-workers, showed that this compound contains bridging alkylidyne groups, $CSiMe_3$, which, along with the tungsten atoms, form planar rings, $\overbrace{W-C-W-C}$. As expected the complex was found to contain a

W-W single bond.[86]

Sancho has found that $[W(CCMe_3)(CH_2CMe_3)_3]_2$ can be prepared in 60% yield via the interaction of $W(OMe)_3Cl_3$ and $6Me_3CCH_2MgCl$ in ether.[40] Employing Me_3SiCH_2MgCl in the above reaction we isolated a new alkylidyne complex, $W(CSiMe_3)(CH_2SiMe_3)_3$. This formally W(VI) product is analogous to Wilkinson's W(V) alkylidyne except that no metal-metal bonding is required to account for its diamagnetism. Scheme I summarizes the reactions of WCl_6, WCl_4, and $W(OMe)_3Cl_3$ with Me_3SiCH_2MgCl. Although we can isolate pure $W(CSiMe_3)(CH_2SiMe_3)_3$ via high-vacuum distillation in 60% yield, the $^{31}C\{^1H\}$ NMR spectrum shows that this crude orange oil contains ~90% $W(CSiMe_3)(CH_2SiMe_3)_3$ and ~10% $[W(CSiMe_3)(CH_2SiMe_3)_2]_2$. A summary of NMR data for these alkylidyne complexes, as well as for $W_2(CH_2SiMe_3)_6$, are given in Table I. This reaction demonstrates that

TABLE I. NMR Data for Tungsten Trimethylsilylmethyl Complexes[a]

	$W_2(CH_2SiMe_3)_6$[b]	$[W(CSiMe_3)(CH_2SiMe_3)_2]_2$[b]	$W(CSiMe_3)(CH_2SiMe_3)_3$[c]
$\underline{^{13}C}$			
$CH_2Si\underline{Me}_3$	4.7	3.0	2.4
$CSi\underline{Me}_3$		2.2	2.1
$\underline{C}H_2SiMe_3$	78.6 (J_{CW}=78)	69.0 (J_{CW}=79)	75.7 (J_{CW}=79)
$\underline{C}SiMe_3$		353 (J_{CW}=173)	344 (J_{CW}=174)
$\underline{^{1}H}$			
$CH_2Si\underline{Me}_3$	0.13	0.03	0.04
$CSi\underline{Me}_3$		0.28	0.19
$C\underline{H}_2SiMe_3$	1.74(J_{CW}=10.0)		0.72 ($^2J_{HW}$=10.3)

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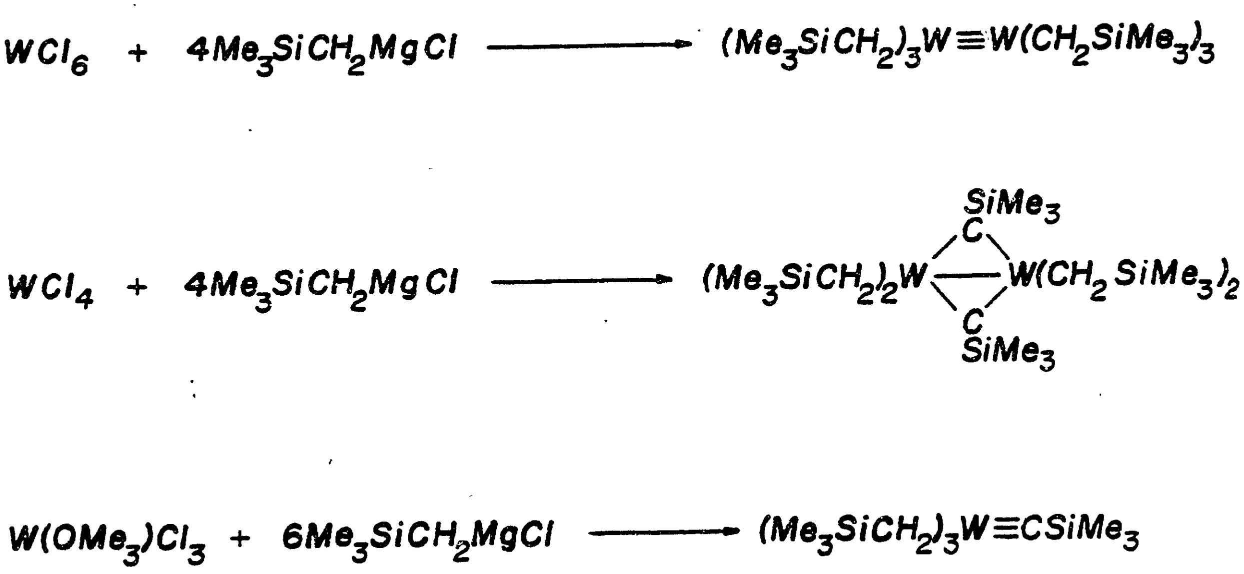
[a] Chemical shifts given in ppm relative to tetramethylsilane in d_8-toluene or d_6-benzene. Coupling to ^{183}W given in Hz. [b] Data from references 84 and 85. [c] This work.

