producing alkoxy radicals. Where their orientation and kinetic energy is such that they can be contained by their dipole attraction, then disproportionation occurs to the path 2a products. The monotonically decreasing rate constant k_t observed in the sequence MeO_2, EtO_2, $iPrO_2$, $tBuO_2$[24] could then be accounted for by an activation energy changing from 2 kcal for MeO_2 to the observed 9 kcal for t-BuO_2. Measured from the tetraoxide (R_2O_4) these activation energies would range from 11 to 18 kcal. *H/D isotopic effects which have been reported have recently been shown by Mendenhall and Quinga to also occur in hyponitrite decompositions where only the 2b path is available.[27]

A last word on the subject of cage effects in gas reactions. In mass spectrometry we frequently find quite extensive rearrangements. In the fission of an excited cation AB^+ (produced by the electron bombardment of

AB) to produce A^+ + B fragments, we will expect a relatively long range attraction arising from ion–dipole or ion-induced dipole forces. Either of these can extend out to 6 to 9 Å and result in an extended cage effect leading to multiple encounters between A^+ and B. Such secondary encounters could produce some of the rearrangements observed without requiring very complex and tight transition states.[28,29]

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High-Oxidation-State Molybdenum and Tungsten Alkylidyne Complexes

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Carbon forms triple bonds to few elements besides itself, nitrogen, and oxygen. The first triple bonds between a transition metal and a monosubstituted carbon atom were found by Fischer in chromium, molybdenum, and tungsten complexes of the type M-(CR)(CO)$_4$(halide).[1] Molybdenum and tungsten complexes of the type $M(C$-t-$Bu)(CH_2$-t-$Bu)_3$ that were discovered several years later[2] at first appeared to be only a rather limited class of distant cousins of the Fischer complexes, but as more derivatives of the type $M(CR)X_3$ were prepared, it became apparent that these "alkylidyne" complexes, in which the metal can be said to be in its highest possible oxidation state (6+), comprise a large and varied class, at least for Mo and W.

Evidence that related high-oxidation-state alkylidene complexes[3] catalyze the olefin metathesis reaction[4-6] fueled speculation that some Mo or W alkylidyne complexes might catalyze the rare acetylene metathesis reaction (eq 1). We now know that some high-oxida-

$$2\ RC{\equiv}CR' \rightleftharpoons RC{\equiv}CR + R'C{\equiv}CR' \qquad (1)$$

tion-state alkylidyne complexes do indeed catalyze the metathesis of acetylenes remarkably efficiently, and

that some do not. We have begun to understand why. We also have begun to understand the relationship between alkylidyne complexes and complexes that contain other types of multiple bonds, such as metal-carbon double bonds,[5,6] metal–metal triple bonds,[7] or metal–nitrogen triple bonds.[8]

Preparation of Alkylidyne Complexes

$W(C$-t-$Bu)(CH_2$-t-$Bu)_3$ can be prepared relatively simply in ~50% yield by adding $W(OMe)_3Cl_3$ to 6 equiv of neopentylmagnesium chloride (eq 2).[9] The

$$W(OMe)_3Cl_3 + 6NpMgCl \xrightarrow{ether}$$
$$W(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3 \qquad (2)$$
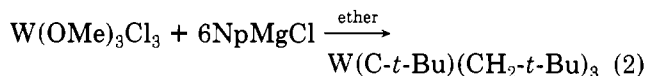
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yield is reproducible and the reaction can be carried out on a relatively large scale (20–30 g of product). Mo(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$ can be prepared in 35% yield by adding MoO$_2$Cl$_2$ to 6 equiv of neopentylmagnesium chloride.[10] Although the mechanism is unknown, in each case it is suspected that a neopentyl ligand is converted smoothly into a neopentylidyne ligand by two sequential "α-hydrogen abstraction"[3] or α-deprotonation reactions in a M(6+) neopentyl complex. Both W(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$ and Mo(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$ are yellow, volatile, highly soluble in hydrocarbons, relatively stable thermally (they can be distilled in a good vacuum), and extremely sensitive to air. Since the neopentyl ligand almost exclusively has been successful in α-hydrogen abstraction reactions to give tantalum and niobium alkylidene complexes,[3] we do not expect a family of tungsten or molybdenum trialkyl alkylidyne complexes to be prepared via analogous alkylation routes. So far the only other known species are of the type M(CSiMe$_3$)(CH$_2$SiMe$_3$)$_3$ (M = Mo[11] or W[12]).

The chemistry of molybdenum and tungsten neopentylidyne complexes began to develop rapidly after the high-yield reactions shown in eq 3 were discovered

$$M(C\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3 + 3\ HCl + dme \rightarrow$$
$$cis,mer\text{-}M(C\text{-}t\text{-}Bu)Cl_3(dme)\quad(3)$$
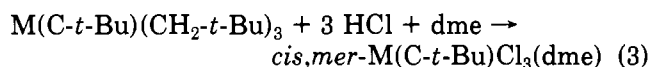
(dme = 1,2-dimethoxyethane).[9,10] A variety of M(C-*t*-Bu)X$_3$ complexes then could be prepared relatively straightforwardly. We were especially interested in complexes in which X is a sterically bulky alkoxide such as O-*t*-Bu,[9] 2,6-C$_6$H$_3$-*i*-Pr$_2$ (DIPP),[13] or OCMe(CF$_3$)$_2$,[14] since we knew that *tert*-butoxide ligands were essential for olefin metathesis activity by Nb and Ta neopentylidene complexes.[5c] We felt that bulky alkoxides would be more desirable than small alkoxide ligands, since bulky alkoxides cannot bridge strongly between metals; smaller alkoxides bridge and therefore lead to relatively insoluble and poorly characterized oligomers or polymers. Bulky alkoxides also may prevent alkylidyne ligands from combining in a bimolecular reaction to give an acetylene and a molecule containing a metal–metal triple bond (see below).

