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Catalysis by Transition Metals: Metal-Carbon Double and Triple Bonds

Richard R. Schrock

Transition metal complexes have long been used to catalyze reactions of organic molecules (*1*). A relatively simple example is addition of molecular hydrogen to a carbon-carbon double bond in an alkene (olefin) to give an alkane with platinum metal used as the catalyst (*2*). This is a heterogeneous catalytic reaction since the catalyst (a solid) is in a different phase than the reactants (gas or solution). When the catalyst and reactants are in the same phase (usually in solution) the catalytic reaction is said to be homogeneous.

One of the most important and fundamental types of intermediates in a catalytic reaction involving organic molecules is one that contains a metal-carbon single bond, that is, a metal alkyl. A great many well-defined metal alkyl compounds have been isolated, and reactions that are steps in known homogeneous catalytic reactions have been studied in great detail. Yet there are still some reactions of metal alkyls that are not well understood. An important example is polymerization of ethylene (or propylene) by catalysts of the Ziegler-Natta type to give high molecular weight, crystalline polymers, a reaction that was discovered almost 30 years ago (*3*) and is believed to involve growth of an alkyl chain bound to a transition metal by "insertion" of the ethylene into the metal-alkyl (M–R) bond (Eq. 1).

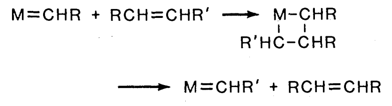
Summary. Several well-characterized transition metal catalysts contain a metal-carbon double bond or a metal-carbon triple bond. In other homogeneous (or heterogeneous) catalyst systems in which the metal is likely to be in a relatively high oxidation state, such as molybdenum(VI) or tungsten(VI), metal-carbon multiple bonds may play an important role. Some recent results suggest that even supposedly well understood reactions such as ethylene polymerization may actually involve catalysts that behave as if they contained a metal-carbon double bond instead of a metal-carbon single bond. The chemistry of metal-carbon double and triple bonds should eventually complement and perhaps overlap the known chemistry of complexes containing metal-oxygen double bonds or metal-nitrogen triple bonds, respectively; unique catalytic reactions involving carbon, nitrogen, and oxygen ligands multiply bonded to transition metals are therefore possible.

$$\mathrm{M{-}R} \xrightarrow{\mathrm{CH_2{=}CH_2}} \mathrm{M{-}CH_2{-}CH_2{-}R} \xrightarrow{\mathrm{(n-1)CH_2{=}CH_2}} \mathrm{M(CH_2CH_2)_nR} \qquad (1)$$

Fischer's discovery of the carbene complex (*4, 5*) $(CO)_5W{=}C(OCH_3)(C_6H_5)$ in 1964 demonstrated that transition metals can form double bonds to carbon (*6*). At about the same time a remarkable unprecedented catalytic reaction called the olefin metathesis reaction was discovered. In this reaction an ill-defined molybdenum, tungsten, or rhenium catalyst (homogeneous or heterogeneous) rapidly establishes the equilibrium shown in Eq. 2 (R and R′ are alkyl groups) from either direction (*7*). About 5 years later it was proposed that the

$$\mathrm{2RCH{=}CHR'} \rightleftharpoons \mathrm{RCH{=}CHR} + \mathrm{R'CH{=}CHR'} \qquad (2)$$

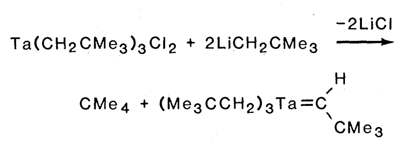
catalyst was a carbene complex and that the reaction consisted of random, reversible formation of all possible metallacyclobutane rings (for instance, Eq. 3). But the fact that complexes such as



$$\mathrm{M{=}CHR} + \mathrm{RCH{=}CHR'} \longrightarrow \begin{array}{c}\mathrm{M{-}CHR}\\ \mathrm{|}\quad\ \mathrm{|}\\ \mathrm{R'HC{-}CHR}\end{array} \longrightarrow \mathrm{M{=}CHR'} + \mathrm{RCH{=}CHR} \qquad (3)$$

$(CO)_5W{=}C(OCH_3)(C_6H_5)$ did not catalyze the metathesis of simple olefins suggested that the as yet uncharacterized metathesis catalysts were probably significantly different from those discovered by Fischer.

A tantalum alkylidene complex (*8*) discovered in 1974 (Eq. 4; Me = CH_3) was the first of many (*9*) that appeared to be fundamentally different from the carbene



$$\mathrm{Ta(CH_2CMe_3)_3Cl_2} + \mathrm{2LiCH_2CMe_3} \xrightarrow{-\mathrm{2LiCl}} \mathrm{CMe_4} + \mathrm{(Me_3CCH_2)_3Ta{=}C}\begin{array}{l}\mathrm{{}^{\diagup}H}\\ \mathrm{{}_{\diagdown}CMe_3}\end{array} \qquad (4)$$

complexes discovered by Fischer. If we view the neopentylidene ligand as a dianion (*8*), it is isoelectronic with an oxo (O^{2-}) ligand and the metal is formally in its highest oxidation state, Ta(V). These types of molecules will react with alkenes as shown in Eq. 3. A few years later related compounds containing a metal-carbon triple bond (alkylidyne complexes) were discovered. These alkylidyne complexes react with alkynes as shown in Eq. 5 and therefore catalyze the almost unknown alkyne metathesis

