Olefin Metathesis. A Mechanistic Study of High-Valent Group 6 Catalysts

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Abstract: The results of an ab initio theoretical mechanistic study are used to suggest that oxo-alkylidene complexes are the active, chain-carrying metathesis catalysts for high-valent Mo, W, and Re complexes and that the oxygen ligand is intimately involved in the catalytic process. Furthermore, we suggest that oxo-alkylidene complexes are formed on supported molybdate and tungstate catalysts and that dioxo precursors can provide a convenient route to formation of well-defined surface catalysts for olefin metathesis and oxidation reactions. The spectator oxo group is suggested to play a central role in stabilizing the critical intermediate in these reactions and may be important in other reactions of metal oxides (e.g., MoO₄²⁻, OsO₄, RuO₄, supported transition-metal oxides).

One of the most intriguing and best studied catalytic reactions in organometallic chemistry is the olefin metathesis reaction.1 It is of potential synthetic utility2 and of industrial importance.3 Formally, the reaction involves a simultaneous cleavage of two olefin double bonds followed by the formation of the alternate double bonds

\[
\text{C}==\text{C} + \text{C}==\text{C} \rightarrow 2\text{C}==\text{C} \quad (A)
\]

where M is an appropriate metal complex. The currently accepted mechanism involves a metal–alkylidene (carbene) complex (that is, M==CR₂) as the active chain-carrying catalyst that reacts with an olefin to form a metallaacyclobutane intermediate (a of Scheme I) that decomposes to form the product olefin (b of Scheme I). This mechanism was proposed by Herrison and Chauvin4 and has been established through detailed (and ingenious) study of isotopic scrambling (Grubbs5 and Katz6) and by indirect evidence such as the synthesis of metallaacylobutenes (Schock)7 and metallaacyclobutanes (Green,8 Puddephatt,9 Whitesides,10 and Ibers11) and by the analysis of the character of polymeric products of cycloolefins (Casey12). Furthermore, Casey13 has synthesized low-valent metallocarbenoid complexes [W(CO)₅CPh₂] that stoichiometrically metathesize olefins. Potential chain-terminating side reactions are the unimolecular decomposition of the metallocycle (reductive elimination), forming a cyclopropane plus the reduced metal complex (c of Scheme I), and the bimolecular decomposition of the carbene complex (d of Scheme I).

As indicated above, there are two general classes of complexes used to mechanistically investigate olefin metathesis: (1) high-valent (generally d⁶) complexes of Mo, W, and Re (these are generally catalytic and often industrially important) and (2) low-valent complexes of Cr, Mo, and W (oxidation state zero); these have been significant in determining the general mechanism for the metathesis reaction but are generally not catalytic and have been of little industrial importance. There are significant differences between the high- and low-valent systems, particularly in the nature of the metal–CR₂ bond. Since only the high-valent class of metathesis complexes have been established to be truly catalytic, this paper will deal exclusively with this type.

Typical recipes for active homogeneous14 high-valent Mo, W, and Re metathesis catalysts involve a combination of various sources of metal [M(0) through M(VI)] with Lewis acids such as

\[
\text{Cl} \quad \text{Al} \quad \text{Cl} \quad \text{C}_2\text{H}_5
\]

under a variety of conditions. A result of this diversity is that a detailed understanding of theligand environment and even the oxidation state of the active catalyst (if there is just one active catalyst) is still lacking. Since the true catalyst is probably in small concentration,15 direct experimental studies on the catalytic system are quite difficult. Further, the industrially important catalysts consist of a metal oxide on an inorganic support, providing additional difficulties for physical studies. In fact, for supported catalysts it has been shown by Hall16 that the metathesis sites

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Scheme I

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(14) (a) It has been suggested that the catalysts thought to be homogeneous may actually be heterogeneous; see, for example, ref 7; (b) Y. Uchida, M. Hidai, and T. Tatsuki, Bull. Chem. Soc. Jpn., 45, 1158 (1972).
(15) Indications are that the active catalyst has a rapid bimolecular decomposition pathway, and hence a stable catalytic system must have the catalyst in small concentration. See, for example, ref 7.
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Figure 1. Energetics ($\Delta G_{300}$ in kcal/mol) for the reaction of C$_2$H$_4$ with the carbene and oxo-alkylidene of Cr.

