$$\langle\mu\rangle^2\{[Fe(\eta^5\text{-}C_9Me_7)_2]^+\} = \langle g\rangle^2\{[Fe(\eta^5\text{-}C_9Me_7)_2]^+\}S(S+1) \quad (2)$$

The calculated moment $\mu_{eff} = 2.09$ is equivalent to the measured moment within the experimental error. For 4, the measured solution magnetic moment $\mu_{eff} = 1.59 \pm 0.2$ μ_B is again in very good agreement with the calculated value of $\mu_{eff} = 1.76$ using the **g** tensors obtained from the EPR spectra.

Solid-State Measurements. Faraday balance magnetic susceptibility measurements in the temperature range 2–300 K indicate that crystals of 2 obeys the Curie Weiss law $\chi^{-1} = C/(T - \Theta)$, with $\Theta = -2.85$ K and an effective moment of 2.09 μ_B. The small negative value of Θ is indicative of weak antiferromagnetic interactions between the radical cations.

Summary

In this paper we have described a convenient synthesis of permethylindene. Treatment of either $FeCl_2 \cdot 2THF$ or $Co(acac)_2$ with the lithium salt of permethylindene (LiInd*) yields the appropriate metal permethylindenyl complexes in good yields. These complexes have low first ionization energies and redox potentials as measured by gas-phase photoelectron spectroscopy and cyclic voltammetry. Both neutral complexes can be oxidized chemically to the monocation. Surprisingly, the Ind* ligand appears to be more electron donating than Cp* for the iron complexes whereas for the cobalt analogue the reverse is found.

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Registry No. 1, 131108-83-3; 2, 137259-36-0; 3, 137259-37-1; 4, 137259-39-3; Li(Ind*), 101960-85-4; tiglic acid, 80-59-1; tigloyl chloride, 35660-94-7; 1,2,3,4-tetramethylbenzene, 488-23-3; 2,3,4,5,6,7-hexamethylindan-1-one, 137175-20-3; heptamethylindene, 86901-30-6.

Theoretical Investigations of Olefin Metathesis Catalysts

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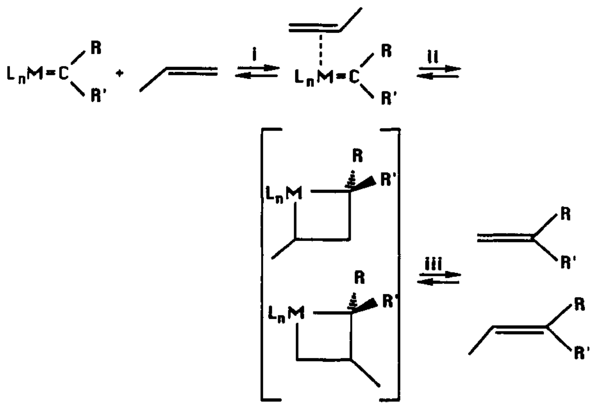
An ab initio analysis of the electronic structure of high-valent, transition-metal alkylidenes as models for olefin metathesis catalysts is presented. The catalyst models studied fall into three categories: "new" metathesis catalyst models—tetrahedral $M(OH)_2(XH)(CH_2)$ complexes; "old" metathesis catalyst models—tetrahedral $MCl_2(Y)(CH_2)$ complexes and alkylidene-substituted Mo metathesis catalysts, $Mo(OH)_2(NH)(=C(H)Z)$. The effect on the bonding caused by modification of either the metal, ligands, or alkylidene substituents is considered. For the new models the minimum energy structures result from maximum metal dπ–ligand pπ bonding and minimum competition among the ligands for the same dπ AO. Rotation about the MC axis increases this competition. The ability of the other multiply bonded ligand (XH) to accommodate the carbene ligand controls the height of the rotation barrier. For Mo and W complexes compression of the M–X–H angle is more facile than that for the Re alkylidene, resulting in a much higher barrier for the latter. A second important result is the greater $M^+{=}C^-$ bond polarity in W versus $Mo(OH)_2(NH)(CH_2)$. Greater polarization correlates with the observed greater metathesis activity for W versus Mo. The bonding in the old models resembles that in the new except for the much greater MC rotational barriers and the lower $M^+{=}C^-$ bond polarity in the former. If greater MC bond polarization does indeed lead to greater reactivity, then one would expect that the old metathesis catalysts are less active compared to their new analogues. Finally, the effects of substitution on the alkylidene ligand of a series of Mo alkylidenes was studied. Electron-withdrawing ligands cause the MC bond length to contract; electron donors have the opposite effect.

I. Introduction

Since the work of Herrison and Chauvin it has been generally accepted that carbene complexes play a pivotal role in transition-metal-catalyzed olefin metathesis, as illustrated in eq 1.[1] The known carbene complexes at that time were the so-called "Fischer-type" carbenes, i.e. a carbene ligand with π-donor substituents attached to a low-valent metal center such as $W(CO)_5(=CMe(OMe))$.[2,3] The carbene C in Fischer-type carbenes is electrophilic and will react with nucleophiles such as phosphines. In 1974 Schrock characterized the first nonheteroatom-stabilized carbene—$(Me_3CCH_2)_3Ta\{=C(H)CMe_3\}$.[4a] This and related compounds, called "Schrock-type" carbenes or alkylidene complexes, were shown to be active in olefin metathesis and polymerization and for the conversion of carbonyl compounds into olefins (the Wittig synthesis).[4,5]



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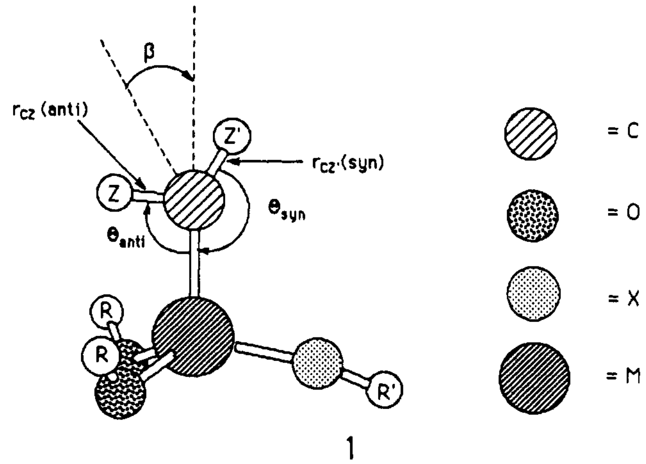
The chemistry of the Schrock-type carbenes is distinct from that of the Fischer-type, since the α-carbon behaves as a nucleophile, as in Wittig-type reactions.