A relatively efficient method of preparing tri-*tert*-butoxide complexes consists of the remarkable reaction shown in eq 4.[15] Even some functionalized acetylenes

$$W_2(O\text{-}t\text{-}Bu)_6 + RC\equiv CR \rightarrow 2\ W(CR)(O\text{-}t\text{-}Bu)_3\quad(4)$$

can be employed. We now know that W$_2$[OCMe$_2$(CF$_3$)]$_6$ and W$_2$(O-*i*-Pr)$_6$(py)$_2$ react with internal acetylenes similarly,[16] Mo$_2$(O-*t*-Bu)$_6$ reacts with terminal acetylenes (but not internal acetylenes) to give Mo(CR)(O-*t*-Bu)$_3$ complexes,[17] and W$_2$(O-2,6-C$_6$H$_3$Me$_2$)$_6$ reacts with internal acetylenes to give tungstacyclobutadiene com-
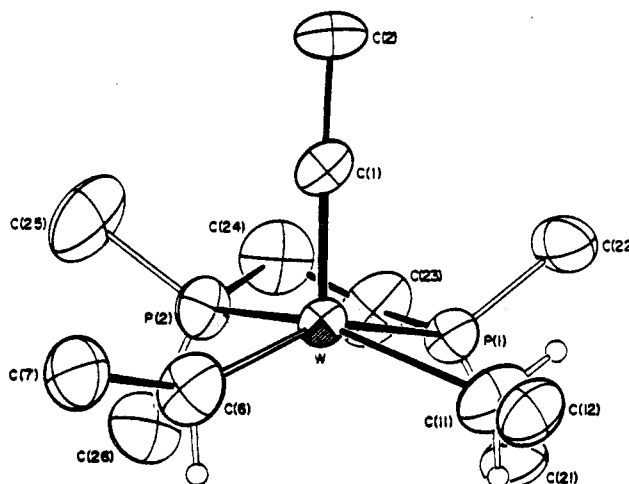
Figure 1. The structure of W(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)-(Me$_2$PCH$_2$CH$_2$PMe$_2$).[24]

plexes[18] (see below) via W(CR)(O-2,6-C$_6$H$_3$Me$_2$)$_3$ intermediates. Nevertheless, the reaction is rare[19] given the relatively large number of complexes containing the metal–metal triple bond.[7] It is interesting to note that W$_2$(O-*t*-Bu)$_6$ also reacts with simple nitriles virtually quantitatively as shown in eq 5.

$$W_2(O\text{-}t\text{-}Bu)_6 + RCN \rightarrow$$
$$W(CR)(O\text{-}t\text{-}Bu)_3 + 1/x\ [W(N)(O\text{-}t\text{-}Bu)_3]_x\quad(5)$$
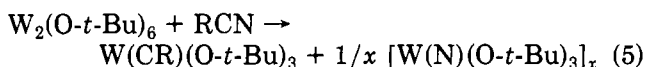
A mechanism for the reaction shown in eq 4 was proposed by analogy with reactions involving metallacyclobutadiene complexes to be discussed below. The crucial intermediate is postulated to be the extremely rare[21] "1,3-dimetallacyclobutadiene" complex,[22] A (equation 6; ligands omitted). It is plausible that a
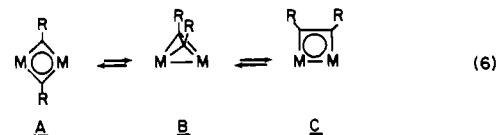
small amount of undetectable A is in rapid equilibrium with observable, relatively unreactive B and/or C under a variety of circumstances, but that A rarely falls apart to give monomeric alkylidyne complexes at a rate that is competitive with the rates of a number of other re-

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actions between A, B, or C and additional equivalents of an acetylene in which a carbon–carbon bond is formed irreversibly.[23a] There is now good evidence that reaction 4 is reversible when R = H.[23b] It is tempting to speculate that the thermodynamics of reaction 4 may be finely balanced in cases other than when R = H and that in general the reaction between compounds containing a W≡W bond and an acetylene may fail for thermodynamic as well as kinetic reasons. Even at this stage it is clear that the cleavage of acetylenes by metal–metal triple bonds to give alkylidyne complexes is the exception rather than the rule, and the circumstances that favor the reaction are very similar to those that are conducive to the metathesis of acetylenes by alkylidyne complexes (see below).