$$\mathrm{M{\equiv}CR'} + \mathrm{RC{\equiv}CR} \longrightarrow \mathrm{M{\equiv}CR} + \mathrm{RC{\equiv}CR'} \qquad (5)$$

reaction. In this article I will discuss the preparation and structure of high-oxidation-state alkylidene and alkylidyne complexes, how they metathesize alkenes and alkynes, and what other reactions involving multiple metal-carbon double or triple bonds have been discovered recently. As we will see, even relatively old catalytic reactions such as alkene insertion into a metal-alkyl bond

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The author is a professor in the Department of Chemistry, Massachusetts Institute of Technology, Cambridge 02139.

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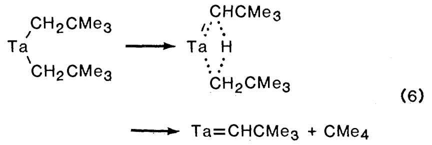
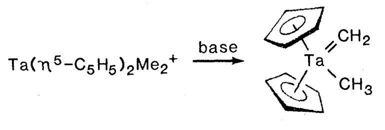
may actually involve alkylidene-like ligands.

All the transition metal complexes discussed here are well-defined compounds that catalyze reactions in solution. There is no good reason why the principles behind this chemistry should not extend to heterogeneous catalytic systems, since all the homogeneous catalytic reactions mentioned here are also catalyzed by heterogeneous catalysts.

Preparation and Structure of Alkylidene and Alkylidyne Complexes

The first tantalum alkylidene complex was prepared by the reaction shown in Eq. 4. The unique aspect of this reaction is what is called α-hydrogen atom abstraction. In its simplest form α-hydrogen atom abstraction consists of migration of a hydrogen atom from the α-carbon atom (the one bound directly to the metal) of one alkyl group to another (Eq. 6). The α-hydrogen atom abstraction reaction has also been observed in complexes containing other alkyl ligands (such as benzyl, CH_2Ph; Ph = C_6H_5) that do not have any hydrogen atoms on their β-carbon atom. An alkylidene ligand can also be formed by removing a proton from the α-carbon atom in a cationic alkyl complex by adding some external base (Eq. 7).

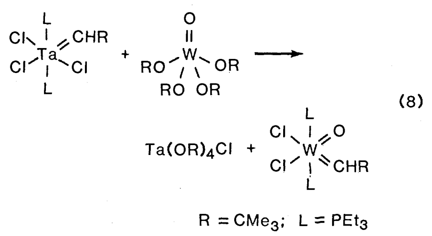




In $Ta(\eta^5\text{-}C_5H_5)_2(CH_3)(CH_2)$ the $Ta{=}CH_2$ bond length (2.03 angstroms) is approximately 10 percent less than the Ta–CH_3 bond length (2.25 Å), and the Ta=C–H angle is ~ 125°.

An unusual structural feature of many tantalum alkylidene complexes is an inordinately large metal–C_α–C_β angle. Instead of ~ 125° it can be as high as 175°. An example is shown in Fig. 1. The reason is believed to be that the metal draws electron density from the C_α–H_α bond toward it and, in effect, partially forms a metal-carbon bond of multiplicity greater than two. As a result, the α-hydrogen atom is placed in a nonclassical bridging position between C_α and Ta, the tantalum-carbon "double bond" is too short (~ 1.90 Å), and the C_α–H_α bond is much longer (1.13 Å) than it should be (1.09 Å). The reason why the methylene ligand in the $Ta(\eta^5\text{-}C_5H_5)_2(CH_3)(CH_2)$ complex above is not distorted is that the metal has already achieved its maximum possible, 18-electron configuration (*10*).

The reaction shown in Eq. 8 was an attempt to prepare $W(CHCMe_3)(OCMe_3)_4$ by exchanging an oxo ligand on tungsten with a neopentylidene ligand on tantalum (in Eq. 8, Et = CH_2CH_3).



The reaction took an entirely different course to give an oxo alkylidene complex (*11*). The most significant feature of tungsten oxo alkylidene complexes is that the neopentylidene ligand is not distorted significantly by the metal. For example, the W=C_α–C_β angle in $W(O)(CHCMe_3)(PEt_3)Cl_2$ is ~ 141° (*12*), the smallest of any observed so far (Fig. 2). It is believed that the electron-deficient metal can acquire electron density more easily from the two nonbonded π-electron pairs on the oxo ligand than it can from the bonding electron pair between C_α and H_α in the neopentylidene ligand. In fact, the oxo ligand is one of the best π-electron donors known (*13*). Recently, it was found that two alkoxide ligands can take over the role of the oxo ligand (*14*) in trigonal bipyramidal molecules of the type $W(CHCMe_3)(OR)_2Cl_2$.