Many of the early olefin metathesis catalysts were multicomponent systems involving a transition-metal salt (typically of Re, Mo, or W), Lewis acid additive (e.g., AlR_3 or SnR_4), and an oxygen source (O_2, an alcohol, etc.)[6-9] Recently, a series of well-characterized, four-coordinate, Lewis acid free, olefin metathesis catalysts have been prepared.[10] Examples of such compounds are W(O-*t*-Bu)$_2$(2,6-diisopropylphenylimide)(C(H)-*t*-Bu) and Re(C-(T-bu))(C(H)-*t*-Bu)(O-T-bu)$_2$.

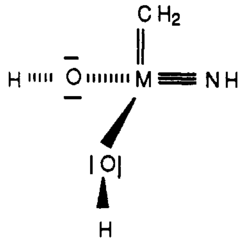
The general structure of these catalysts are depicted in **1**. The observed asymmetric nature of this structure[10] is indicated by the distinct CZ distances and ZCM angles (denoted syn and anti). The angle between the C=M axis and the bisector of the ZCZ′ angle is shown as β. These new catalysts possess interesting chemistry, both in their reactions with olefins and in solution by themselves.[10] For example, there is evidence that a dynamic process is taking place on the NMR time scale at room temperature for these pseudotetrahedral complexes. This process has been ascribed to rotation about the MC bond.[10a-c] Rotation about the MC bond has been observed in alkylidenes[11] and has been studied theoretically.[12]



1

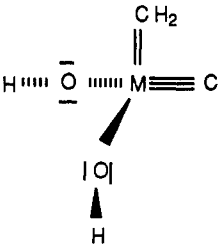
An analysis of ^{13}C NMR chemical shifts and C_α–H coupling constants (J_{CH}) for Mo and W alkylidenes indicates that there are two distinct species in solution.[10a-d] It has been proposed that they are isomers arising from rotation about the MC bond.[10a-c] NMR spectroscopy indicates that $\Delta H^\ddagger \approx 17$ kcal mol^{-1} for internal rotation in substituted Mo and W alkylidene complexes.[10a-c]

The purpose of the present paper is 2-fold. The first is to compare the electronic structures of two classes of metathesis catalyst models. The new metathesis catalysts (those with the general formula $M(OH)_2(XH)(CH_2)$ where M = Mo, W; X = N (**2a**)/M = Re; X = C (**2b**)) are related



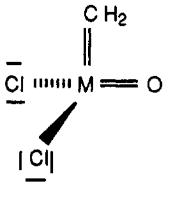
M = Mo, W

2a



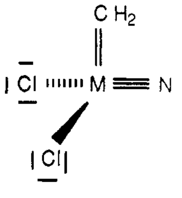
M = Re

2b



M = Mo, W

2c



M = Re

2d

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to the old catalysts (those with the general formula $MCl_2(Y)(CH_2)$ where M = Mo, W; Y = O (**2c**)/M = Re; Y = N (**2d**)). Both types of complex are tetrahedral with two univalent ligands and an ancillary multiply bonded ligand in addition to the carbene.

The second goal is to extend a previous study[13] of alkylidene complexes from methylidene complexes (L_nMCH_2) to more experimentally attainable substituted alkylidenes such as $Mo(OH)_2(NH)(C(H)Z)$ where Z is a non-hydrogen atom or functional group. Molybdenum alkylidene complexes were chosen as subjects for the substituted new metathesis catalyst models in the present study because experience[13] with similar complexes has shown that the calculated geometries concur exceptionally well with experimentally characterized complexes when a moderate basis set and effective core potential size is employed.

The analysis of the molecular and electronic structures of these compounds is qualitatively related to their observed catalytic activity.

II. Calculations

The calculations described herein were carried out at the ab initio level by using the GAMESS quantum chemistry program.[14] All geometry optimizations were carried out at the Hartree–Fock level. Three basis sets are employed in this study.

A. Basis A: The geometry optimizations of the larger, substituted Mo alkylidenes were calculated with a compact basis set utilizing the Hay–Wadt (HW) effective core potentials (ECPs) and valence basis for the transition metals.[15a] The 3-21G basis set was used for the heavy atoms of the main-group second row and hydrogen. The Si atom in the silyl-substituted Mo alkylidenes was described with the Stevens, Basch, and Krauss (SBK) ECP and valence basis[15b] augmented with a d polarization function ($\xi_d = 0.45$). This basis set will be referred to as basis A.

B. Basis B: The 3-21G(d) basis set for C, N, and O atoms and a 3-21G basis for the H atoms was employed in conjunction with the SBK ECPs and valence basis for the geometry optimization of the methylidene complexes.

C. Extended Basis: The extended basis includes SBK ECPs and valence bases for metal and all third-row, main-group elements. For H and second-row, main-group elements the 6-311G basis was employed. Heavy-atom basis sets were augmented with a d polarization function.[16a] The transition metals were augmented with a diffuse d polarization function.[16b]

The bond overlap population (BOP_{AB}) is defined in eq 2 for all atomic orbitals (AOs) X_u and X_v on atoms A and B, respectively. $\mathbf{P}_{uv}$ is the charge-bond order matrix; $\mathbf{S}_{uv}$ is the overlap matrix. The values of $\mathbf{P}_{uv}$ are given by eq 3. The quantities C_{ui}

$$\mathrm{BOP}_{AB} = 2\sum_{u}^{A}\sum_{v}^{B} 2\mathbf{P}_{uv}\mathbf{S}_{uv} \qquad (2)$$

and C_{vi} are the LCAO-MO coefficients of X_u and X_v, respectively, in the molecular orbital (MO) ϕ_i and n_i is the occupation number of ϕ_i.

$$\mathbf{P}_{uv} = \sum_{i} C_{ui}C_{vi}n_i \qquad (3)$$

Stationary points on the potential energy surfaces were located by using the method of Baker.[17a] The force constant matrix was calculated at each stationary point, and vibrational frequencies were determined, in order to characterize the structure as a minimum or transition state. The methods used to obtain intrinsic frequencies and force constants are described elsewhere.[17b] The Boys technique was used to obtain localization of MOs.[18] Electron correlation at the Moller–Plesset, second-order perturbation theory (MP2) level[19] was included to calculate the energy differences between stationary points. Core electrons were not correlated in the MP2 calculations.