Structural and Spectroscopic Characterization

The first high-oxidation-state alkylidyne complex to have its structure determined[24] was W(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(Me$_2$PCH$_2$CH$_2$PMe$_2$), the high yield product of the reaction between W(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$ and Me$_2$PCH$_2$CH$_2$PMe$_2$.[2] It is a distorted square pyramid in which the tungsten–carbon bond lengths are 1.785 (8) Å (W≡C), 1.942 (9) Å (W=C), and 2.258 (9) Å (W–C), and the W–C$_\alpha$–C$_\beta$ bond angles are 175.3 (7)°, 150.4 (8)°, and 124.5 (7)°, respectively (Figure 1). The decreasing tungsten–carbon bond lengths and the increasing W–C$_\alpha$–C$_\beta$ angles nicely illustrate the structural difference between a neopentyl, a neopentylidene, and a neopentylidyne ligand. The two compounds of the type W(CR)(O-*t*-Bu)$_3$ that have been structurally characterized show metal–carbon triple bond lengths of 1.758 (5) Å (R = Ph)[25] and 1.759 (6) Å (R = Bu-*t*);[26] the latter contains two weakly bridging *tert*-butoxide ligands that complete a trigonal bipyramidal coordination geometry about each metal. There are a few other structures of alkylidyne complexes in which the length of the metal–carbon triple bond varies between about 1.75 Å and 1.81 Å in several different geometries and coordination numbers.[27] Tungsten–carbon triple bonds in these "high-oxidation-state" tungsten–carbon triple bonds tend to be somewhat shorter than those in the lower oxidation-state "carbyne" complexes of the type prepared by Fischer.[1]
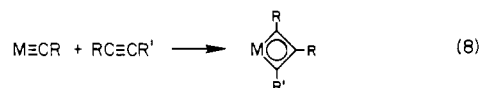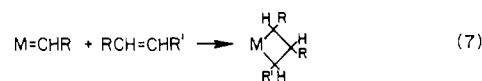
The ^{13}C NMR spectra of Mo(6+) and W(6+) alkylidyne complexes show a characteristic signal for the alkylidyne α-carbon atom 200–400 ppm downfield of Me$_4$Si. Coupling of C$_\alpha$ to tungsten ([183]W, S = $^1/_2$, 14%) is characteristically large (200–300 Hz). Usually the chemical shift and coupling constant of an alkylidyne ligand are both larger than those for an alkylidene ligand. For example, in W(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(PMe$_3$)$_2$ $J_{C≡W}$ = 208 Hz, $J_{C=W}$ = 120 Hz, and J_{C-W} = 80 Hz.[2] While it is usually true in similar complexes that the ^{13}C NMR signal for an alkylidyne ligand's α-carbon atom is found downfield of that for an al-

kylidene ligand's α-carbon atom, there is a significant range where either might be found. In fact in rhenium chemistry there are examples where the ^{13}C NMR signal for an alkylidene ligand's α-carbon atom is found further *downfield* of that for an alkylidyne ligand's α-carbon atom in a given compound.[28]

Metathetical Reactions between Alkylidyne Complexes and Acetylenes

The metathesis of acetylenes (eq 1) was first reported to be catalyzed heterogeneously at 200–450 °C in 1968.[29] The reaction was relatively slow, and oligomerization of the acetylene was a major side reaction. The first homogeneous system consisted of Mo(CO)$_6$ in the presence of excess phenol in refluxing toluene.[30] What are probably related homogeneous catalyst systems have been discovered recently.[31] No active species have been identified in any such system.

The acetylene metathesis reaction is not nearly as well-known as the olefin metathesis reaction, the mechanism of which was studied extensively during the early 1970's. All the evidence was consistent with the key step being addition of an olefin to an alkylidene complex to give an unstable metallacyclobutane ring (eq 7). It seemed plausible that the key step in acetylene

$$M=CHR + RCH=CHR' \longrightarrow M \overset{H,R}{\underset{R'H}{\diagup\!\!\!\diagdown}}\overset{H}{R} \qquad (7)$$

$$M≡CR + RC≡CR' \longrightarrow M \overset{R}{\underset{R'}{\diagdown\!\!\!\bigcirc\!\!\!\diagup}} R \qquad (8)$$

metathesis might be analogous (eq 8).[32] Since we had just shown that high oxidation-state tungsten alkylidene complexes would react with olefins to give new alkylidene complexes and products of olefin metathesis,[5a] we believed it possible that a compound such as W(C-*t*-Bu)(O-*t*-Bu)$_3$ would metathesize acetylenes. This turns out to be the case if the acetylene is disubstituted.[33] Although no metallacycles are observed, the expected new alkylidyne complexes can be observed *in situ*. The rate of metathesis is highest for dialkylacetylenes such as 3-heptyne (greater than 10 turnovers per s at 25 °C). When the two ends of the acetylene are rather different (electronically or sterically), the rate can decrease dramatically because degenerate metathesis steps become the most favored. We suspect that the early, empirically derived systems also involve M(6+) alkylidyne complexes as the catalytically active species. Low rates could be ascribed either to inherently low catalyst activity—acetylene metathesis is a rare and finely balanced reaction, as we shall see—or to a low concentration of active species.