Alkylidyne complexes are formed by an α-hydrogen atom abstraction reaction (Eq. 9) which is related to the reaction that produces alkylidene complexes (Eq. 6). An important example is shown in Eq. 10 (*15*). Typical tantalum-carbon or tungsten-carbon triple bond lengths are

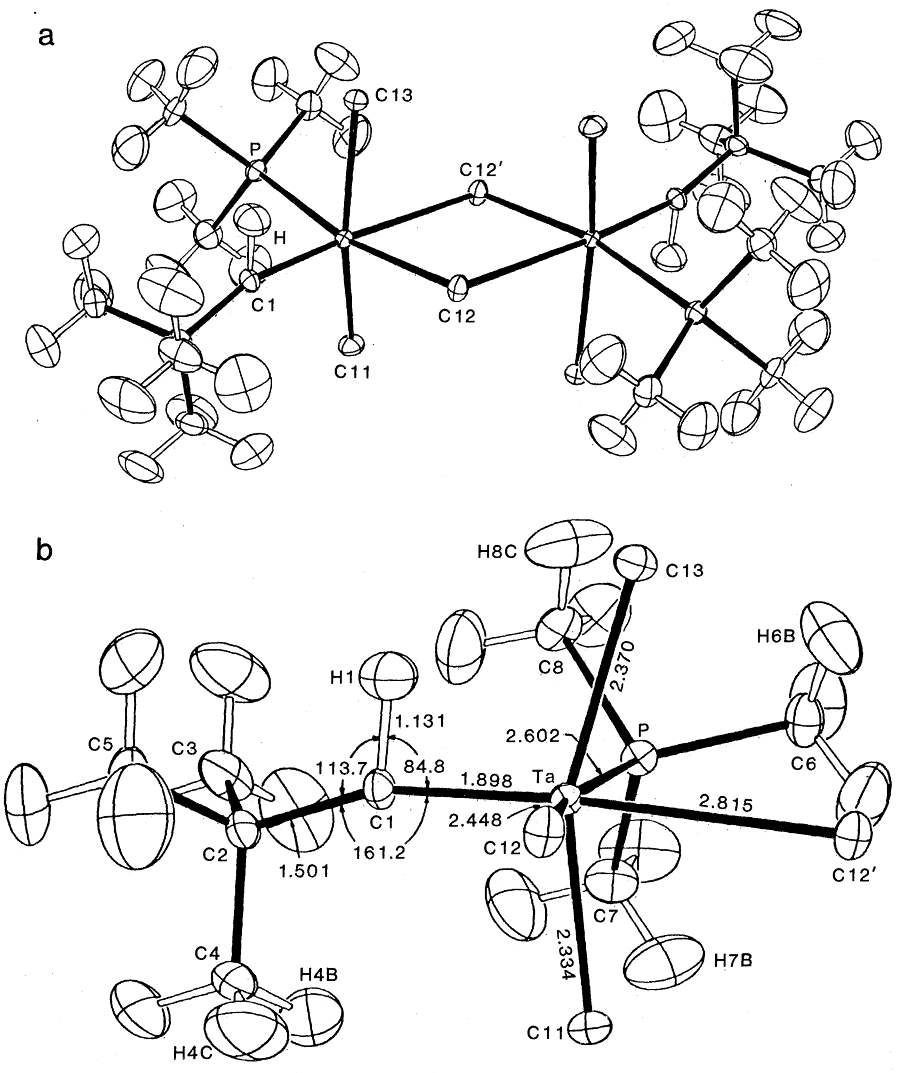


Fig. 1. (a) Computer-generated (ORTEP II) drawing of $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$; (b) detail of half the structure. Except for H1, all hydrogen atoms have been omitted for clarity.

~ 1.80 Å, ~ 10 percent shorter again than double bond lengths. The $M{\equiv}C_{\alpha}$–C_{β} angle is usually within a few degrees of 180°, as it should be by analogy with an alkyne.

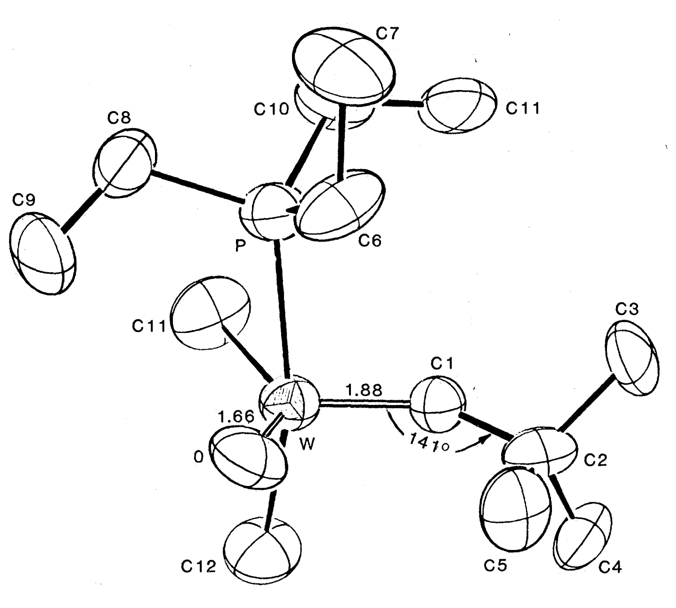
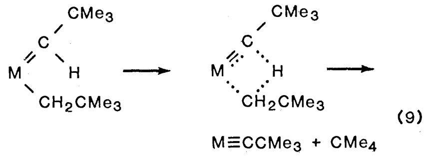


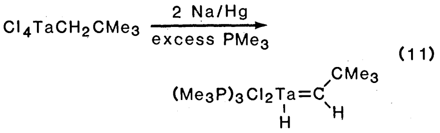
Fig. 2. ORTEP II drawing of W(O)(CHCMe$_3$)(PEt$_3$)Cl$_2$. All hydrogen atoms have been omitted for clarity.