Table I. Metal–Ligand π MOs for "New" Metathesis Catalyst Models[a]

orbital[b]	energy[c]	composition[d]
	Canonical MOs	
$Mo(OH)_2(NH)(CH_2)$		
MC π	−9.51	Mo 49; C_α 44; O 3 each; N 1
MN $\pi_\perp$	−11.31	Mo 10; C_α 0; O 13 each; N 62
MN $\pi_\parallel$	−11.60	Mo 25; C_α 4; O 4 each; N 64
$W(OH)_2(NH)(CH_2)$		
MC π	−9.26	W 45; C_α 50; O 2 each; N 1
MN $\pi_\perp$	−11.34	W 11; C_α 0; O 11 each; N 67
MN $\pi_\parallel$	−11.51	W 22; C_α 4; O 3 each; N 65
$Re(OH)_2(CH)(CH_2)$		
MC_α π	−8.88	Re 34; C_α 46; O 8 each; C_{sp} 4
MC_{sp} $\pi_\perp$	−10.88	Re 43; C_α 0; O 6 each; C_{sp} 45
MC_{sp} $\pi_\parallel$	−10.89	Re 50; C_α 4; O 2 each; C_{sp} 37
	Localized MOs[e]	
$Mo(OH)_2(NH)(CH_2)$		Mo 46; C 54
$W(OH)_2(NH)(CH_2)$		W 41; C 59
$Re(OH)_2(CH)(CH_2)$		Re 44; C 56

[a] The MO energies and compositions of the MOs that most closely correspond to the metal–ligand π-bonding MOs are given. These values were obtained by using the extended basis described in the Calculations. [b] This is the description of the MOs primary character. Being canonical, i.e. delocalized, MOs, they also possess contributions from other atoms. [c] The MO energies are quoted in eV. [d] The distribution of the MO, in percentage terms that is comprised of basis functions centered on a particular atom. The contributions from hydrogen atoms are not included. [e] These MOs were localized by using the Boys procedure.

The atoms-in molecules (AIM) technique is designed to reveal information about the molecule by analyzing the topology of the total charge density (ρ).[20] Critical points are points at which the first derivative of ρ is zero. At a bond critical point (bcp) the curvature is positive along the bond axis and negative along axes orthogonal to the bond axis. The charge density at the bcp is an indicator of bond strength: as ρ increases, the bond strength increases.

III. Results and Discussion

A. Comparison of Metathesis Catalysts. 1. Geometry of the New Metathesis Catalyst Models. Some interesting differences (e.g., the distribution of electron density in the MC bond) were predicted in the electronic structure of those alkylidenes that are models of the catalysts used[10] in olefin metathesis.[13] This fact, coupled with observed experimental differences (specifically, the greater metathesis activity of W versus Mo alkylidene catalysts and the higher tolerance of functional groups for the latter[10a,b]) led to a more detailed investigation. The geometries used for the new metathesis models (obtained from ab initio geometry optimization[13] using Basis B) are summarized in **3**. The experimental values in **3** are given in parentheses. The minimum energy structures for the Mo and W methylidenes are those in which the MCH_2 plane is parallel to the CMN plane. This structure is referred to throughout as the parallel geometry. The pseudotet-

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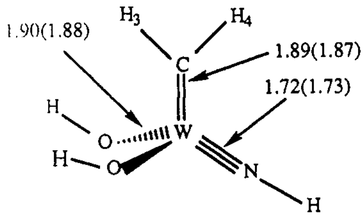
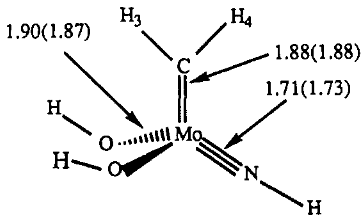


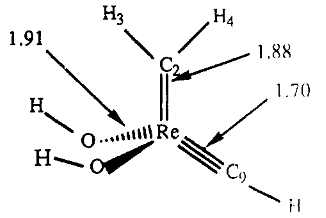
Angles (degrees)
O-W-O = 107 (110)
O-W-C = 108 (110)
O-W-N = 115 (112)
C-W-N = 103 (103)
W=C-H$_3$ = 115
W=C-H$_4$ = 131
W-N-H = 171

3a



Angles (degrees)
O-Mo-O = 108 (107)
O-Mo-C = 107 (109)
O-Mo-N = 116 (115)
C-Mo-N = 102 (100)
Mo=C-H$_3$ = 115
Mo=C-H$_4$ = 130
M-N-H = 170

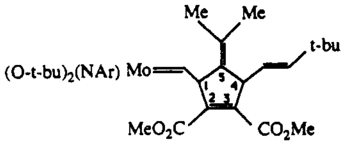
3b



Angles (degrees)
O-Re-O = 113
O-Re-C$_2$ = 110
O-Re-C$_9$ = 112
C$_9$-Re-C$_2$ = 97
Re-C$_2$-H$_3$ = 113
Re-C$_2$-H$_4$ = 132
Re-C$_9$-H$_{10}$ = 177

3c

rahedral Mo and W alkylidene complexes that have been structurally characterized all possess this parallel arrangement.[10a-d] The agreement between the calculated minima (**3a** and **3b**) and the experimental structures, **3**, with respect to the bond lengths and bond angles of the heavy atoms, is excellent. The experimental Mo bond lengths and angles were obtained from an X-ray diffraction analysis of **4**.[10b] Note the similarity between the W and



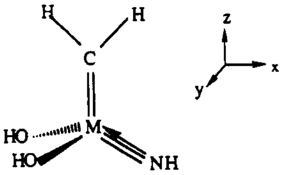
4

Mo alkylidene geometries, both calculated and experimental. Calculated metal–heavy atom bond lengths differ by 0.01 Å or less; heavy atom–metal–heavy atom angles differ by ≤3° for analogous bond angles in the W and Mo complexes, **3a** and **3b**.