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Figure 2. The structure of $W(C_3Et_3)(O-2,6-C_6H_3-i-Pr_2)_3$.[13]

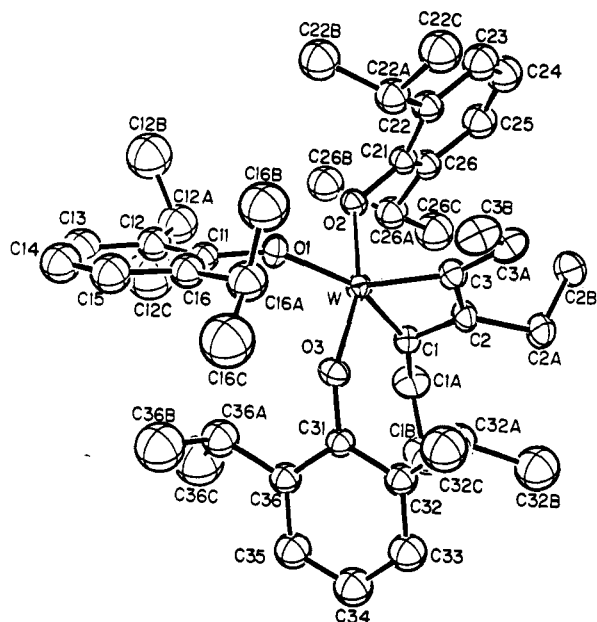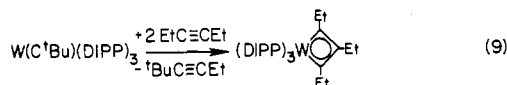**Figure 3.** A view of the WC_3 ring in $W(C_3Et_3)(O-2,6-C_6H_3-i-Pr_2)_3$.

It became possible to prepare a variety of alkylidyne complexes containing functionalities in the alkylidyne ligand through reactions analogous to that shown in eq 4. It was found that $W(CY)(O-t-Bu)_3$ complexes in which Y was electron-withdrawing (CN, CO_2Et) did not react with 3-heptyne at all, while complexes in which Y was σ- or π-donating (S-*t*-Bu or NMe₂) still metathesized 3-heptyne readily.[15] Other studies showed that the reactivity of $W(CR)X_3$ species varied markedly with the nature of X; species in which X = NMe_2[34a] or $2,6-(i-Pr)_2C_6H_3S$[34c] will not react with internal acetylenes. Therefore we conclude that the W≡C bond behaves as if it were polarized $W(\delta+)\equiv C(\delta-)$ and that its reaction with an acetylene can be viewed in terms of activation of that acetylene toward nucleophilic attack by coordination to the electrophilic tungsten center.

We presumed the intermediate in acetylene metathesis reactions to be a hitherto virtually unknown type of organometallic species,[35] a metallacyclobutadiene complex (eq 8). When OR is $O-2,6-C_6H_3-i-Pr_2$ (DIPP), $OCH(CF_3)_2$, or $OCMe(CF_3)_2$, metallacyclobutadiene complexes can be observed and isolated. In the example shown in eq 9 it is proposed that the first-formed α-

$$W(C^tBu)(DIPP)_3 \xrightarrow[-^tBuC\equiv CEt]{+2\,EtC\equiv CEt} (DIPP)_3W\underset{Et}{\overset{Et}{\bigcirc}}Et \quad (9)$$

tert-butyl-substituted tungstacyclobutadiene complex rapidly loses t-BuC≡CEt to give (unobservable) W-(CEt)(DIPP)₃, which then reacts rapidly with a second equivalent of 3-hexyne to give the observed tungstacyclobutadiene product. Steric crowding must cause

t-BuC≡CEt to be lost readily from the initial metallacyclobutadiene ring, since the triethyl-substituted metallacyclobutadiene ring only slowly loses 3-hexyne (see below).

An X-ray structural study of $W(C_3Et_3)(DIPP)_3$ (Figures 2 and 3) shows it to be a crowded, distorted trigonal bipyramidal molecule containing a strictly planar, almost symmetrical WC_3 ring.[13] (The molecule can be described equally well as a distorted square pyramid containing three basal phenoxide ligands.) The most interesting features of the ring system are the relatively short W-C_α bond lengths (roughly halfway between those characteristic of *double* (1.90–2.00 Å) and *triple* (1.75–1.80 Å) tungsten–carbon bonds) and a distance between the metal and C_β that is roughly the equivalent of a tungsten–carbon single bond length (2.15–2.20 Å). The short W···C_β distance has been ascribed to overlap of a d orbital with the totally symmetric MO of the C_3 fragment.[36] The slight distortion of the tungstacyclobutadiene ring (Figure 3) is just outside experimental error and suggests that 3-hexyne is in the process of leaving the ring. The structure of $W(C_3Et_3)[OCH-(CF_3)_2]_3$[14] overall is remarkably similar to that of W-$(C_3Et_3)(DIPP)_3$, except the WC_3 ring is virtually symmetric; i.e., there is no structural evidence that 3-hexyne is in the process of being lost.

$W(C_3Et_3)(DIPP)_3$,[13] $W(C_3Et_3)[OCH(CF_3)_2]_3$,[14] and $W(C_3Et_3)[OCMe(CF_3)_2]_3$[14] all will metathesize 3-heptyne at rates that qualitatively are (respectively) slow, fast, and very fast. By measuring the rate of incorporation of 3-hexyne-d_{10} into the WC_3Et_3 ring, it was found that $W(C_3Et_3)(DIPP)_3$ reacts with 3-hexyne-d_{10} at a rate that is independent of the concentration of 3-hexyne-d_{10}, as expected for rate-limiting loss of 3-hexyne from the WC_3Et_3 system to give putative W-(CEt)(DIPP)₃. However, $W(C_3Et_3)[OCH(CF_3)_2]_3$ reacts with 3-hexyne-d_{10} in a *bi*molecular fashion. We propose that the associative mechanism is favored in this case because the $OCH(CF_3)_2$ ligand is smaller and more electron-withdrawing than the DIPP ligand. It is too small to force the acetylene out of the metalacycle or