Figure 2. Energetics ($\Delta G_{300}$ in kcal/mol) for the reaction of C$_2$H$_4$ with the carbene and oxo-alkylidene of Mo.

correspond to less than 1% of the Mo present at the surface. The theoretical calculations presented here$^{17}$ will concentrate on determining the detailed ligand environment of high-valent metathesis catalysts, developing an understanding of why particular ligands are desirable, and suggesting a mechanistic understanding of the initiation step for supported catalysts.

Theoretical Studies

Since WCl$_5$ can be used as the starting point for metathesis catalysts,$^{18,19}$ the simplest catalyst consistent with Scheme Ia is

Thus, as the first step in our studies, we examined the cycloaddition step postulated in the Herrison-Chauvin mechanism (1). As indicated in Figures 1a, 2a, and 3a, we find that process 1 is not favorable, with $\Delta G_{300} = +25$, +15, and +10 kcal mol$^{-1}$ for M = Cr, Mo, and W, respectively.$^{20}$ The bonding in the metallacycle is not strong enough to compensate for the loss of the $\pi$ bonding.

A. Bonding in Mono- and Dioxo Systems. In order to learn more about such metallacycle formations and possible initiation steps for supported catalysts, we considered some related processes, (2) and (3). Here we found that reaction 2 is quite

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$^{20}$ The calculations$^{21}$ were all-electron ab initio by using a valence double-$f$ basis on all centers except for the Cl. The Cl was described by using the SHC effective core potential$^{22}$ to replace the Ne core and a valence basis that was contracted to minimum basis for TiCl$_4$. Generalized valence bond (GVB) calculations were carried out, correlating all bonds to the metal except for metal–Cl bonds. These GVB orbitals were then used in a full configuration interaction (GVB-CI calculation for each molecule, leading to the energies used to obtain $\Delta E$ for the various processes.$^{23}$ Vibrational frequencies (estimated, experimental, or calculated) were used with $\Delta E$ to obtain $\Delta H$ at 0 K and were also used in conjunction with moments of inertia to calculate $C_I$ and thereby $\Delta H$ at 300 K and also to generate $\Delta S$, which were used to obtain the $\Delta G_{300}$.


$^{23}$ These calculations do not use f functions. Related calculations$^{24}$ on Cl,Ti=O and Cl,TiH$_2$ indicate that omission of these functions weakens the M=O bond by 5.2 kcal and the two M–H bonds by a total of 5.1 kcal. For Cl,Mo=O, the experimental value of the Mo–O bond is 106.5$^{25}$ about 4.5 kcal higher than the value obtained without f functions.

endothermic, \( \Delta G_{300} = +54 \) and +49 kcal mol\(^{-1}\) for Cr and Mo, respectively, whereas reaction 3 is quite exothermic, \( \Delta G_{300} = -14 \) and -21 kcal mol\(^{-1}\) for Cr and Mo, respectively. Further analysis of the wave functions shows that these differences arise from a fundamental difference in the metal-oxo bonds for the monooxo species 3 as compared to the dioxo species 5.

In the dioxo species each oxo group makes a \( \sigma \) bond and a \( \pi \) bond to the metal, leaving a nonbonding lone pair on the oxygen perpendicular to the bond axis (a normal nonbonding oxygen lone pair just as in a ketone). The orbitals for one of the metal-oxo bonds are shown in Figure 4. Thus, of the six valence electrons on the metal, two are involved in partially ionic \( \sigma \) bonds to the two Cl, two are involved in covalent \( \sigma \) bonds to the two oxygens, and two are involved in covalent \( \pi \) bonds to the two oxygens.

In the monooxo species, four of the six valence electrons on the metal are involved in partially ionic \( \sigma \) bonds to the four Cl and two are involved in bonds to the oxygen. However, in this case the stable configuration has both of these latter electrons in \( d\pi \) orbitals making two covalent \( \pi \) bonds with the oxygens (see Figure 5bc), while the lone pair on the oxygen is aligned with the bond axis (\( \sigma \)) pointing at the empty \( d\sigma \) orbital of the metal (see Figure 5a). The result is a triple bond involving two electrons from the metal and four from the oxygen, quite analogous to the bond in CO. The dioxo system cannot make this triple bond since use of both \( \pi \) orbitals for a triple bond to one oxo group would deprive the second oxygen of the \( \pi \) orbitals for its bonds (further, the \( \pi \) orbital needed to make a second \( \pi \) bond to one oxo group is destabilized by the lone-pair orbital on the second oxo group and by the metal-\( O \) \( \sigma \) bond). This situation for the dioxo complex is analogous to \( CO_2 \) where there is only a double bond to each oxygen, whereas the monooxo complex makes a triple bond just as in CO.