The parallel structure for a Re alkylidene complex is also predicted (**3c**), although the C_s geometry possesses one imaginary frequency corresponding to a change in the H—O—Re=C torsional angles. It is anticipated that the essential features of the bonding will not be significantly altered by hydroxyl group orientation. A Re alkylidene has been characterized.[10o] A crystal structure determination has not been made and would be very interesting. Nevertheless the agreement between theory and experiment for the Mo and W complexes lends confidence to the assertion that the Re structure is essentially correct, except for placement of the hydroxyl protons.

2. Electronic Structure of the New Metathesis Catalyst Models. The electronic structure of the parallel, new metathesis catalysts conforms in large part with the picture one would deduce from the Lewis structures drawn in 2. The metal–ligand π-bonding MOs are shown for $Mo(OH)_2(NH)(CH_2)$ in Figure 1. The MOs of the W and Re complexes resemble those of $Mo(OH)_2(NH)(CH_2)$ in shape but differ in the percentage of orbital density on the various atoms (Table I). The orbitals pictured, as well as the calculated properties discussed in this section, were obtained with the extended basis at the geometries determined by using basis B optimization and shown in **3**.

In each of the parallel structures the three MOs that most closely correspond to the M–L π-bonding MOs are the three highest occupied MOs. The MO that most closely corresponds to the MC_α π-bonding orbital is invariably the HOMO. As can be seen from inspection of Figure 1, the MOs are reasonably covalent. The MN $\pi_\perp$ bonding MO (approximately perpendicular to the M=C bond axis) is somewhat more polarized toward N than the MC π MO is toward C_α (cf. Figure 1b vs 1c). Thus, one might represent the bonding in Mo and $W(OH)_2(NH)(CH_2)$ as in **5**, to describe the near-linear M–N–H moiety and



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the highly polarized (dative) nature of the M–N interaction. As expected, the ReC_{sp} bond is more covalent than the MN bond. A plot of the ReC_{sp} $\pi_\perp$ MO (Figure 1d) shows it to be evenly distributed between the Re and C_{sp} (43% Re, 45% C_{sp}).

A Mulliken population analysis shows that the M=C bond is more polarized in the W complex ($W^{+2.19}$=$C^{-0.88}$) than in the Mo complex ($Mo^{+1.92}$=$C^{-0.77}$). The Re analogue is $Re^{+1.72}$=$C^{-0.73}$. There is experimental support for greater M^+=C^- polarization in W versus Mo alkylidenes: the ^{13}C NMR spectra of analogous Mo[10n] and W[10d] metathesis catalysts show that the chemical shifts on the Mo complexes are more positive (i.e. less shielded), consistent with greater negative charge on the C_α for the W complexes. To further explore the polarization of the WC versus MoC bond, a density difference (DENDIF) map and the Boys localized MOs were constructed in the following manner:

(a) DENDIF Map. Since the core electrons of the metal are replaced with a pseudopotential, $W(OH)_2(NH)(CH_2)$ and $Mo(OH)_2(NH)(CH_2)$ have the same number of electrons. A plot of the DENDIF map for the total electron density of $Mo(OH)_2(NH)(CH_2)$ minus the total electron density of $W(OH)_2(NH)(CH_2)$ is shown in Figure