(34) (a) $W(CEt)(NMe_2)_3$ will not metathesize 3-heptyne[11] even though it has been shown that "$W(C-t-Bu)(N-i-Pr_2)_3$" will metathesize phenyltolylacetylene;[34b] we believe an impurity in the latter system is the actual catalyst. One possibility is $W(C-t-Bu)(N-i-Pr_2)_2Cl$. (b) Leigh, G. J.; Rahman, M. T.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1982**, 541. (c) Murdzek, J. S.; Blum, L.; Schrock, R. R., unpublished results.
(35) (a) A Rh[35b] and an Ir[35c] complex had been reported which formally contained a metallacyclobutadiene ring. These MC_3 rings are structurally significantly different from those found in acetylene metathesis systems. (b) Frisch, P. D.; Khare, G. P. *Inorg. Chem.* **1979**, *18*, 781. (c) Tuggle, R. M.; Weaver, D. L. *J. Am. Chem. Soc.* **1970**, *92*, 5523.
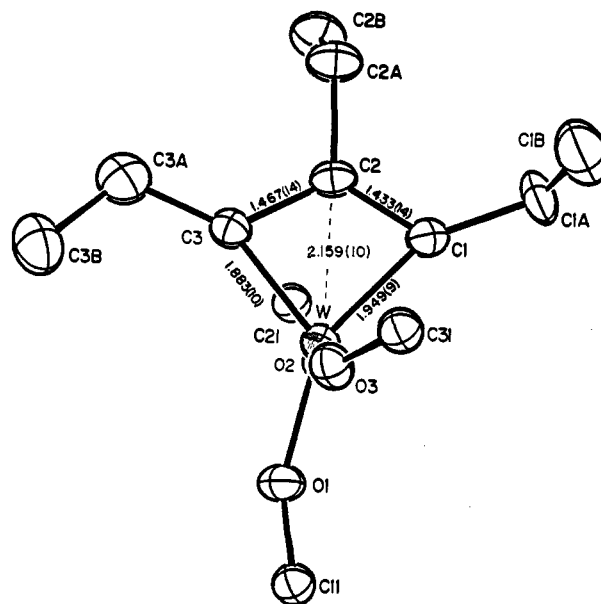
(36) Bursten, B. E. *J. Am. Chem. Soc.* **1983**, *105*, 121.

to prevent coordination of an additional equivalent of an acetylene. A planar metalabenzene complex (eq 10,

$$W(C_3Et_3)(OR)_3 + EtC\equiv CEt \rightleftarrows (RO)_3W(C_5Et_5) \quad (10)$$

OR = $OCH(CF_3)_2$) is a reasonable intermediate to propose for this "associative" mechanism. Interestingly, $W(C_3Et_3)[OCMe(CF_3)_2]_3$ again reacts with internal acetylenes in a *dissociative* fashion. This result must be ascribed solely to a significant increase in steric crowding within the coordination sphere of the complex compared to steric crowding in $W(C_3Et_3)[OCH(CF_3)_2]_3$. We conclude that more than one mechanism for acetylene metathesis is possible, although the one proposed initially by Katz,[32] and the one that we found predominates in the few systems we have studied so far, may be the most common. We also can conclude that steric factors could be at least as important as electronic factors in determining whether a species is active or not.

Since the first empirically derived homogeneous acetylene metathesis catalyst systems were based upon $Mo(CO)_6$,[30] we felt it important to show that complexes of the type $Mo(CR')(OR)_3$ also will metathesize acetylenes. Several were prepared, the most interesting series where R' = t-Bu and OR = O-t-Bu, $OCMe_2(CF_3)$, $OCMe(CF_3)_2$, or O-2,6-C_6H_3-i-Pr_2(DIPP).[10] Surprisingly, $Mo(C$-t-Bu)(O-t-Bu)$_3$ simply *does not react* with ordinary dialkylacetylenes. However, $Mo(C$-t-Bu)$-[OCMe_2(CF_3)]_3$ reacts slowly, and $Mo(C$-t-Bu)[OCMe-(CF_3)_2]_3$ and $Mo(C$-t-Bu)(DIPP)$_3$ react moderately fast; all three will metathesize 3-heptyne. However, in contrast to analogous tungsten systems, the only molybdacyclobutadiene complex that has been observed so far is $Mo(C_3Et_3)(DIPP)_3$, and it is stable only at low temperature; at 25 °C it dissociates completely into $Mo(CEt)(DIPP)_3$ and 3-hexyne. The molybdenum study showed that as far as acetylene metathesis is concerned, the major difference between Mo and W can be described as a lower affinity of Mo for the acetylene. Since molybdenum and tungsten are virtually the same size, we simplistically refer to Mo as being less electrophilic.