The energetic consequence of these effects is that the \( M=O \) bond of the monooxo species 3 is 82 kcal for Cr and 102 kcal for Mo, whereas the \( M=O \) bond in the dioxo species is 51 kcal for Cr and 79 kcal for Mo. Thus the triple bond is 31 kcal stronger than the double bond for Cr and 23 kcal stronger for Mo.

The larger strength (31 kcal for Cr, 23 kcal for Mo) in the metal-oxo bond of 3 vs. that of 5 explains part of the difference between reaction 2 and reaction 3 (total difference 68 kcal for Cr and 60 kcal for Mo); however, this accounts for only about half the difference and indeed, including only this effect, reaction 3 would still be quite endothermic. The critical effect responsible for making 3 exothermic has to do with a change in character between reaction 2 and reaction 3 (total difference 68 kcal for Cr and 79 kcal for Mo).

B. The Oxo-Alkylidene and Metallacycle Formation. The above studies suggested to us \(^{17}\) that an oxo-alkylidene

\[
\begin{align*}
\text{Cl}_2M\text{=O} & + H_2C\equiv CH_2 \\
\text{Cl}_2M(H\equiv CH_2) & = \text{Cl}_2M\text{=O} + H_2C\equiv CH_2
\end{align*}
\]

would favor formation of metallacycles

\[
\begin{align*}
\text{Cl}_2M\text{=O} & + H_2C\equiv CH_2 \\
\text{Cl}_2M(H\equiv CH_2) & = \text{Cl}_2M\text{=O} + H_2C\equiv CH_2
\end{align*}
\]

because of conversion of the double-bond spectator oxo group in 7 to a triple bond in 8. Indeed, as shown in Figures 1b, 2b, and 3b, the calculations \(^{17}\) lead to just this result, with \( \Delta G_{300} = -20 \), -24, and -18 kcal for \( M = \text{Cr}, \text{Mo}, \text{and W} \), respectively. On the other hand, the potential side reaction is much less favorable (\( \Delta G \) = +12, +2, +0 kcal for \( M = \text{Cr}, \text{Mo}, \text{and W} \), respectively) because here the spectator group is an alkylidene that provides only a double bond in both 7 and 9.

As a result of these studies, we have suggested \(^{17}\) that the oxo-alkylidene 7 is the active intermediate in the high-valent
metathesis catalysis by Mo and W. Further, the active metathesis catalyst for the Re system is suggested to be a trichloro-oxc-metathesis catalysis by Mo and W. Further, the active metathesis alkylidene complex.

C. Comments on Electronic Structure. In normal oxidation state formalism, the metal in 3 or 5 would be considered to be fully oxidized, M(VI), the oxo groups would be considered as O^2-, and the chlorides as Cl^- . Thus the metal is described as d^5 . Similarly, the alkylidene in 1 or 7 would be considered as 2-CR^2 and the metals are M(VI) or d^0 . In addition, the M-C and M-O bonds of the metallacycles in 2, 4, 6, and 8 would be considered as ionic (C or O ), so that these metals are also M(VI) or d^0 . Such a formalism has the advantage of being simple and unambiguous; however, we believe that it is oversimplified.

Our wave functions indicate that the M-Cl bonds for 1-8 are indeed quite ionic and suggest that the Cl can rather accurately be pictured as chloride ions, Cl^- . However, the remaining bonds in 1-8 are quite covalent and should be viewed as involving localized d orbitals on the metal paired into valence bonds with appropriate ligand orbitals. Since each d orbital is paired with a different ligand orbital, the four d electrons are in different orbitals. Thus the electron density distributions on the metals for 5-8 are all best described as high-spin d^4 configurations [M-(II)] rather than d^5 configurations [M(VI)]. However, since each of these d orbitals is involved in a bond pair with a ligand orbital, the spectroscopic transitions are expected to correspond essentially one-to-one with those that would have arisen from a d^6 configuration with the bond pairs each completely ionic toward the appropriate ligand.