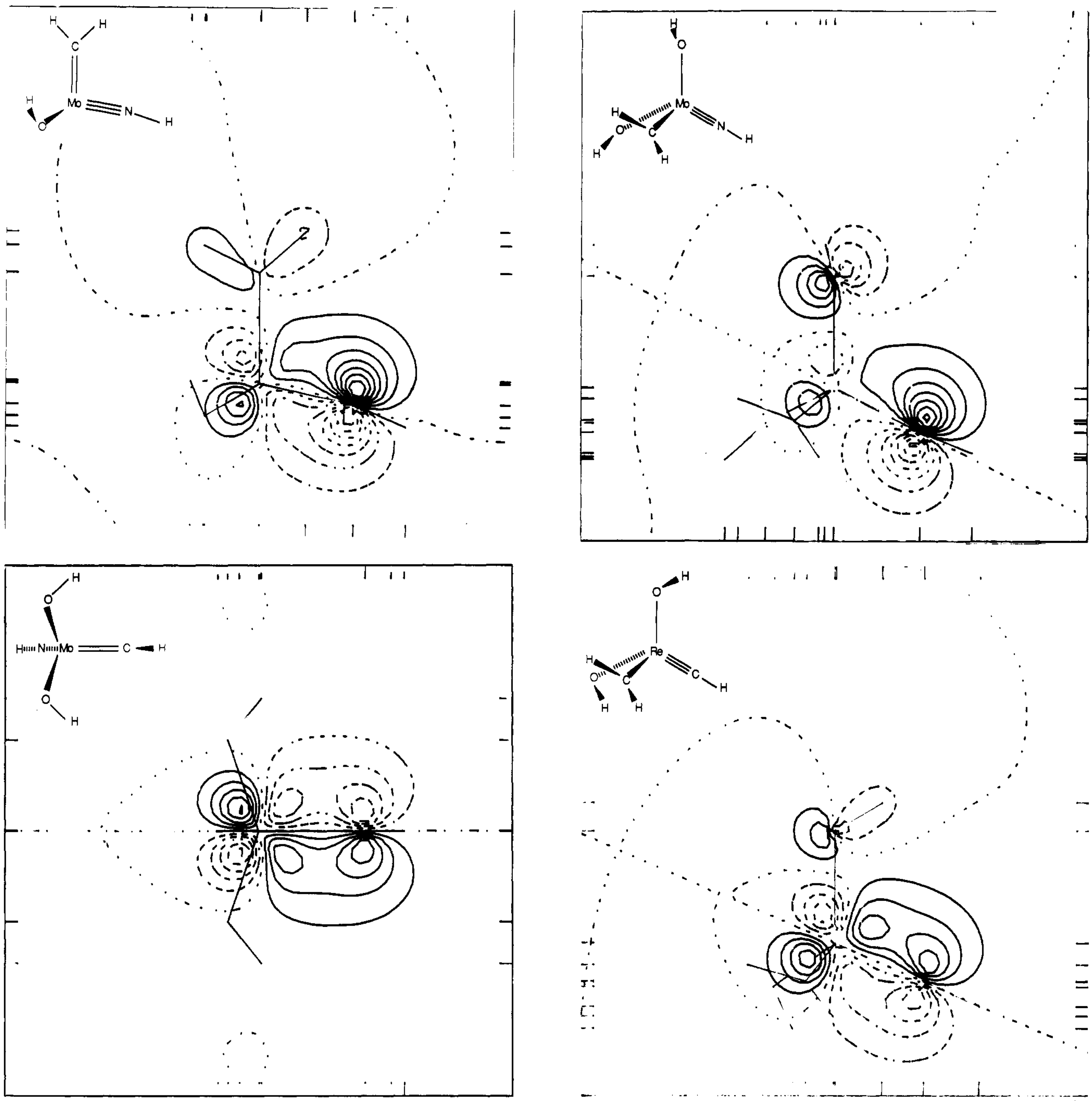

Figure 1. Metal–ligand π MOs for $Mo(OH)_2(NH)(CH_2)$ plotted for, (a, top left) MoN $\pi_{\parallel}$ in the C–Mo–N plane, (b, top right) MoN $\pi_{\perp}$ in the O–Mo–N plane, and (c, bottom left) MoC_{α} π in the plane that is perpendicular to the MCH_2 plane and passes through the MC bond. Figure 1d (bottom right) is ReC_{sp} $\pi_{\perp}$ of $Re(OH)_2(C_{sp}H)(CH_2)$ in the O–Re–C_{sp} plane. The lowest contour shown is 0.05 bohr$^{-3/2}$; the increment between successive contours is 0.05 bohr$^{-3/2}$.

2. The DENDIF map is plotted in the C_s plane. These plots were carried out at the Mo minimum to facilitate comparison.[21] The negative contours in the electron density (signifying greater electron density in the W compound in this region) are near the carbon end. The positive contours surrounding the metal end of the MC bond indicate that electron density is greater in the Mo complex in this region.

(b) Localized MOs. To ascertain that the difference in electronic distribution between the W and Mo methylidenes is due to electron density in the MC bonding region, the canonical molecular orbitals were localized by using the Boys procedure.[18] Localizing the MOs reveals two symmetry-equivalent bent or "banana" metal–carbon MOs. When the electron density of the two localized metal–carbon MOs (LMOs) in W is subtracted from that of Mo, a DENDIF map analogous to that obtained for the total electron density is obtained.

The orbital density of these localized metal–carbon MOs is consistent with greater polarization for the WC bond than for the MoC bond. This is shown quantitatively in Table I. The experimental work of Schrock and co-workers has demonstrated that W catalysts are more reactive (i.e., they have higher turnover numbers, where a turnover is the number of moles of product yielded per mole of catalyst as a function of time) and more tolerant of func-

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[21] Since their geometries are very similar ($\Delta r_{ave} \leq 0.005$ Å; $\Delta\theta \leq 0.6°$) little accuracy is lost if one subtracts the total electron density (or some clearly defined portion of it) of the W minimum from the Mo minimum. A repeat of these DENDIF calculations on the W and Mo complexes at their respective minima does not change either the total density or the metal–carbon density difference.

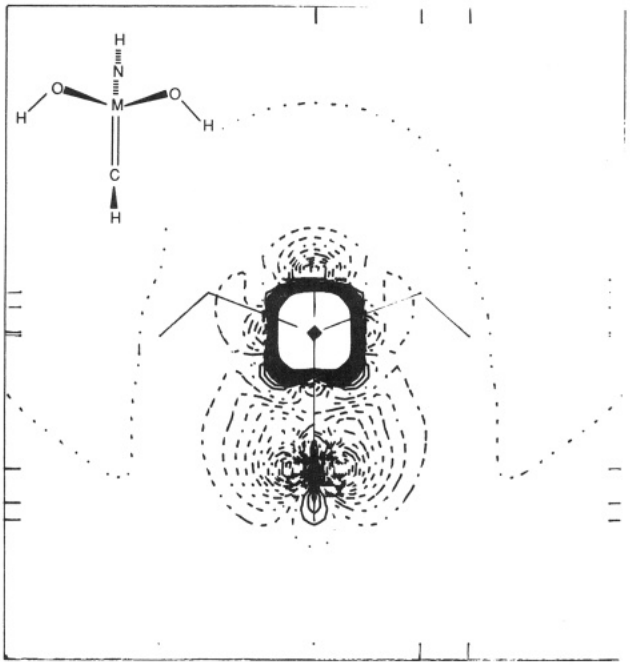


Figure 2. Density difference (DENDIF) maps for the total electron density for $W(OH)_2(NH)(CH_2)$ subtracted from $Mo(OH)_2(NH)(CH_2)$ plotted in the mirror plane. The outermost contour is 0.001 bohr$^{-3/2}$, and the increments between successive contour lines is 0.001 bohr$^{-3/2}$.