In contrast to internal acetylenes, metathesis of terminal acetylenes has not yet been observed. One possible reason is that the reaction stands a good chance of being degenerate, as in fact has been observed in the case of $Mo(C$-t-Bu)(O-t-Bu)$_3$;[10] it reacts with $RC\equiv CH$ to give t-$BuC\equiv CH$ and the new alkylidyne complex, $Mo(CR)(O$-t-Bu)$_3$. A second reason is that although disubstituted metallacyclobutadiene complexes form (a structure of one is known[37]), they tend to lose the β proton to give "deprotiocycles" (eq 11)[10,38] two structures

$$W(C_3{}^tBu_2H)(OR)_3 + 2\,py \xrightarrow{-ROH} \begin{array}{c} py \\ py \end{array}\!\!\!\!W \qquad (11)$$
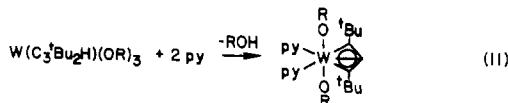
of which are known.[10,38b] A third possible reason is that methylidyne complexes are unlikely to be nearly as stable as substituted alkylidyne complexes.[15,23b] Finally, any ethyne that is generated is likely to be much more reactive (irreversibly) with organometallic intermediates
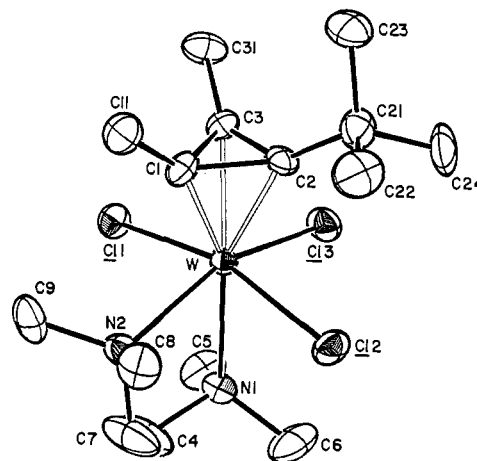
Figure 4. The structure of $W(C_3Me_2$-t-Bu)Cl$_3$-$(Me_2NCH_2CH_2NMe_2)$.[39]

than a disubstituted acetylene.

η^3-Cyclopropenyl and η^5-Cyclopentadienyl Complexes

A tautomeric form of a planar MC_3 ring is a tetrahedral arrangement (an η^3-cyclopropenyl complex). η^3-Cyclopropenyl complexes are known to form from planar metallacyclobutadiene complexes by addition of a nitrogenous base (eq 12, Figure 4).[39] This type of

$$W(C_3{}^tBuMe_2)Cl_3 + TMEDA \longrightarrow \qquad (12)$$
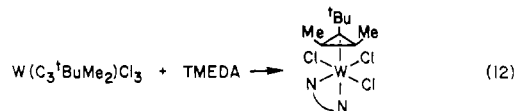
reaction contrasts with that between trialkoxide tungstacyclobutadiene complexes and (e.g.) pyridine where an acetylene is lost to give an alkylidyne complex.[14] A second example of a η^3-cyclopropenyl complex is that formed upon addition of an acetylene to a tris(carboxylate) tungsten alkylidyne complex.[40] In neither case is the resulting complex a catalyst for the metathesis of acetylenes. In each case if lithium *tert*-butoxide is added to the η^3-cyclopropenyl complex, alkylidyne complexes of the type $W(CR)(O$-t-Bu)$_3$ are formed in high yield. On the basis of these results we suspect that η^3-cyclopropenyl complexes may be energetically accessible under a variety of conditions, even when only planar metallacyclobutadiene rings are observable. The current hypothesis, however, is that only a planar MC_3 ring can lose an acetylene to give an alkylidyne complex, just as only a planar 1,3-M_2C_2 ring (equation 6) can break up into alkylidyne complexes.

If a dialkylacetylene is added to complexes of the type $W(C_3R_3)Cl_3$ then η^5-cyclopentadienyl complexes are formed.[39] η^3-Cyclopropenyl complexes could be intermediates, but we prefer the proposal that a "tungstabenzene" complex forms, possibly one that is closely related to that proposed as an intermediate in the associative acetylene metathesis mechanism (eq 10). Instead of losing an acetylene, however, this "tungstabenzene" complex collapses to form a C_5 ring. We do not expect formation of η^5-cyclopentadienyl complexes to be reversible.

(37) Churchill, M. R.; Ziller, J. W. *J. Organomet. Chem.* **1985**, *286*, 27.
(38) (a) Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1986**, *5*, 1411. (b) Churchill, M. R.; Ziller, J. W. *J. Organometal. Chem.* **1985**, *281*, 237.

(39) Schrock, R. R.; Pedersen, S. F.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1984**, *3*, 1574.
(40) Schrock, R. R.; Murdzek, J. S.; Freudenberger, J. H.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1986**, *5*, 25.

Wittig-like Reactions of Alkylidyne Complexes

Tantalum and niobium alkylidene complexes are known to react with the carbonyl function in a Wittig-like manner.[3a] Therefore, we felt that complexes that are active acetylene metathesis catalysts might react with nitriles as shown in eq 13. This is the case

$$M\equiv CR + R'C\equiv N \rightarrow M\equiv N + RC\equiv CR' \quad (13)$$

in some instances, although the reaction does not seem as general as that between alkylidyne complexes and acetylenes. So far it is known that $W(CEt)(O\text{-}t\text{-}Bu)_3$ reacts in 1 h at 25 °C with acetonitrile to give [W-$(N)(O\text{-}t\text{-}Bu)_3]_x$, while $W(C\text{-}t\text{-}Bu)(DIPP)_3$ (DIPP = O-2,6-C_6H_3-i-Pr_2) yields red $[W(N)(DIPP)_3]_x$ rapidly at 25 °C.[41] Yet other acetylene metathesis catalysts such as $W(CR)[OCMe(CF_3)_2]_3$ do not react readily at 25 °C with acetonitrile.[11] We assume for now that the intermediate in such reactions is a planar azametallacyclobutadiene complex in which the nitrogen atom is adjacent to the metal.