SCHEME I. TUNGSTEN ALKYLATIONS



$$WCl_6 + 4Me_3SiCH_2MgCl \longrightarrow (Me_3SiCH_2)_3W{\equiv}W(CH_2SiMe_3)_3$$

$$WCl_4 + 4Me_3SiCH_2MgCl \longrightarrow (Me_3SiCH_2)_2W(\mu\text{-}CSiMe_3)_2W(CH_2SiMe_3)_2$$

$$W(OMe_3)Cl_3 + 6Me_3SiCH_2MgCl \longrightarrow (Me_3SiCH_2)_3W{\equiv}CSiMe_3$$

a W(VI) trimethylsilylmethyl alkyl complex can be obtained from simple alkylation techniques. The alkoxide ligands on $W(OMe)_3Cl_3$ help stabilize tungsten, relative to reduction, and yields high-valent complexes. As the reports of $[W(CSiMe_3)(CH_2SiMe_3)_2]_2$ noted, the alkylation chemistry of WCl_6 is complex and both W(V) and W(III) products can be observed.[84,85] Although we observe a similar effect our reaction of $W(OMe)_3Cl_3$ with $6Me_3SiCH_2MgCl$ produced tungsten complexes that were ~90% W(VI) and only ~10% W(V). No W(III), i.e., $W_2(CH_2SiMe_3)_6$, was observed.

While this manuscript was in preparation Chisholm and co-workers reported the preparation of $W(CSiMe_3)(CH_2SiMe_3)_3$ (W(VI)) from WCl_6 and $LiCH_2SiMe_3$ (6 equiv) in 16% isolated yield.[131] It's puzzling why the reaction of WCl_6 with a lithium reagent provided a W(VI) product while the reaction with Me_3SiCH_2MgCl gave reduced products (vide supra).

EXPERIMENTAL

Preparation of $W(CSiMe_3)(CH_2SiMe_3)_3$ (VII-61)

$W(OMe)_3Cl_3$ (5.0 g, 13.04 mmol) was dissolved in thf (25 mL) and slowly (~3 hr) added dropwise to Me_3SiCH_2MgCl (74 mL, 1.0 M soln in ether) at -78°C. After the addition was complete the lime-green slurry was slowly warmed to ca. 25°C (~2 hr) and the reaction turned red-brown. The reaction was stirred 8 hr, filtered through a Celite pad, evaporated to an orange-red oil, extracted with pentane (2x100 mL), and evaporated to crude product. The oil was purified via distillation (65-80°C) in vacuo (< 0.1 μ) to yield 4.0 g of bright yellow solid (58% yield).