Because of the usual oxidation state formalism, the CR^2 group of 1 or 7 is often referred to as 2-CR^2. We want to emphasize that this description is not a good approximation to the actual form of the wave functions. We find that the M=CR^2 bond is a very covalent double bond involving (i) a dσ orbital in the metal paired with a hybridized carbon orbital (sp^2σ) and (ii) a dπ orbital on the metal paired with a π orbital on the carbon. Thus the bond is an ordinary double bond (analogous to that in olefin) and the CR^2 part of the system is essentially identical with the ground state of a simple alkylidene or carbene (one electron in sp^2σ and one in πc combined to yield a triplet state). Consequently, we recommended that the M=CR^2 bond be described as a metal alkylidene double bond.

The bonding in the metal—CR^2 compounds discussed above (all high-valent metals) is quite different from that in the low-valent systems (CO)rWCPH2. In the latter case, the CPH2 has the character of a singlet carbene with an empty π orbital and a doubly occupied σ orbital (sp^2σ) pointing at the metal. Thus the bond here is basically a coordinate bond (not unlike that in CO) with possible dπ back-bonding (as also in CO). As a result, there is a very low rotational barrier here. In contrast, the high-valent systems lead to a σ bond and a π bond between metal and CR^2 and exhibit high rotational barriers.

We should note here that the above very covalent description of the M=O, M=CR^2, M=O, and M=C bonds is contingent upon having at least two ionic bonds to the metal (M=Cl here). The ionic character in these two bonds makes the metal positive and unwilling to lose further electrons to the O or C groups. Similar behavior is expected if the two Cl^- are replaced by two other electronegative ligands, e.g., F^-, OR, or even cyclopentadienyl anions. However, if the Cl ligands are replaced by alkyl groups, the M=O and M−O bonds are expected to become much more ionic, reducing or eliminating the triple character found in 3, 6, and 8.

Figure 5. The GVB orbitals involved in the oxo bond of ClMo==O.

Other ligands may also perform analogously to the spectator oxo group in stabilizing the metalloane, e.g., 7 to 8. For example, we find that an imino group NR can form a triple bond to the metal

\[ \text{M}==\text{NR} \]

with two π bonds and a donor-acceptor σ bond analogous to

\[ \text{M}==\text{O} \]

in 3, 6, or 8 or a double bond (π and σ) to the metal

\[ \text{M}==\text{N} \]

analogous to M==O in 5 and 7. However, the spectator imino stabilization appears to be approximately half as great as spectator oxo stabilization. This smaller stabilization could be an advantage since it might allow metathesis without the need for a Lewis base.
Table I. Energies for Bimolecular Decomposition Modes of Oxo-Alkylidenes (6), (7), and (8)

<table>
<thead>
<tr>
<th>M</th>
<th>olefin formation (6)</th>
<th>ketone formation (7)</th>
<th>dioxygen formation (8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>-44</td>
<td>-44</td>
<td>+15</td>
</tr>
<tr>
<td>Mo</td>
<td>-6</td>
<td>-1</td>
<td>+69</td>
</tr>
<tr>
<td>W</td>
<td>-2</td>
<td>+3</td>
<td>+73</td>
</tr>
</tbody>
</table>

Table II. Trends in Bond Strength (kcal/mol) within the Same Column

<table>
<thead>
<tr>
<th>molecule</th>
<th>bond strength</th>
<th>difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Cl)₂Ti-O</td>
<td>140b</td>
<td>-89</td>
</tr>
<tr>
<td>(Cl)₂(O)Cr-O</td>
<td>51b</td>
<td></td>
</tr>
<tr>
<td>(Cl)₂Ti-CH₃</td>
<td>78b</td>
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<td>(Cl)₂(O)Cr-CH₃</td>
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<td>-30</td>
</tr>
<tr>
<td>Ti-(O-t-Bu)ₜₜ</td>
<td>104a</td>
<td></td>
</tr>
<tr>
<td>V-(O-t-Bu)ₜₜ</td>
<td>90b</td>
<td>-32</td>
</tr>
<tr>
<td>Cr-(O-t-Bu)ₜₜ</td>
<td>72a</td>
<td></td>
</tr>
</tbody>
</table>

Table IV. GVB Orbital Overlaps for Metal-Alkylidene Bonds

<table>
<thead>
<tr>
<th>molecule</th>
<th>σ bond</th>
<th>π bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Cl)₂Ti-CH₃</td>
<td>0.74</td>
<td>0.41</td>
</tr>
<tr>
<td>(Cl)₂(O)Cr-CH₃</td>
<td>0.60</td>
<td>0.39</td>
</tr>
<tr>
<td>(Cl)₂(O)Mo-CH₃</td>
<td>0.74</td>
<td>0.53</td>
</tr>
</tbody>
</table>

(see sections E and F). Thus both metallacycle formation and decomposition might be approximately thermoneutral.