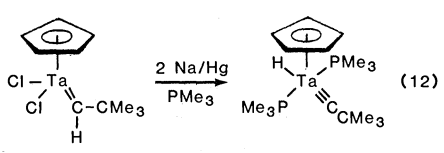
(9)

$$WCl_6 + 6LiCH_2CMe_3 \longrightarrow (Me_3CCH_2)_3W{\equiv}CCMe_3 \quad (10)$$

An important reaction that is related to α-hydrogen atom abstraction is what has been called α-hydride elimination (*16*). Here the α-hydrogen atom migrates from an α-carbon atom to the metal, rather than to the α-carbon atom of another alkyl ligand. This can occur only when the complex that results is isoelectronic with other alkylidene or alkylidyne complexes. Therefore, the initial alkyl or alkylidene complexes must first be reduced by two electrons. Examples are shown in Eqs. 11 and 12. Not surprisingly, α-hydride elimination is reversible; that is, Ta(CHCMe$_3$)(H)(PMe$_3$)$_3$Cl$_2$ is in equilibrium with Ta(CH$_2$CMe$_3$)(PMe$_3$)$_3$Cl$_2$.

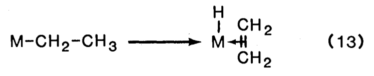


(11)



(12)

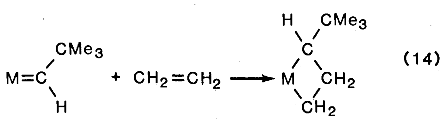
None of the alkyl complexes I have mentioned so far contain hydrogen atoms on a β-carbon atom. Formation of a carbon-carbon double bond by β-hydride elimination (Eq. 13) is believed to be faster than formation of a metal-carbon double bond by α-hydrogen atom abstraction or α-hydride elimination.



(13)

Reaction of Alkylidene Complexes with Alkenes

The niobium and tantalum alkylidene complexes whose reactions with alkenes have been studied most thoroughly are octahedral complexes, for example, Ta(CHCMe$_3$)Cl$_3$(PMe$_3$)$_2$ (*17*). Each member of the class of M(CHR)X$_3$L$_2$ complexes (M = Nb or Ta; R = CMe$_3$ or Ph; X = Cl or Br; L = an alkyl phosphine ligand) reacts with an alkene to give an intermediate metallacyclobutane complex (for instance, Eq. 14). Since β-hydrogen atoms are now present, a process related to that shown in Eq. 13 converts the metallacyclobutane ring into an olefin (Eq. 15). Another possible fate of the metallacyclobutane complex, and a step that is the heart of the alkene metathesis reaction, is re-formation of the other possible alkylidene complex, a methylene complex, by loss of *t*-butylethylene (Eq. 16). Evidently, rearrangement of the metallacyclobutane ring is faster than cleavage of the ring. If we are interested in catalytically metathesizing alkenes we might begin by attempting to slow down the rate of rearrangement of the metallacyclobutane ring.



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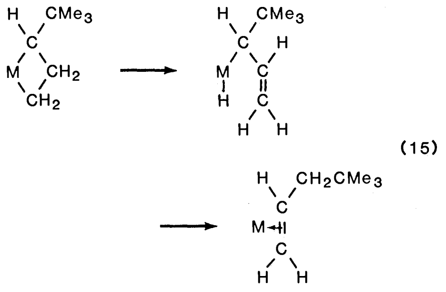
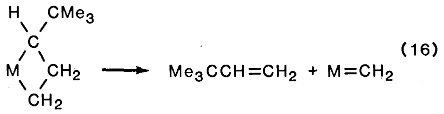


(15)



(16)

On the basis of some related work involving rearrangement of metallacyclopentane (MC$_4$) rings (*18*) we believed that replacing some chloride ligands with alkoxide ligands would yield that result. Indeed, Ta(CHCMe$_3$)(OCMe$_3$)$_2$Cl(PMe$_3$)$_2$ reacts with ethylene to give only cleavage products (Eq. 17). Ta(CH$_2$)(OCMe$_3$)$_2$Cl(PMe$_3$)$_2$ cannot be isolated because it decomposes readily (Eq. 18) by a process that is probably re-