Similar reasoning suggested that some alkylidyne complexes might react with the carbonyl function as shown in eq 14. Although $W(CEt)(O\text{-}t\text{-}Bu)_3$ does not

$$M(CR)(OR')_3 + Me_2C{=}O \rightarrow$$
$$M(O)(RC{=}CMe_2)(OR')_3 \quad (14)$$

react readily with acetone at room temperature, $W(C\text{-}t\text{-}Bu)(DIPP)_3$ does react rapidly to give well-characterized, red, crystalline $W(O)(t\text{-}BuC{=}CMe_2)(DIPP)_3$ virtually quantitatively. Analogous reactions with benzaldehyde, formaldehyde, dimethylformamide, and ethyl formate give analogous oxo–vinyl complexes at variable rates, that with dimethylformamide being the slowest. Analogous products are obtained in reactions involving the tungstacyclobutadiene complex, W-$(C_3Et_3)(DIPP)_3$, although the reaction is significantly slower, as the metallacycle must first lose 3-hexyne. It seems reasonable to view the reaction as consisting first of coordination of the carbonyl oxygen to the electrophilic metal center followed by nucleophilic attack by the alkylidyne α carbon atom on the now strongly positively polarized carbonyl carbon atom. The oxa-tungstacyclobutadiene ring then rearranges as shown in eq 15. Since the coordination sphere is relatively
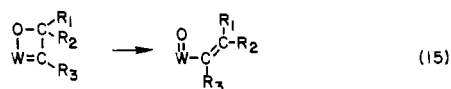
crowded, there is some stereoselectivity toward formation of the product in which the largest group (R_1 or R_2) is cis to R_3. Reactions related to that shown in eq 14 have been observed with isocyanates[42] and imines.[11]

Wittig-like reactions of alkylidyne complexes might eventually prove useful in organic synthesis if easier routes to alkylidyne complexes can be found.

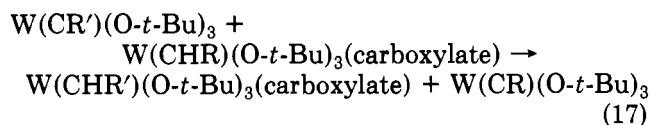## Protonation of Alkylidyne Complexes

Since alkylidyne complexes appear to be polarized $M(\delta+){\equiv}C(\delta-)$, and appear to be formed by sequential deprotonations of alkyl ligands (α-hydrogen abstraction reactions), it should be possible to protonate alkylidyne complexes. If the reaction can be controlled so that the

incipient alkylidene ligand is not protonated further to give an alkyl ligand, then it should be possible to prepare alkylidene complexes in this fashion. This route could be a useful complement to those that rely on α-abstraction in an alkyl complex.

In a recent study[43] we showed that $W(CR)(O\text{-}t\text{-}Bu)_3$ complexes can be protonated by hydrogen halides, phenols, or carboxylic acids to give neopentylidene complexes that are closely related to those discovered by Osborn[6] (eq 16). Analogous reactions employing
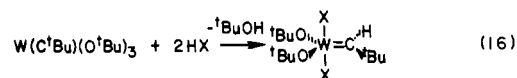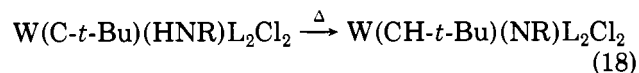

complexes in which the alkylidyne ligand contains β-protons are sometimes successful, although the only relatively stable class of compounds are of the type $W(CHR)(O\text{-}t\text{-}Bu)_3$(carboxylate). Interestingly, such species will react with $W(CR')(O\text{-}t\text{-}Bu)_3$ complexes as shown in eq 17, thus establishing what was before only suspected, that alkylidyne complexes can form by deprotonating alkylidene complexes, here even where

$$W(CR')(O\text{-}t\text{-}Bu)_3 +$$
$$W(CHR)(O\text{-}t\text{-}Bu)_3(\text{carboxylate}) \rightarrow$$
$$W(CHR')(O\text{-}t\text{-}Bu)_3(\text{carboxylate}) + W(CR)(O\text{-}t\text{-}Bu)_3 \quad (17)$$

suspected, that alkylidyne complexes can form by deprotonating alkylidene complexes, here even where β-protons are present in the alkylidene ligand.

In an early study an interesting proton transfer from an amido nitrogen atom to an alkylidyne carbon atom was discovered (eq 18).[27a] In $W(C\text{-}t\text{-}Bu)(HNR)L_2Cl_2$

$$W(C\text{-}t\text{-}Bu)(HNR)L_2Cl_2 \xrightarrow{\Delta} W(CH\text{-}t\text{-}Bu)(NR)L_2Cl_2 \quad (18)$$

$$L = PMe_3 \text{ or } PEt_3$$

the neopentylidyne and amido ligands presumably occupy cis positions in order to avoid competition between the two d orbitals used to form the triple bond and the d orbital that receives a pair of donated π electrons from the amido nitrogen ligand. The phosphine ligands are trans. It is suspected that the planar amido ligand lies in the C–W–N plane and that H_α points toward the neopentylidyne α-carbon atom, as found in the analogous $W(C\text{-}t\text{-}Bu)(HPPh)(PEt_3)_2Cl_2$ complex.[27a] The α-proton transfers in a first-order manner. The fact that NEt_3 is a catalyst for this reaction suggests that the proton on nitrogen may be partially or wholly removed by the amine and then readded to the neopentylidyne ligand's α-carbon atom. Similar reactions between $[W(C\text{-}t\text{-}Bu)Cl_4]^-$, water, base, and phosphine gave previously reported,[44] analogous $W(CH\text{-}t\text{-}Bu)$-$(O)L_2Cl_2$ complexes, presumably via intermediate W-$(C\text{-}t\text{-}Bu)(OH)L_2Cl_2$.