Other possible spectator ligands for metallacycle stabilization are alkoxy and sulfo ligands; however, we have not yet tested these cases.

D. Chain Termination Steps. In analyzing the possible role of oxo-alkylidene intermediates in reactions, we should consider the possible chain termination steps (6)-(8). As indicated in Table

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<th>difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Cl)₂Ti-O</td>
<td>51b</td>
<td>28</td>
</tr>
<tr>
<td>(Cl)₂(O)Mo-O</td>
<td>79b</td>
<td>23</td>
</tr>
<tr>
<td>(Cl)₂(O)Cr-CH₃</td>
<td>48b</td>
<td></td>
</tr>
<tr>
<td>(Cl)₂(O)Cr-CH₃</td>
<td>71b</td>
<td></td>
</tr>
<tr>
<td>Ti-(O-t-C₃H₇)ₜₜ</td>
<td>106a</td>
<td></td>
</tr>
<tr>
<td>V-(O-t-C₃H₇)ₜₜ</td>
<td>126a</td>
<td>20</td>
</tr>
<tr>
<td>Cr-(O-t-C₃H₇)ₜₜ</td>
<td>130a</td>
<td>4</td>
</tr>
</tbody>
</table>

a Average bond energy, from ref 36. b Theoretical calculations.

Figure 6. Effect of a Lewis base (LB) and π complexation of the olefin upon the energetics (ΔG° in kcal/mol) for the reaction of C₈H₄ with oxo-alkylidenes.

goes across a row of the periodic table and increase as one goes down a column. (This in turn results from general trends in sizes of d orbital.) Table IV shows the σ and π bond overlaps for three complexes, verifying this effect.

E. Solvation Effects. In order to relate our theoretical studies to the experimentally relevant systems, it is necessary to include possible differential effects due to solvation. Fortunately the postulated intermediates are uncharged and the solvents used for metathesis are aprotic solvents such as benzene, chlorobenzene, hexane, or CCl₄, for which estimates of solvation effects are most straightforward. Little in the way of quantitative data on such effects is yet available; however, some preliminary calculations provide a basis for estimates.

From studies on the interaction of Cl₂Ti-O with H₂C=CH₂, we find a complexation enthalpy of 18 kcal. This interaction depresses the reactant side effects of the cycloaddition reactions 1-5 by a corresponding amount. Similar calculations are underway for models of the Cr and Mo complexes where this effect is ~10-15 kcal.
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Figure 7. Effect of a Lewis acid (LA) and π complexation of the olefin upon the energetics (∆G<sub>298</sub> in kcal/mol) for the reaction of C<sub>2</sub>H<sub>4</sub> with oxo-alkylidenes.

Figure 8. The full catalytic cycle for metathesis by W oxo-alkylidene with Lewis base present (energies are ∆G<sub>298</sub> in kcal/mol).

In addition, metathesis solutions generally contain Lewis bases such as C<sub>1</sub>-, amines, or phosphines which we find to cause differential effects on the rate of metathesis; see, for example, ref 24. This is verified by a shortening of both the M—O and M—C double bonds by ~0.05 Å. The strengthening of the W—C and W—O bonds is apparent from the shortening of these bonds in going from Cl<sub>3</sub>W(O)(CH<sub>2</sub>)<sub>3</sub>(PR<sub>3</sub>) to Cl<sub>3</sub>W(O)(CH<sub>2</sub>)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub> due to increased steric interactions.

Figure 9. The full catalytic cycle for metathesis by W oxo-alkylidene with Lewis acid present (energies are ∆G<sub>298</sub> in kcal/mol).