tionalities, such as carboxyl groups, than analogous Mo catalysts for the metathesis of internal olefins.[10] For example, $Mo(OCMe(CF_3)_2)_2$(*N*-2,6-diisopropylphenyl)(=C(H)-*t*-bu) will metathesize 500 equiv of *cis*-2-pentene to an equilibrium mixture of olefins in 2 min (250 turnovers/min), while the tungsten analogue will metathesize at least 3700 equiv in 5 min (≥740 turnovers/min) at 25 °C in toluene.[10n] Without a detailed knowledge of the mechanism, one cannot predict with certainty what effect modifications have on metathesis. However, it seems reasonable that these observed differences can be related to the increased electron deficiency of the metal in the W complexes. For example, making the OR group more electron withdrawing increases the activity of W(=C(H)-*t*-bu)(NAr)$(OR)_2$ by up to 3 orders of magnitude in the metathesis of *cis*-2-pentene.[10a] With a high-valent transition-metal complex and olefin present in solution, a plausible first step in olefin metathesis is the coordination of the olefin to the metal (see eq 1). The coordination of an olefin is expected to result from donation from the olefin π MO into a low-lying vacant MO on the metal. Back-bonding from occupied metal MOs into the olefin π^* should be minimal since the metal is formally d^0. With a larger positive charge on W it is expected that coordination of the olefin to the catalyst will be more facile than for the Mo case. Also, olefins with oxygen donor groups will be more likely to coordinate to the metal as the charge on the metal increases, making the W complex more susceptible to deactivation by monomers with these functionalities. Donor group coordination will block olefin coordination sites and slow the rate of olefin metathesis.

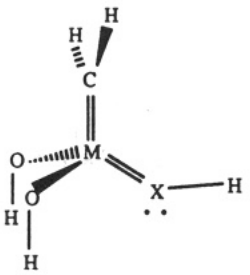
3. Transition States for M=C Bond Rotation in New Metathesis Catalyst Models. The MC rotation process has been intensively studied by Schrock and coworkers[10a-d] due to its possible importance in olefin metathesis. If, as the NMR studies suggest, the properties of the two rotamers are different, then one rotamer could react with olefins at a faster rate to form the metallacyclobutane intermediate. The rate of interconversion would then be a critical component in determining catalyst activity.

Table II. Transition State Structures for "New" Metathesis Catalysts[a]

	$Mo(OH)_2$-$(NH)(CH_2)$	$W(OH)_2$-$(NH)(CH_2)$	$Re(OH)_2$-$(CH)(CH_2)$
$M{=}C_\alpha$	1.88	1.89	1.90
$C_\alpha{-}H_\alpha$	1.08	1.09	1.09
$M{-}O$	1.88	1.88	1.88
$M{=}X^b$	1.76	1.76	1.75
$M{=}C_\alpha{-}H$	122	122	121
$M{=}X{-}H$	134	140	151
$X{=}M{=}C_\alpha$	110	112	115
$O{-}M{=}C_\alpha$	107	106	105
$O{-}M{=}X$	105	105	103
$O{-}M{-}O$	124	122	127
$H{-}O{-}M{=}C_\alpha$	±123	±125	±132
$H{-}X{=}M{=}C_\alpha$	0.0	0.0	0.0
f^c	8	10	22

[a] Geometries for M=C rotation obtained by using basis B are reported: bond lengths in angstroms, angles in degrees. [b] For the Mo and W complexes X = N; for the Re complex $X = C_{sp}$. [c] The flap angle, *f*, as described in 8 is given in degrees.

The most plausible transition-state structures for MC bond rotation are those in which the MCH_2 plane is perpendicular (or nearly perpendicular) to the CMX plane, as depicted in **6**. Perpendicular stationary points similar to **6** have been isolated as transition states with basis B for Re, Mo, and W complexes (Table II); the imaginary frequency corresponds to MC rotation, yielding the previously described minima.



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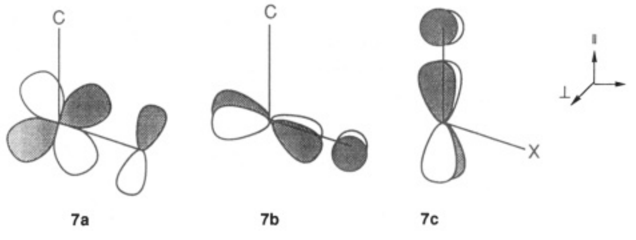
Fascinating changes in the conformations of the ligands are brought about as a consequence of MC rotation. Many of these changes are tied to competition between the multiply bonded ligands for the dπ AOs (the t_2 set in these pseudotetrahedral complexes). Since the metal is d^0, the orientation of the π-bonding ligands will be that conformation which maximizes dπ-pπ bonding. Only when the MCH_2 and XMC planes are parallel does each ligand π orbital have its own metal dπ AO with which to maximize overlap for bonding, **7**. Upon rotation of the MC bond, a conflict between the C pπ and the X $\pi_\parallel$ AOs for overlap with the d_{xz} arises. As a result, coordination about the X ligand changes from approximately linear in the minima (**3a** and **3b**) to more noticeably bent in the transition states (Table II). The MC rotation (Table II) increases the MX bond lengths by an amount (≈0.05–0.06 Å) greater than



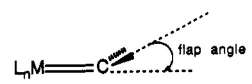
7a **7b** **7c**

Table III. Geometries of Minima and Transition States for "Old" Metathesis Catalyst Models[a]

	$MoCl_2(O)(CH_2)$	$WCl_2(O)$-(CH_2)	$ReCl_2(N)(CH_2)$
Minima			
M=C	1.91	1.88	1.88
M=Y	1.64	1.66	1.61
M—Cl	2.34	2.33	2.33
$M=C—H_3$	126	127	128
$M=C—H_4$	120	118	118
Y=M=C	102	102	98
Cl—M=C	103	106	105
Cl—M—Cl	113	112	121
Y=M—Cl	117	115	112
$Y=M—C—H_3$	0	0	0
Transition States			
M=C	1.91	1.89	1.95
M=Y	1.67	1.69	1.64
M—Cl	2.30	2.29	2.29
$M=C—H_3$	119	120	118
$M=C—H_4$	119	120	118
Y=M=C	111	111	114
Cl—M=C	108	106	110
Cl—M—Cl	117	120	117
Y=M—Cl	106	106	103
α^b	29	23	35

[a] The bond lengths (in angstroms) and angles (in degrees) for models of the "old" metathesis catalysts obtained from ab initio optimization (using basis sets described in the text) are reported; Y = O for M = Mo and W and Y = N for M = Re. [b] This angle is the flap angle defined in 8.

it increases the MC bond lengths (0.00–0.02 Å). There are also small changes in the geometry about C_α—the C_α coordination goes from planar to pyramidalized: the flap angle, 8, is ≈9° for both the W and Mo methylidenes. This



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pyramidalization at C_α lowers the metal–carbon π-bonding interaction.