^1H NMR (C_6D_6, 250 MHz, ppm): 0.717 (s, 6, $C\underline{H}_2SiMe_3$, $^2J_{HW}$ = 10.3), 0.189 (s, 9, $CSi\underline{Me}_3$), 0.044 (s, 27, $CH_2Si\underline{Me}_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 62.8 MHz, ppm): 344.0 (s, J_{CW} = 173.6, $\underline{C}SiMe_3$), 75.69 (t, J_{CH} = 109.9, J_{CW} = 79.3, $\underline{C}H_2SiMe_3$), 2.39 (q, J_{CH} = 119.0, $CH_2Si\underline{Me}_3$), 2.10 (q, J_{CH} = 119.0, $CSiMe_3$).

APPENDIX III

THE PREPARATION OF DIHAPTO ACYL COMPLEXES OF TANTALUM

RESULTS AND DISCUSSION

The interest in the selective reductive coupling of CO with H_2 has prompted the study of early transition metal alkyl complexes with carbon monoxide. Floriani has reported $(\eta^5\text{-}C_5H_5)_2Zr(COMe)Me$ prepared from $(\eta^5\text{-}C_5H_5)_2ZrMe_2$ and CO.[132] He has found the carbon monoxide to be bonded in a side-on (η^2) fashion. This was proposed since the IR spectrum displays a low energy CO stretch at 1545 cm^{-1} and was established by crystal structure determination. The Zr-O distance is 2.290(4)Å. Bercaw and co-workers have found that the pentamethylcyclopentadienyl derivative, $(\eta^5\text{-}C_5Me_5)_2ZrMe_2$, reacts with CO to yield $(\eta^5\text{-}C_5Me_4)Zr(COMe)Me$ (ν_{CO} = 1537 cm^{-1}) which rapidly absorbs a second equivalent of CO to yield the 2,3-butenediolate complex, $(\eta^5\text{-}C_5Me_5)\overline{Zr(O(Me)C{=}C(Me)O})$ in which two molecules of carbon monoxide have been coupled.[133] The only report of the insertion of CO into a metal-carbon bond of tantalum was by Schrock and Wood.[134] They found that $(\eta^5\text{-}C_5Me_5)TaMe_XCl_{4-X}$ (X = 2,3,4) reacts readily with one equivalent of CO to give stable η^2-acetone complexes. When X = 3 or 4 these complexes react with a second equivalent of CO to give $(\eta^5\text{-}C_5Me_5)Ta(O)X(O(Me)C{=}CMe_2)$. Labelling experiments support the contention that the enolate complex is a result of an intramolecular reductive coupling of two CO molecules which may proceed via the η^2-acetone moiety.

We have recently found that tantalum mono-alkyl complexes of the type $(\eta^5\text{-}C_5Me_5)Ta(R)X_3$ (R = CH_2CMe_3, CH_2SiMe_3; X = Cl, Br) react with carbon monoxide (either one equivalent or excess) to yield η^2-acyl complexes, $(\eta^5\text{-}C_5Me_5)Ta(\eta^2\text{-}COR)X_3$. No acyl complexes of tantalum have been reported.[135] These complexes are described as dihapto because the acyl carbon atom is found far downfield at ~300 ppm in the $^{13}C\{^1H\}$ NMR spectrum. $(\eta^5-C_5H_5)_2Zr(\eta^2-COC_6H_5)(C_6H_5)$[136] and $(\eta^5-C_5H_5)_2Zr(\eta^2-COCH_2CMe_3)-Cl$[137] have acyl carbon resonances at 301 ppm and 319 ppm, respectively, in the $^{13}C\{^1H\}$ NMR spectra. The C-O stretching frequencies for the Zr complexes are found at 1505 cm^{-1} and 1550 cm^{-1}, respectively, in the IR spectra in solution.