Discussion of Experimental Results

A. The Role of Oxygen. Several experiments provide evidence confirming our findings that the stable, high-valent metathesis catalyst is an oxo-alkylidene. First, Basset et al. found that oxygen-containing compounds (O<sub>2</sub> or alcohols) accelerate the metathesis reaction and that chlorine is essential for metathesis. Second, Muettterties<sup>19</sup> and co-workers have shown that catalytic amounts of oxygen are essential for the generation of active stable metathesis catalysts for high-valent tungsten. As discussed in section A of Theoretical Studies, our studies suggest that two electronegative ligands on the metal are important in allowing the spectator oxo group to form the triple bond stabilizing the metallacycle intermediates. However, the chlorine used in our studies (and in the experiments) could probably be replaced by other electronegative ligands such as alkoxides if the carbon portion of the ligand could be made inert. The experiments, which suggested that halide is essential, utilized alkoxide ligands (OCH<sub>3</sub>), which definitely are not inert to 6 abstraction and other forms of catalyst degradation.

More recently, Osborn<sup>27</sup> and co-workers have generated Mo and W complexes that will metathesize olefins without standard cocatalysts. For example, reaction of


Figure 7 (Lewis bases) and Figure 7 (Lewis acids) for Cr, Mo, and W. The resulting catalytic cycles are illustrated in Figures 8 and 9. These studies suggest the importance of balance between the metal (W here), the other ligands around the metal (Cl here), the Lewis acid or base, and the solvent. Changes in these quantities could lead to a large ∆G for one or another of the steps and to a large decrease in the rate of reaction.

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Heterogeneous Catalysts with Lewis acid present (energies are ∆G<sub>298</sub> in kcal/mol).

which according to our studies should do metathesis.

The most significant experiment establishing the role of oxo-
alkyldienes in metathes is recently reported by Schrock and co-
workers. They synthesized high-valent complexes of Mo and W such as

\[
\begin{align*}
\text{Cl}_2\text{Mo} + \text{PR}_3 & \rightarrow \text{Cl}_2\text{MoPR}_3 \\
\text{Cl}_2\text{W} + \text{PR}_3 & \rightarrow \text{Cl}_2\text{WPR}_3
\end{align*}
\]

and showed that these complexes metathesize terminal and internal
oleins without cocatalysts. Recently, Muetterties and co-
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\end{align*}
\]

B. Supported Catalysts. Based on the theoretical studies, we
suggest that molybdyl and tungstenyl chlorides should be very
useful in generating supported catalysts that can be systematically
used to detect the role of oxo-alkylidene intermediate.

To verify the energetic similarity of dioxo and oxo-alkylidene
complexes, we suggest that reaction of ketones with Schrock’s
oxo-alkylidene complex should generate oleins and a dioxo
complex. If isolated, this dioxo complex should react with oleins
to regenerate an oxo-alkylidene complex. This reaction has
precedent in Tebbe’s stabilized titanium-alkylidene complex that
has been developed into a reasonable synthetic reagent for the
formation of oleins. The titanium system is not reversible due to
secondary reactions and the tremendous difference in bond
strengths between the oxo and alkylidene complexes for Ti com-
plexes (see Table I).

C. Role of Lewis Acids and Bases. Some comments on the role
of Lewis acids and bases is relevant here. As discussed in section
D of Theoretical Studies, we find that the dominant role of the
Lewis acid or base is to decrease the gap between the metallocyclic
intermediate and the alkylidene complex, thereby decreasing the
activation energy for the metallocyclic decomposition. Further,
the Lewis base increases the electron density at the metal center,
strengthening the M=C double bond and thereby decreasing the
importance of the bimolecular decomposition pathways [d of Scheme I and (4)], allowing metathesis and polymerization pathways
to dominate. With the surface loading high, stoichiometric C=C bond
cleavage should dominate.

A. Olefin Oxidation. As discussed in section A of Theoretical
Studies we find that high valent dioxo complexes (such as Cl_M-
(=O)_2) will react to form metalla-cycloolexetane intermediate (a
of Scheme II). This metalla-cycloolexetane intermediate can decompose in several ways, it can decompose to form the previously mentioned
oxo-alkylidene complex (b of Scheme II), an epoxide (c of Scheme II), or the precursor to a chlorohydrin (d of Scheme II). Each
of these products has been observed in alkene oxidation by chromyl chloride.28,34,47,52

\[
\begin{align*}
\text{C}_2\text{H}_4 + \text{Cl}_2\text{CrO}_2 & \rightarrow \text{C}_2\text{H}_4\text{Cl} + 2\text{Cl}_2\text{O} \\
\text{C}_2\text{H}_4 \text{Cl} + \text{H}_2\text{O} & \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{HCl}
\end{align*}
\]