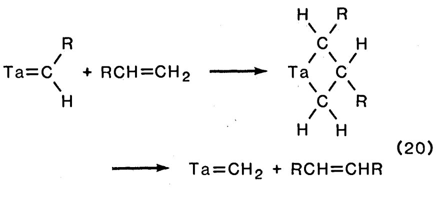
$$\begin{array}{l} Ta(CHCMe_3)(OCMe_3)_2ClL_2 \xrightarrow[]{\text{excess } C_2H_4} \\ \quad Me_3CCH{=}CH_2 + Ta(CH_2)(OCMe_3)_2ClL_2 \\ \quad (L = PMe_3) \end{array} \quad (17)$$

$$\begin{array}{l} 2Ta(CH_2)(OCMe_3)_2ClL_2 \longrightarrow \\ \quad Ta(CH_2{=}CH_2)(OCMe_3)_2ClL_2 \\ \quad + Ta(OCMe_3)_2ClL_2 \end{array} \quad (18)$$

lated to the bimolecular decomposition of Ta(η^5-C$_5$H$_5$)$_2$(CH$_2$)(CH$_3$) to give, among other things, Ta(η^5-C$_5$H$_5$)$_2$(CH$_2$=CH$_2$)(CH$_3$) (*19*). When a terminal alkene is added to Ta(CHCMe$_3$)(OCMe$_3$)$_2$ClL$_2$ the reaction proceeds largely as shown in Eq. 19. The Ta(CHR)

$$\begin{array}{l} Ta(CHCMe_3)(OCMe_3)_2ClL_2 \xrightarrow{RCH{=}CH_2} \\ \quad Me_3CCH{=}CH_2 + Ta(CHR)(OCMe_3)_2ClL_2 \end{array} \quad (19)$$

(OCMe$_3$)$_2$ClL$_2$ complexes do not decompose bimolecularly nearly as fast as Ta(CH$_2$)(OCMe$_3$)$_2$ClL$_2$ does. Therefore they live long enough to react with more RCH=CH$_2$, and they can do so either in a "productive" (Eq. 20) or "degenerate" (Eq. 21) sense. But the methylene complex (Eq. 20) must still be formed in

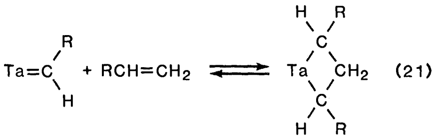


(20)

Table 1. Productive metathesis of acetylenes in toluene at 25°C. Initial metathesis products formed rapidly (> 90 percent yield). The rate was measured after initial metathesis products had formed but while more than 90 percent of initial acetylene reactant remained. Unless otherwise noted, the error in k is on the order of ±10 percent (three to seven measurements).

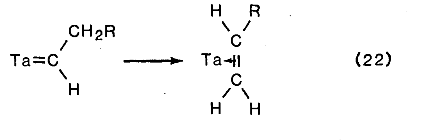
Catalyst	Acetylene	k (M^{-1} sec^{-1})
$\mathrm{W(CCMe_3)(OCMe_3)_3}$	$\mathrm{PhC{\equiv}CEt}$	8.1×10^{-3}
$\mathrm{W(CCMe_3)(OCMe_3)_3}$	p-$\mathrm{MeC_6H_4C{\equiv}CPh}$	8.9×10^{-2}
$\mathrm{W(CCMe_3)(OCMe_3)_3}$	$\mathrm{PrC{\equiv}CEt}$	~ 3

order to catalytically metathesize a terminal alkene to give ethylene and the internal alkene. Since the methylene complex decomposes, terminal alkenes cannot be metathesized catalytically.



(21)

One might expect internal alkenes (RCH=CHR′) to be metathesized catalytically starting with $\mathrm{Ta(CHCMe_3)(OCMe_3)_2ClL_2}$ since formation of $\mathrm{Ta(CH_2)(OCMe_3)_2ClL_2}$ is not possible. This is the case, but, unfortunately, the catalytic activity is not long-lived. A new problem has arisen. The alkylidene ligands in the two intermediate complexes, $\mathrm{Ta(CHR)(OCMe_3)_2ClL_2}$ and $\mathrm{Ta(CHR')(OCMe_3)_2ClL_2}$ (R may be $\mathrm{CH_3}$; R′ = $\mathrm{CH_2CH_3}$), contain β-hydrogen atoms. Although these alkylidene complexes do not decompose readily in a bimolecular reaction, the alkylidene ligands do rearrange readily to alkenes (Eq. 22). This β-hydride elimination reaction is related to those shown in Eqs. 13 and 15.



(22)

The study of niobium(V) and tantalum(V) alkylidene complexes showed that, although certain complexes have some of the necessary properties to metathesize alkenes, bimolecular decomposition of alkylidene complexes, rearrangement of metallacyclobutane rings, and rearrangement of alkylidene ligands are three ways in which an alkylidene ligand is removed from the catalytic cycle and the potential catalytic alkene metathesis reaction thereby prevented. In retrospect, it is not surprising that tantalum and niobium alkylidene complexes do not metathesize alkenes well; niobium and tantalum do not form good metathesis catalysts in the classical "black-box" catalyst systems (*7*). Conversely, since tungsten is one of the three classical catalysts, it was gratifying to find that isolated tungsten(VI) alkylidene complexes do metathesize alkenes.

$\mathrm{W(O)(CHCMe_3)L_2Cl_2}$ reacts with terminal alkenes in the presence of a trace of a Lewis acid such as $\mathrm{AlCl_3}$ (*20*) to yield a mixture of the two possible alkylidene complexes that result from cleavage of the two possible initial metallacyclobutane rings (for instance, Eq. 23).