The foregoing observations concerning the changes that take place in the geometry of the Mo and W complexes upon rotation about the MC bond raise several interesting points with respect to an olefin metathesis pathway. First, the large reorientation of the non-carbene ligands suggests that steric interactions between ligand substituents (e.g., replacing the imido H with a 2,6-diisopropylphenyl group or the hydroxyl proton with a *tert*-butyl group), brought about by the electronic changes which accompany MC rotation, may play an important role in determining the height of the barrier.

A second important conclusion that can be deduced from the transition-state results is that if NH is replaced with a π-bonding ligand stronger than NH, then the MC rotational barrier will increase. The old catalysts in which the NH^{2-} and CH^{3-} are replaced by O^{2-} and N^{3-}, respectively, for the group VIB and Re complexes may be expected to fall into this category. As will be discussed below, this hypothesis is borne out by ab initio results.

B. Old Metathesis Catalyst Models. 1. Geometries of the Old Metathesis Catalyst Models. The old metathesis catalyst models were optimized by using basis B. As with the new alkylidenes, the minimum energy structures are those with the parallel geometry. The pertinent geometric details for the C_s minima and transition states are listed in Table III.

Although similar in geometry, the energetics of MC rotation change markedly upon going from the new to old catalysts. As seen in Table III, the rotational barriers in the old catalysts are 2–3 times larger than those calculated for the new models. The methylene ligand distorts more as a result of the increased competition for the dπ AOs in the old transition states versus the new. There is a greater degree of pyramidalization in the old catalysts about C_α (measured by the flap angle, 8, 29° (Mo), 23° (W), and 35° (Re)). For the new metathesis catalysts f = 8° (Mo), 10° (W), and 22° (Re).

2. Electronic Structure of the Old Metathesis Catalyst Models. The frontier orbitals of all compounds considered here are dominated by the π symmetry AOs of the metal and ligands. When compared to the new catalyst models, the π-bonding MOs of the old models are much more delocalized over the whole molecule. The greater "spreading out" of the frontier MOs over the metal and ligands makes comparisons between the canonical MOs not as straightforward as for the new metathesis catalysts.

A quantitative comparison of the π bonds in the old and new models is facilitated by localization of the canonical MOs. The Boys LMOs[18] obtained from the extended basis canonical MOs for the old catalysts are summarized in eqs 4a–c. The analogous results for the new catalysts are given

$$MoCl_2(O)(CH_2):\quad \sigma_{MC} = 30\%\ Mo + 70\%\ C/\pi_{MC} = 73\%\ Mo + 27\%\ C \qquad (4a)$$

$$WCl_2(O)(CH_2):\quad \tau_{MC} = 46\%\ W + 54\%\ C \qquad (4b)$$

$$ReCl_2(N)(CH_2):\quad \tau_{MC} = 51\%\ W + 49\%\ C \qquad (4c)$$

$$Mo(OH)_2(NH)(CH_2):\quad \tau_{MC} = 46\%\ Mo + 54\%\ C \qquad (5a)$$

$$W(OH)_2(NH)(CH_2):\quad \tau_{MC} = 41\%\ W + 59\%\ C \qquad (5b)$$

$$Re(OH)_2(CH)(CH_2):\quad \tau_{MC} = 44\%\ W + 56\%\ C \qquad (5c)$$

in eqs 5a–c. The notations σ, π, and τ are used to describe σ, π, and mixed "banana" bonds, respectively. The M^+C^- polarization in the M=C bond is greater in the new than in the old metathesis catalysts. Since the CH bonds are nearly equivalent in the two sets of compounds (≈62% C and 38% H), this means that there is roughly 0.2–0.3 electrons more on C_α in the new metathesis catalysts (summing over the σ and π or two "banana" bonds).

The differences between the old and new metathesis catalyst models has interesting implications with respect to an olefin metathesis mechanism. First, the greater metathesis activity and lower functional group tolerance of the new W metathesis catalysts (vs Mo) is seen to correlate with a polarization of the MC bond in $W(OH)_2(NH)(CH_2)$ greater than in $Mo(OH)_2(NH)(CH_2)$. The greater MC polarization in the new (vs old) catalysts would also suggest generally greater reactivity for the new catalysts. Second, the significantly greater rotational barriers for the old metathesis catalyst models suggests that if the M=C rotational process is integral to olefin metathesis, as demonstrated by the experimental work,[10] then this part of the olefin metathesis mechanism could act as a bottleneck for the old catalysts.

C. Substituted Mo Alkylidenes. 1. Geometries. In the present context a substituted alkylidene is taken to be a methylidene complex in which the methylene ligand has been modified by replacing one of the hydrogen atoms with another atom or functional group. The large majority of Mo and W metathesis catalysts that have been synthesized and characterized are monosubstituted alkylidenes, $L_nM=C(H)Z$, where Z is typically an alkyl or silyl group.[10] The larger size of the substituted complexes requires the use of the compact basis A for their geometry