Scheme I shows the preparation of $(\eta^5-C_5Me_5)Ta(\eta^2-COCH_2CMe_3)Cl_3$ from the alkyl precursor and CO. The "oxycarbene" resonance structure has been proposed by Bercaw to explain the reaction chemistry of his bis-pentamethylcyclopentadienyl zirconium system.[133,138] The geometry of our η^2-acyl complexes was established by preparing the bis-tert-butoxide and/or the bis-tert-butylthiolate derivatives displayed in the Scheme. In both cases the tert-butyl groups gave only a single singlet in the ^1H and ^{13}C NMR spectra. The methylene protons of the neopentyl group are observed as a singlet by ^1H NMR. $(\eta^5-C_5Me_5)Ta(\eta^2-COCH_2SiMe_3)Cl_3$ was shown to be a monomer by cryoscopic molecular weight determination in cyclohexane (calcd; 538. found; 526). A pseudo-octahedral geometry in which the oxygen atom of the inserted carbon monoxide occupies an axial position explains the above results. Table I lists the tantalum η^2-acyl complexes prepared and gives the $^{13}C\{^1H\}$ NMR data. The most interesting feature is that the acyl carbon of $(\eta^5-C_5Me_5)Ta(COCH_2CMe_3)(OBu^t)_2Cl$ is found at 286 ppm while in $(\eta^5-C_5Me_5)Ta(COCH_2CMe_3)(SBu^t)_2Cl$ it is observed at 194 ppm (in the range of η^1-acyl carbon atoms). This might be ascribed to the lower electronegativity of sulfur vs. oxygen. The $\eta^5-C_5Me_5$ ring carbon chemical shifts for the six complexes should be compared.