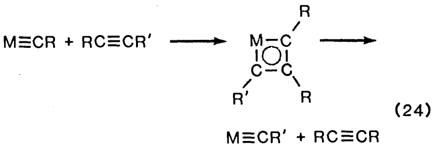
$$\mathrm{W(O)(CHCMe_3)L_2Cl_2} \xrightarrow{\mathrm{CH_2{=}CHMe}} \mathrm{W(O)(CHMe)L_2Cl_3 + W(O)(CH_2)L_2Cl_3} \quad (23)$$

Both the ethylidene complex and the methylene complex [the only isolable "high-oxidation-state" methylene complex besides $\mathrm{Ta(\eta^5{-}C_5H_5)_2(CH_2)(CH_3)}$] can be isolated. Therefore, the oxo alkylidene complex will slowly catalytically metathesize both internal and terminal alkenes. Complexes of the type $\mathrm{W(CHCMe_3)(OR)_2Br_2}$ will also metathesize olefins, especially rapidly in the presence of aluminum halides (*14*). In each case it seems likely that the π-electron donor ligands (oxo or alkoxide, respectively) retard formal reduction of W(VI) to W(IV)—that is, they slow down the rate of rearrangement of intermediate tungstenacyclobutane rings (Eq. 15) and probably also slow down the rate of rearrangement of intermediate alkylidene complexes in which β-hydrogen atoms are present in the alkylidene ligand (as in Eq. 22). At the same time the rate of cleavage of intermediate tungstenacyclobutane rings to give an alkene and an alkylidene complex may increase markedly. Although aluminum halides are not required as cocatalysts (*21*), they increase the rate of alkene metathesis enormously, possibly by forming cationic alkylidene complexes. For example, addition of one or two equivalents of $\mathrm{AlCl_3}$ to $\mathrm{W(O)(CHCMe_3)(PEt_3)_2Cl_2}$ in polar, noncoordinating solvents such as dichloromethane or chlorobenzene yields $\mathrm{[W(O)(CHCMe_3)L_2Cl]^+AlCl_4^-}$ and $\mathrm{[W(O)(CHCMe_3)L_2]^{2+}(AlCl_4^-)_2}$ (L = $\mathrm{PEt_3}$), some of the longest lived metathesis catalysts we have prepared.

It is now fairly certain that tungsten(VI) alkylidene complexes must be present in the classical black-box alkene metathesis systems. One of the remaining important questions concerning the classical alkene metathesis catalyst is how the initial alkylidene ligand forms. Although it now seems likely that there are many routes to alkylidene complexes, some form of α-hydrogen atom abstraction is almost certainly an important step in many, if not most, cases.

Reaction of Tungsten Alkylidyne Complexes with Alkynes

If W(VI) alkylidene complexes will metathesize alkenes, will W(VI) alkylidyne complexes react with alkynes to give new alkylidyne complexes (Eq. 24) and thereby catalyze the metathesis of alkynes (Eq. 25)? The only known homogeneous alkyne metathesis catalyst is inefficient and its composition is unknown (*22*). Alkylidyne complexes such as $\mathrm{(CO)_5BrW{\equiv}CPh}$, one of numerous species prepared by Fischer over the last decade (*23*), do not catalyze the alkyne metathesis reaction. We should now not be surprised by that fact, since they contain W(IV), the "wrong" oxidation state.



(24)

$$2\mathrm{R'C{\equiv}CR} \rightleftharpoons \mathrm{R'C{\equiv}CR' + RC{\equiv}CR} \quad (25)$$

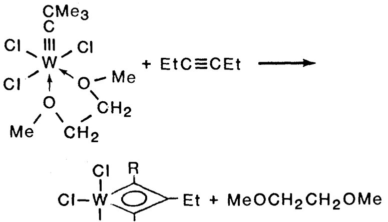
The first known tungsten(VI) alkylidyne complex (*15*), $\mathrm{(Me_3CCH_2)_3W{\equiv}CCMe_3}$, serves as a starting material for preparing blue $\mathrm{[NEt_4][Cl_4W{\equiv}CCMe_3]}$ (Eq. 26), and from it white $\mathrm{(Me_3CO)_3W{\equiv}CCMe_3}$. The $\mathrm{(Me_3CO)_3W{\equiv}CCMe_3}$ reacts rapidly with diphenyl acetylene as shown in Eq. 27 to give orange-red, sublimable $\mathrm{(Me_3CO)_3W{\equiv}CPh}$. Therefore, unsymmetrical alkynes such as $\mathrm{EtC{\equiv}CPh}$ and $\mathrm{PrC{\equiv}CPh}$ (where Pr = $\mathrm{CH_2CH_2CH_3}$) are catalytically metathesized by $\mathrm{(Me_3CO)_3W{\equiv}CCMe_3}$ (*24*). Some estimates of the initial rate of productive metathesis of several acetylenes are shown in Table 1. The most impressive is the metathesis of 3-heptyne. In neat 3-heptyne at 25°C it is estimated that on the order of one to ten

$$\mathrm{(Me_3CCH_2)_3W{\equiv}CCMe_3} \xrightarrow[\mathrm{NEt_4Cl}]{\mathrm{3HCl}} \mathrm{[NEt_4][Cl_4W{\equiv}CCMe_3]} \xrightarrow{\mathrm{3LiOCMe_3}} \mathrm{(Me_3CO)_3W{\equiv}CCMe_3} \quad (26)$$