We believe that $W(CH\text{-}t\text{-}Bu)(NR)L_2Cl_2$ is the lower energy species in the reaction shown in eq 18 as a result of a strong pseudo triple bond formed between tungsten and the imido ligand, a situation that probably will depend heavily upon the electronic effect of R and that of the alkylidyne ligand substituent (here *tert*-butyl). (The W=NR bond is a pseudo triple bond since the electron pair on N is donated strongly to W to give a species in which the W–N–R angle approaches 180°.[8])

(41) Freudenberger, J. H.; Schrock, R. R. *Organometallics* 1986, 5, 398.

(42) Weiss, K.; Schubert, U.; Schrock, R. R. *Organometallics* 1986, 5, 397.

(43) Freudenberger, J. H.; Schrock, R. R. *Organometallics* 1985, 4, 1937.

(44) Wengrovius, J. H.; Schrock, R. R. *Organometallics* 1982, 1, 148.

It is intersting to note, however, that it may be difficult to lose a proton entirely from the coordination sphere of either complex in eq 18 (e.g., eq 19), as the four π

$$W(CH\text{-}t\text{-}Bu)(NR)L_2Cl_2 \xrightarrow{\hspace{1cm}}$$
$$W(C\text{-}t\text{-}Bu)(NR)L_2Cl + HCl \quad (19)$$

components of the $W{\equiv}C\text{-}t\text{-}Bu$ triple bond and those of the $W{\equiv}NR$ pseudo triple bond would then have to compete with each other for d orbitals of π symmetry.

Recently[45] a variation of the reaction shown in eq 18 has been employed to prepare a precursor to a wide variety of complexes of the type $W(CH\text{-}t\text{-}Bu)(NAr)X_2$ (eq 20; Ar = 2,6-diisopropylphenyl). That in which X

$$W(C\text{-}t\text{-}Bu)(dme)Cl_3 + (Me_3Si)NH(2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2) \rightarrow$$
$$W(C\text{-}t\text{-}Bu)(HN\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(dme)Cl_2 \quad (20)$$

is $OCMe(CF_3)_2$ is a relatively efficient catalyst for the metathesis of cis-2-pentene and the most successful so far for the metathesis of methyl oleate. If $Me_3SiCH{=}CH_2$ is added to $W(CH\text{-}t\text{-}Bu)(NAr)[OCMe(CF_3)_2]_2$, then a tungstacyclobutadiene complex can be isolated whose structure is a distorted trigonal bipyramid in which the bent WC_3 ring is found to occupy equatorial positions (cf. Figure 2). Interestingly, $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ does *not* react with ordinary olefins. Therefore the principles of olefin metathesis appear to parallel those of acetylene metathesis; five-coordinate trigonal bipyramidal metallacyclic intermediates seem to be

(45) Schaverien, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2771.

favorable, and more electron-withdrawing alkoxide ligands produce more active catalysts.

Comments and Conclusions

It is especially pleasing to see how the chemistry of molybdenum and tungsten alkylidyne complexes is developing in relation to other chemistry characteristic of the heavier, earlier transition metals, i.e., that of alkylidene complexes and complexes that contain a metal–metal triple bond. High-oxidation-state alkylidyne complexes, like alkylidene complexes, appear to be "natural products" in organometallic chemistry involving alkyl complexes in this part of the periodic table, even in circumstances that one might think would yield solely reduced species. We expect that much of what has been learned can be extended to rhenium(7+) chemistry, if suitable starting materials can be synthesized. This approach to high-oxidation-state organometallic chemistry is revealing new molecules, unique types of bonding of carbon-containing fragments to metals, and potentially useful stoichiometric reactions. An important future direction is the application of what we have learned toward the controlled design of metathesis catalysts with well-defined and predictable properties.

Electrophilic Metal Carbenes as Reaction Intermediates in Catalytic Reactions

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Catalytic methods for the decomposition of diazo compounds have been know for more than 80 years, and their uses for a variety of carbenoid transformations are well established.[1] The term "carbenoid" was first applied to these processes in 1966[2] to infer that the reacting species was neither a free carbene nor an activated diazo compound but, rather, a carbene bound to a transition metal, as originally suggested by Yates in 1952.[3] This model was adopted for catalytic cyclopropanation reactions with limited evidence, primarily based on asymmetric induction through the the use of chiral copper and cobalt catalysts,[4] that supported the actual participation of the metal during addition to olefins. The discovery of stable metal carbene complexes and demonstration of their compatibility for stereospecific olefin cyclopropanation[5] lent further support to transient metal carbene intermediates in catalytic processes. However, metal carbene involve-

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(3) Yates, P. *J. Am. Chem. Soc.* **1952**, *74*, 5376.
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