For example, we suggest that the concentration-dependent rate
acceleration found for amines is due to an initial formation of a monoamine complex that is a better catalyst (as discussed above for phosphines), followed by the eventual
formation of the diame complex that should be catalytically inactive (this has been shown to be the true for phosphines by Schrock).30,35

The general accelerating effect of Lewis bases (amines) is well
documented for heterogeneous catalysts, again consistent with
our expectations. As experimental test of this dual role of
phosphines would be to study the rate of catalysis by the Schrock
compound II as a function of phosphine concentration for very
low concentrations. A complication here is the possible use of
Cl as a Lewis base in the absence of phosphine.

Implications

Our findings have implications for several related homogeneous
reactions such as olefin oxidation by Cl_2CrO_2, KMnO_4, and OsO_4
and for the initiation process of the supported metathesis reaction.
The homogeneous oxidation reactions will be discussed in subsection A and supported metathesis will be discussed in subsection B.

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\]

The energetics for the oxidation of ethylene by chromyl chloride are shown in Figure 10. These energetics confirm the proposal (Sharpless) that the metallacyclooxetane is a likely common precursor for all of the observed oxygen-containing products and rule out the direct addition (ene) reaction characteristic of oxidation by KMoO₄ and OsO₄ (e of Scheme II). It is noteworthy that Cl₂CrO₂ does not react to form significant diol product, whereas KMoO₄ and OsO₄ dominantly form diols without significant epoxide formation. This differential reactivity is easily understood in terms of stabilization due to spectator oxo groups. Starting from the respective metallacyclooxetane intermediates

\[ \text{6} \xrightarrow{\text{Cl}_2\text{CrO}_2} \ \text{7} \]

\[ \text{11} \xrightarrow{\text{KMoO}_4} \ \text{12} \]

\[ \text{13} \xrightarrow{\text{OsO}_4} \ \text{14} \]

the difference is apparent. That is, for Cl₂CrO₂ the shift involves reaction with a strong metal oxo triple bond, preventing (9), whereas for both KMoO₄ and OsO₄ the reaction is with an oxo double bond with a spectator oxo converting to an oxo triple bond thus enhancing (10) and (11) and driving the formation of species 12 and 14. (These latter two systems may go directly to 12 or 14 without passing through 11 or 13.)

As discussed in section C of Theoretical Studies, a major difference between Cr and Mo compounds is the general increase in bond strength of 15 kcal per bond. This effect manifests itself in strong relative disfavoring of any reductive elimination pathway for molybdenum. For Mo, the C=C bond cleavage pathway will dominate the reductive elimination of epoxides or chlorohydrins, and as will be discussed in section B it is likely through this pathway that MoO₃ and WO₃ are activated for metathesis on a polymer support. The energetics for these processes are summarized in Figure 11 for molybdenum.

B. Supported Catalysts. An understanding of the precise character of the surface sites responsible for heterogeneous metathesis is of both general mechanistic and industrial interest. A precise understanding of sites and mechanism could be useful in developing modified procedures allowing more economical activation of the surface with a possible increase in the concentration of active catalytic sites (currently ~1%). The two most likely surface sites on calcined molybdates or tungstenates are 15 and 16, where 15 is analogous to 5 and 16 is analogous to 3. Energetically these two surface sites are quite similar. Although these sites lead to very similar physical characteristics (e.g., the metal-oxygen stretching frequency is very similar), they should lead to enormous differences catalytically. Thus species 15 should react with olefins to form oxo-alkylidenes (see eq 12), whereas species 16 should be inert to attack at the oxo group since the metallacyclooxetane intermediate (eq 13)

\[ \text{M} = \text{W} \]

should be energetically inaccessible (\(\Delta G = 444 \text{ kcal} \)). Thus we are suggesting that if the surface is prepared in a manner that maximizes the concentration of species 15 an active metathesis catalyst will be generated simply by the addition of olefin, even at room temperature! In fact, we believe that this has been experimentally observed. Recently, Hall has found that there is a concentration dependence to the reaction pathway for olefins over supported WO₃. At low olefin concentrations, olefin isomerization is observed, while at high olefin concentration, metathesis occurs. Our interpretation of these results is as follows. If the surface sites are mainly species 16, activation to species 15 is required. Two possible procedures involve H₂ and a final abstraction process. The first possibility (eq 14) involves addition of H₂ across an M-O bridge bond, followed by olefin addition across the M-H bond, leading to an alkyl group (ethyl in this case) that can undergo an α abstraction to yield an oxo-carbene that
initiation processes, (13), (14), and (15), should depend upon 
reaction conditions; each may occur in some systems. Since these 
processes yield different products, it should be possible to design 
experiments to test these predictions and to establish which occur 
in various circumstances.