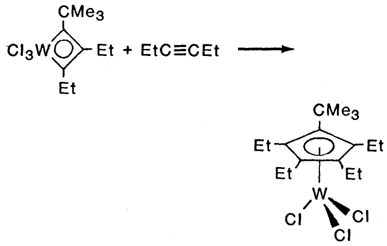
$$\mathrm{(Me_3CO)_3W{\equiv}CCMe_3 + PhC{\equiv}CPh} \longrightarrow \mathrm{(Me_3CO)_3W{\equiv}CPh + Me_3CC{\equiv}CPh} \quad (27)$$

metathesis steps per second are carried out by each molecule of catalyst. Some of the most active homogeneous catalysts known have turnover numbers of ~ 100 per second.

We found that metathesis of alkynes is the exception rather than the rule (*25*). When alkoxide ligands are not present a tungstenacyclobutadiene complex is formed which is relatively stable toward cleavage to reform an alkylidyne complex (Eq. 28, for example). Furthermore, it readily reacts with a second equivalent of alkyne to give a cyclopentadienyl complex (Eq. 29, for example). The metal is thereby reduced from tungsten(VI) to tungsten(IV). Interestingly, alkyne metathesis activity in the system involving $(Me_3CO)_3W\equiv CR$ catalysts eventually does cease (in days), and when it does, catalytically inactive cyclopentadienyl complexes can be isolated. We can conclude that alkoxide ligands slow down the rate of reduction of the metal [formation of W(IV) cyclopentadienyl complexes] and probably also enhance the rate of cleavage of the tungstenacyclobutadiene ring to give $(Me_3CO)_3W\equiv CR$ complexes. This role for *t*-butoxide ligands is analogous to their role (and that of the oxo ligand) in alkene metathesis, as discussed in the previous section.



(28)



(29)

Metathesis-Like Reactions of Other Triple Bonds

In thinking about the possibility of metathesis-like reactions of other $W\equiv X$ bonds, we noted that we had never observed $(Me_3CO)_3W\equiv CR$ to decompose to give $RC\equiv CR$ and $(Me_3CO)_3W\equiv W(OCMe_3)_3$, one of many dimeric compounds of molybdenum, tungsten, or rhenium that contain triple (or quadruple) bonds (*26*). We found this surprising for two reasons: metal-metal triple and quadruple bonds are thought to be extremely strong (and formation of them therefore thermodynamically quite favorable), and bimolecular decomposition of alkylidene complexes to give olefins is probably a major decomposition pathway in all homogeneous alkene metathesis reactions. Therefore, we attempted to add alkynes to $(Me_3CO)_3W\equiv W(OCMe_3)_3$ (*27*). This reaction was successful (Eq. 30). We were surprised, since compounds containing metal-metal triple bonds, including their reactions with alkynes, have been the subject of a good deal of research in the last decade (*26*). We soon found that of the several common compounds containing a metal-metal triple bond [including $(Me_3CO)_3Mo\equiv Mo(OCMe_3)_3$] none reacted with alkynes the way $(Me_3CO)_3W\equiv W(OCMe_3)_3$ does. Therefore it appears once again that the alkoxide ligand (or, more specifically, perhaps the *t*-butoxide ligand) is a rather special ligand. It is possible also that at least in this reaction tungsten is a rather special metal.

$$(Me_3CO)_3W\equiv W(OCMe_3)_3 + EtC\equiv CEt \xrightarrow[\text{fast}]{25^\circ C} 2(Me_3CO)_3W\equiv CEt \qquad (30)$$

The observations above prompted two questions. First, do organonitriles, in which the carbon-nitrogen bond dissociation energy is approximately 215 kilocalories per mole (compared to a $C\equiv C$ bond energy of ~ 200 kcal/mole in alkynes) also react with $W_2(OCMe_3)_6$? They do, as shown in Eq. 31. The nitrido ligand is isoelectronic with the alkylidyne ligand. Therefore it is not surprising to find that nitrido complexes analogous to alkylidyne complexes can be formed. Interestingly, nitrido complexes also will form (slowly) by the reaction shown in Eq. 32. Hence it appears that tungsten prefers to bond to the more electronegative atom (N). This finding is similar to the observation that a tantalum alkylidene complex can be converted into an isoelectronic imido complex, and the imido complex into an oxo complex (*28*), as shown in Eq. 33.

$$(Me_3CO)_3W\equiv W(OCMe_3)_3 + CH_3CN \xrightarrow[\text{fast}]{25^\circ C} (Me_3CO)_3W\equiv CCH_3 + (Me_3CO)_3W\equiv N \qquad (31)$$

$$(Me_3CO)_3W\equiv CR + RC\equiv N \longrightarrow (Me_3CO)_3W\equiv N + RC\equiv CR \qquad (32)$$