Scheme I

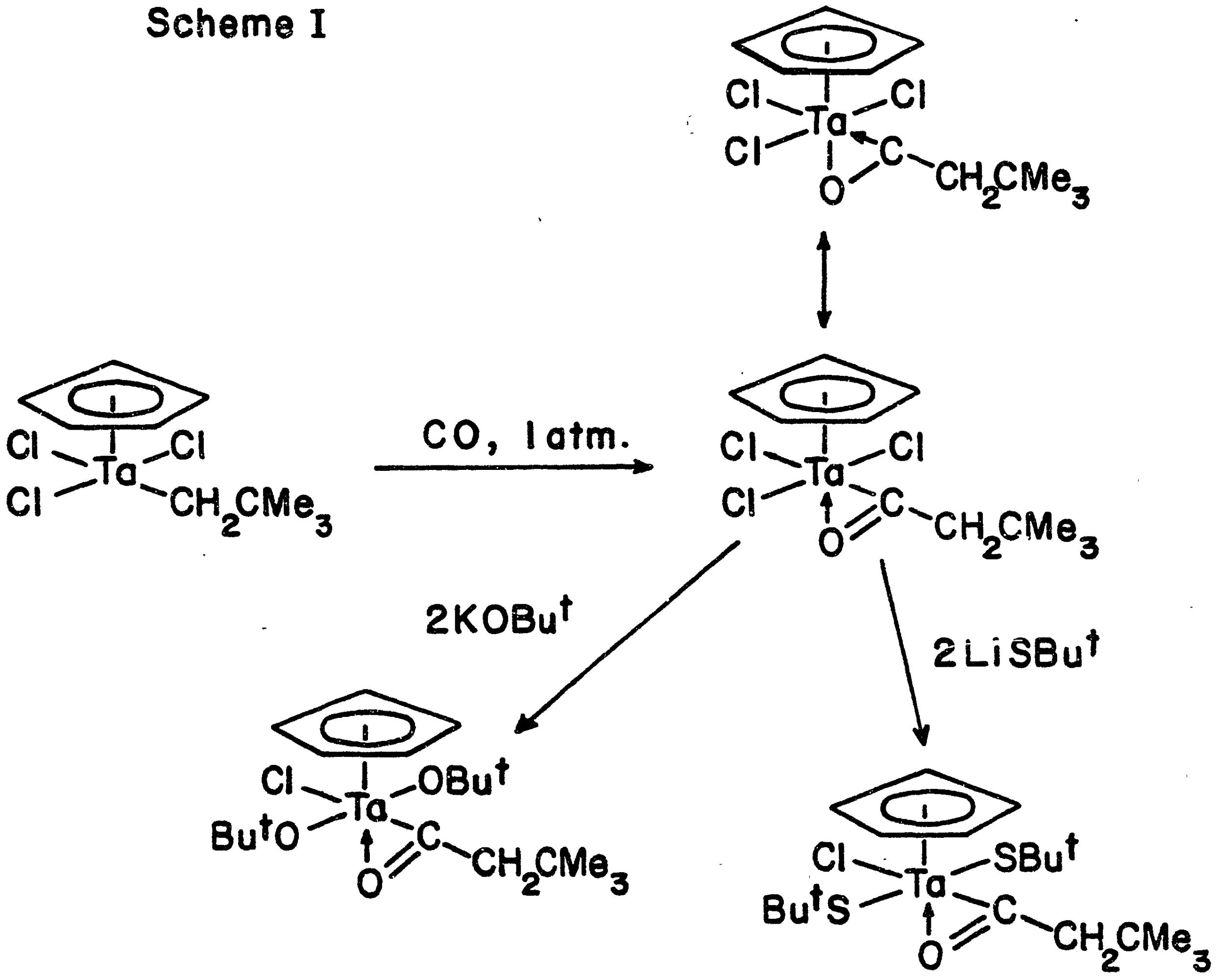


TABLE I. ^{13}C NMR Data for Tantalum η^2-Acyl Complexes[a]

Complex	η^2-$\underline{C}$=O	η^5-$\underline{C_5}Me_5$	η^5-$C_5\underline{Me_5}$	$\underline{CH_2}ZMe_3$[b]	$CH_2\underline{C}Me_3$	$CH_2Z\underline{Me_3}$[b]	$X\underline{C}Me_3$[c]	$XC\underline{Me_3}$[c]
Cp"Ta(η^2-$COCH_2SiMe_3$)Cl_3 (N15-25-I)[d]	304.6	130.3	11.9	39.6		0.3		
Cp"Ta(η^2-$COCH_2SiMe_3$)Br_3 (N22-31-X)	301.9	131.0	13.0	40.2		0.2		
Cp"Ta(η^2-$COCH_2CMe_3$)Cl_3 (N22-52-II)	314.7	130.7	11.8	54.9	31.4	30.1		
Cp"Ta(η^2-$COCH_2CMe_3$)(OBu^t)Cl_2 (N22-56-III)	314.4	125.5	11.5	55.1	31.9	29.8	84.0	30.5
Cp"Ta(η^2-$COCH_2CMe_3$)$(OBu^t)_2$Cl[e] (N22-29-IV)	285.6	119.9	12.2	54.3	31.9	29.7	80.5	31.2
Cp"Ta(η^2-$COCH_2CMe_3$)$(SBu^t)_2$Cl (N22-47-IV)	193.6	119.7	13.0	52.4	31.7	32.0	109.1	34.7

[a] Spectra run in C_6D_6 or $CDCl_3$ at 308K unless otherwise noted. Gated decoupled spectra show acyl carbons as singlets. [b] Z = Si or C. [c] X = O or S. [d] Notebook reference. [e] T = 243 K in $CDCl_3$.