Summary

In summary, we suggest that oxo-alkylidene complexes are the 
stable metathesis catalysts for high-valent Mo, W, and Re com-
plexes and that the oxygen ligand is intimately involved in 
the catalytic process. Furthermore, we suggest that similar oxo-
alkylidene complexes can be formed on supported catalysts and 
that dioxo precursors may provide a convenient route to formation 
of well-defined surface catalysts for olefin metathesis and oxidation 
reactions. The spectator oxo group is suggested to play a central 
role in stabilizing the critical intermediate in these reactions and 
may be important in other reactions of metal oxides (MnO4-,
OsO4, RuO4, supported transition-metal oxides).

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Registry No. 3 (M = Cr), 57414-29-6; 13 (M = Mo), 13814-75-0; 5 
(M = Cr), 14977-61-8; 6 (M = Mo), 13637-68-8; 6 (M = Cr), 79899-
75-5; 6 (M = Mo), 79899-76-6; 6 (M = W), 79899-77-7; 7 (M = Cr), 
74670-62-5; 7 (M = Mo), 74670-63-6; 7 (M = W), 75213-82-0; 8 (M 
= Cr), 79899-78-8; 8 (M = Mo), 79899-79-9; 8 (M = W), 79899-80-2; 
(Cl2)Ti-O, 13780-39-7; (Cl2)Ti-CH3, 79899-81-3; Ti-(O-t-Bu)4, 3087-
39-6; V-(O-t-Bu)4, 10585-27-0; Cr-(O-t-Bu)4, 10585-25-8; Ti-(O-i-
C3H7)4, 546-68-9; Zr-(O-i-C3H7)4, 2171-98-4; Hf-(O-i-C3H7)4, 2171-
99-5; C5H10, 74-85-1.

Functionally Polymerized Surfactant Vesicles. Synthesis 
and Characterization

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Abstract: Bis[2-(10-undecenoyloxyacarbonyl)ethyl]dimethylammonium bromide (1), bis[2-(10-undecenoyloxyacarbonyl)ethyl][2-hydroxyethyl]methylammonium bromide (2), bis[2-(10-undecenoyloxyacarbonyl)ethyl]amidophosphoric acid (3), bis[2-(10-undecenoyloxyacarbonyl)ethyl]-2-sulfoethylamine (4), allylbis[2-(dodecanoyloxyacarbonyl)ethyl]methylammonium bromide (5), and dimethyl-α-hexadecyl[10-(p-vinylcarboxanilloido)decyl]ammonium bromide (6) have been synthesized. The predominantly single compartment bilayer vesicles formed from these surfactants could be polymerized either by exposure to ultraviolet irradiation or by the use of azoisobutyronitrile (AIBN) as an initiator. The presence of vesicles (unpolymerized and polymeric) has been demonstrated by electron micrography. 1H NMR, gel filtration, phase transition, turbidity changes, substrate entrapment, and permeability. Rates of light initiated polymerization of vesicles prepared from 6 have been found to be first order (k = 0.10 min-1 at 25 °C; [6] = 0.33 and 0.20 mg/1.0 mL of H2O) and independent of the concentration of 6. Under identical conditions, polymerization of 6 in methanol has occurred at a very much slower rate, and no polymerization has been observed at higher concentrations (2 mg of 6/2 mL of MeOH). Polymerized vesicles are considerably more stable and less permeable and have reduced rates of turbidity changes compared to their unpolymerized counterparts.

Completely synthetic surfactant vesicles are increasingly being utilized in photochemical solar energy conversion, reactivity control, and drug delivery. Recognizing the need for enhanced stability, Regen reported the synthesis of a polymerized surfactant vesicle from (CH3)2N+(C16H33)[(CH2)10OC=O]C-