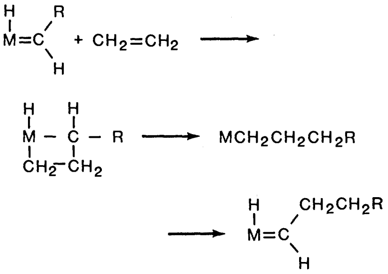
$$Ta=CHCMe_3 \xrightarrow[-PhCH=CHCMe_3]{+PhN=CHPh} Ta=NPh \xrightarrow[-Me_2C=NPh]{+Me\overset{O}{\overset{\|}{C}}Me} Ta=O \qquad (33)$$

The second question is whether molecular nitrogen, whose $N\equiv N$ bond strength is ~ 225 kcal/mole, reacts with $W_2(OCMe_3)_6$. At up to 100 atmospheres and 80°C it does not. Molecular nitrogen, unlike alkynes or nitriles, coordinates most strongly to relatively electron-rich metals in lower oxidation states (*29*), that is, it is a poor nucleophile. Therefore, the reaction of N_2 with $W_2(OCMe_3)_6$, like many reactions of N_2, probably failed for kinetic rather than thermodynamic reasons.

Ethylene Polymerization

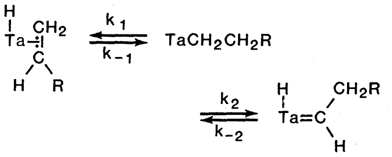
I mentioned earlier in this article that tantalum neopentylidene hydride complexes can be prepared by reducing Ta(V) neopentyl complexes by two electrons. An example is shown in Eq. 11. Since a hydride ligand is rarely unreactive in organometallic chemistry, an interesting question is how alkylidene hydride complexes react with alkenes.

Green $Ta(CHCMe_3)(H)L_3I_2$ ($L = PMe_3$) in toluene reacts slowly with excess ethylene to give a pale green polymer (*30*). Protonolysis of this pale green polymer with HCl yields a white polymer, which was shown by field desorption mass spectroscopy to consist of primarily alkenes, C_nH_{2n}, where $n = 50$ to 100 and is both even and odd. The mechanism by which the polymers are believed to form is shown in Eq. 34. The odd-carbon polymers result from growth of a polymer that contains the original C_5 fragment and termination of that growth by formation of an alkene. The even-carbon polymer is authentic polyethylene. The polymer mixture is pale green since it contains some "living" polymer, $Ta[CH(CH_2CH_2)_nCH_3](H)L_3I_2$, which is destroyed by HCl to give even-carbon alkanes, $CH_3(CH_2CH_2)_nCH_3$, which can be observed in small amounts in the mass spectrum.



(34)

One of the most interesting aspects of the mechanism shown in Eq. 34 is the last step, an α-elimination reaction to give the new alkylidene hydride complex. Such a proposal appears contrary to common sense, that is, "more favorable" β-hydride elimination to give an olefin hydride complex. But our results do not necessarily imply that β-elimination to give an alkene hydride complex is relatively slow. As shown in Eq. 35 it is possible that although K_2 is greater than K_1, k_1 is greater than k_2 ($K_1 = k_1/k_{-1}$, $K_2 = k_2/k_{-2}$)—that is, β-elimination


(35)

could still be faster—if the olefin hydride complex also is relatively stable toward displacement of $CH_2{=}CHR$ by ethylene under the reaction conditions employed here.

The alkylidene hydride catalyst closely resembles a Ziegler-Natta ethylene polymerization catalyst (*3*), except that the chain length with the tantalum catalyst is actually comparatively short. It has been proposed that alkylidene hydride complexes may be responsible for the stereospecific polymerization of propylene by Ziegler-Natta catalysts (*31*). However, an enormous amount of circumstantial evidence favors the accepted mechanism (*32*) of ethylene and propylene polymerization (Eq. 1), and growth of a polymer chain has been observed directly on a lutetium center (*33*). Although lutetium is, strictly speaking, not a transition metal, it resembles typical transition metals that are active in Ziegler-Natta systems.

Rather than attempt to choose between the two mechanisms, it should be pointed out that it is possible, on the basis of what I discussed earlier in this article, that an alkyl ligand in some alkyl complexes of titanium, vanadium, or chromium (typical Ziegler-Natta catalysts) may be severely distorted toward being an alkylidene hydride (Eq. 36). It would not be surprising if such an alkyl complex were to behave as an alkylidene hydride complex behaves. Such molecules will be difficult to observe since they may be some of the truly rapid alkene polymerization catalysts.


(36)

Conclusions

Metal-carbon double and triple bonds are natural and important features of the organometallic chemistry of metals in their highest possible oxidation state. Since molybdenum, tungsten, and rhenium form a large variety of oxo, imido, and nitrido complexes, high-oxidation-state alkylidene and alkylidyne complexes of these metals should be most numerous. High-oxidation-state complexes are active for methathesis-like catalytic reactions if the metal is surrounded with ligands that are compatible with the high oxidation state; rapid reduction of the metal and catalyst deactivation are thereby avoided. There seems to be some evidence that reactions of M≡M bonds, M≡C bonds, and M≡N bonds are related; therefore, "heteroatomic" methathesis-like reactions of triple bonds are a good possibility.

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