The IR spectra of the η^2-acyl complexes were not extremely informative as no obvious C-O bands were observed between 1700 cm^{-1} and 1400 cm^{-1} in nujol or fluorlube mulls. An FT-IR study in chloroform solution was performed with the assistance of J. Mitchener. The spectrum of $(\eta^5-C_5Me_5)Ta(CH_2SiMe_3)Br_3$ and $(\eta^5-C_5Me_5)Ta(\eta^2-COCH_2SiMe_3)Br_3$ differ in only one respect: a medium-strength band at 1214 cm^{-1} is observed for the η^2-acyl complex. This is quite low in energy for an acyl C-O stretching frequency but organic ether carbon-oxygen single bond stretching modes are found in this region. Obviously no definitive statement can be made without a ^{13}C-labelling study. $(\eta^5-C_5Me_5)Ta(\eta^2-COCH_2CMe_3)Cl_3$ also shows a peak ~ 1200 cm^{-1}. $(\eta^5-C_5Me_5)Ta(\eta^2-COCH_2CMe_3)(OBu^t)_2Cl$ and $(\eta^5-C_5Me_5)Ta(\eta^2-COCH_2CMe_3)(SBu^t)_2Cl$ have absorbances at 1598 cm^{-1} and 1624 cm^{-1} which may be ascribed to C-O stretching modes.

$(\eta^5-C_5Me_5)Ta(\eta^2-COCH_2SiMe_3)Cl_3$ does not react with H_2 at 40 psi and RT and decomposes above 70°C. It does however react with PMe_3. Although not fully investigated the PMe_3 appears to attack the "carbene-like" acyl carbon since the methylene protons of the neopentyl group are found as a doublet ($^2J_{HP} \simeq 3$ Hz) in the ^1H NMR (N60-3A-II). The alkyl precursor, $(\eta^5-C_5Me_5)Ta(CH_2SiMe_3)Cl_3$, does not coordinate PMe_3 in toluene until ~223 K. Interestingly $(\eta^5-C_5Me_5)Ta(\eta^2-COCH_2CMe_3)(OBu^t)_2Cl$ does not react with PMe_3.

Much chemistry remains to be done in this fascinating area.

EXPERIMENTAL

$(\eta^5\text{-}C_5Me_5)Ta(\eta^2\text{-}COR)X_3$ (R = CH_2SiMe_3, CH_2CMe_3; X = Cl, Br) complexes were prepared from the alkyl precursors and carbon monoxide in a glass bomb at ~30-40 psi. The alcoxy and thiolate complexes were prepared using $KOBu^t$ and $LiSBu^t$ in toluene, respectively. The elemental analysis for $(\eta^5\text{-}C_5Me_5)Ta(\eta^2\text{-}COCH_2SiMe_3)Cl_3$ was correct: Anal. calcd. for $TaC_{15}H_{26}SiOCl_3$: C, 33.50; H, 4.87. Found: C, 33.92; H, 5.04.

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Biographical Note

Scott M. Rocklage was the first of five children born to Gerald and Mary Lou Rocklage 10 miles south of San Francisco in Burlingame, California on July 28, 1954. His family moved to San Jose in 1962 and he attended public schools there. He was involved in FFA (Future Farmers of America) and other agrarian pursuits at Willow Glen High School, where he graduate from in 1972. He began his undergraduate career at San Jose State University as a Marine Biology major but changed his major to chemistry after his sophomore year. The author transferred to U.C. Berkeley in September, 1976 and performed undergraduate research with Dr. Leonard Bjeldanes on the chemistry of flavonoids and then with Dr. Craig L. Hill on the synthesis and reactivity of iron-sulfur protein analogues and manganese porphyrins. He was fortunate to be introduced to inorganic chemistry by Dr. Ken Raymond. The author received the B.S. degree in Chemistry, with honors, in June 1978.

In September, 1978 he began a pre-doctoral program at the Massachusetts Institute of Technology and chose to perform his graduate work with Dr. Richard Schrock in organotantalum, organotungsten, and early transition metal inorganic chemistry. In addition to synthetic and reaction chemistry he specialized in the uses of multi-nuclear magnetic resonance spectroscopy in product characterization and structural assignment. He completed the requirements for the Ph.D. degree in December, 1981. In January, 1982 the author will begin his career outside academia at Catalytica Associates, Inc. in Santa Clara, California.

He was married on June 26, 1977 to Julie L. Bellandi. On February 27, 1981 Julie and Scott brought their first son, Matthew, into the world.