Table IV. Geometry of Ethylidene Complexes and Comparison with Experiment[a]

	syn	anti	TS	methylidene	expt[b]
$Mo{=}C_\alpha$	1.90	1.91	1.90	1.88	1.88
$C_\alpha{-}H_\alpha$	1.09	1.08	1.08	1.07 (syn)[c]	
$C_\alpha{-}C_\beta$	1.51	1.52	1.52	1.08 (anti)	1.52
$Mo{-}O$	1.88	1.88	1.86 (1.85)	1.87	1.87
$Mo{\equiv}N$	1.68	1.68	1.76	1.67	1.73
$Mo{=}C_\alpha{-}C_\beta$	134	123	129	128 (syn)	140
$Mo{=}C_\alpha\text{-}H$	113	125	116	120 (anti)	
$M{\equiv}N{-}H$	169	167	147	168	172
$Mo{-}O{-}H$	147	146	139 (140)	148	152
$C{=}Mo{-}O$	107	106	105 (106)	108	109
$C_\alpha{=}Mo{\equiv}N$	101	102	112	102	100
$N{\equiv}Mo{-}O$	118	118	105 (106)	117	115
$O{-}Mo{-}O$	105	105	122	105	107
$C_\alpha{=}Mo{-}O{-}H$	±11.4	±11.7	142 (−139)	±13.6	
$C_\alpha{=}Mo{\equiv}N{-}H$	180	180	−3	180	180
$C_\beta{-}C_\alpha{=}Mo{\cdots}H_\alpha$	180	180	−166	180	
f	0	0	10.9	0	0

[a] Angles are reported in degrees; bond lengths are reported in angstroms. These values were calculated by using basis A. [b] Experimental values (where applicable) are from compound 4.[10b] [c] Syn and anti refer to the H atoms on the methylidenes that are cis and trans, respectively, to the imido group.

optimization. As with the methylidene complexes, the minimum energy structures possess the parallel geometry. Note the good agreement between the Mo methylidene structure calculated with basis A (Table IV) and the larger basis B (**3b**). Pertinent bond lengths and angles for the Mo alkylidene complex 4 are also listed in Table IV.[10b] The other substituted Mo alkylidenes have nearly identical geometrical parameters except where noted below.

The MoC bond is slightly shorter in the silyl-substituted minima (1.87 Å syn, 1.86 Å anti) than in the methyl-substituted minima (1.90 Å syn, 1.91 Å anti). Fluorine has the opposite effect on the MC bond length (1.95 Å syn, 1.96 Å anti). Methyl substitution lengthens the MC bond slightly (≈0.02 Å) in the Mo ethylidene relative to the MC bond in the Mo methylidene complex. The syn isomer is that in which the non-hydrogen substituent on C_α is cis to the NH group; the anti isomer is formed by a 180° rotation of the alkylidene group about the MC bond. The M═C—Z angle is always larger for the syn substituent than for the anti. A measure of the distortion is half the difference in the syn and anti M═C—Z angles: $\beta = (\theta_{syn} - \theta_{anti})/2$. For reference, $\beta = 4°$ for the methylidene complex. In the Mo ethylidene complex the syn rotamer is more distorted ($\beta = 11°$) than the anti rotamer ($\beta = 1°$). This might have been guessed on steric grounds. The discrepancy between the syn ($\beta = 8.5°$) and anti distortions ($\beta = 6°$) is much less for the silyl-substituted complex. With the electron-withdrawing fluorine the anti distortion ($\beta = 4.5°$) is actually slightly larger than the syn distortion ($\beta = 4°$).

As with the Mo methylidene complex, the stationary points in which the CHZ plane is approximately perpendicular to the CMN plane are transition states. The imaginary modes correspond to rotation about the MC bond. The MC rotational barriers of the Mo alkylidenes are in most cases insensitive to the carbene substituent. The MP2 rotational barriers (including ZPE) at the basis A level are (in kcal mol^{-1}) 13.0 (Z = H), 13.6 (Z = Me), 14.2 (Z = SiH_3), and 28.5 (Z = F). Experimental enthalpies of activation ($\Delta H^\ddagger$) for the NMR dynamic process fall in the range 12.7 ± 0.3 kcal mol^{-1} for $W(C(H)SiMe_3)(NAr)(OAr)$ to 22.8 ± 2.1 kcal mol^{-1} for $Mo(C(H)CMe_2Ph)(NAr)(OTB)_2$, where Ar = 2,6-diisopropylphenyl and OTB = 2-*tert*-butylphenoxide, with an average $\Delta H^\ddagger$ of 18 kcal mol^{-1}.[10c] The calculated rotational barriers for the methyl- and silyl-substituted Mo alkylidenes concur with the range of observed $\Delta H^\ddagger$, lending support to the assertion[10c] that the process being studied by NMR spectroscopy is a MC rotation process. The agreement between theory and experiment also suggests that the interconversion of rotamers proceeds by a straightforward route (i.e., MC rotation) and not by a different pathway (e.g., transformation from tetrahedral to square-planar coordination and then back to tetrahedral coordination). Test calculations on square-planar Mo methylidenes showed them to be much higher in energy (≈40 kcal mol^{-1} and ≈20 kcal mol^{-1} above the parallel minimum and perpendicular transition state, respectively, at the basis A/HF level for $Mo(OH)_2(NH)(CH_2)$).

2. Electronic Structure of Substituted Mo Alkylidenes. The nature of the substituents is expected to have a profound influence on the electronic structures of the metathesis catalysts. The bond overlap populations (BOP), Mulliken atomic charges, MC and CH force constants, LMO populations, and several properties calculated by using the atoms-in-molecules (AIM) method[20] are listed in Table V for the substituted Mo alkylidenes. These properties were calculated by using the extended basis at the minima obtained with basis A.

There are three properties in Table V that are related to the bond strength: the force constant (k), the bond

Table V. Calculated Properties of $Mo({=}C(H)Z)(OH)_2(NH)$[a]

	Z = H	Me(anti)	Me(syn)	SiH_3(anti)	SiH_3(syn)	F(syn)	F(anti)
			BOP				
$Mo{=}C_\alpha$	0.66	0.58	0.56	0.66	0.64	0.48	0.52
$C_\alpha{-}H_\alpha$	0.70/0.76	0.78	0.72	0.74	0.70	0.74	0.68
			AIM[b]				
(i) R_M/R_C[c]	1.89/1.67	1.90/1.71	1.90/1.70	1.90/1.62	1.90/1.63	1.90/1.80	1.90/1.80
ρ[d]	0.186	0.177	0.178	0.197	0.193	0.155	0.155
(ii) R_C/R_H	1.34/0.72; 1.34/0.70	1.33/0.70	1.34/0.72	1.33/0.70	1.34/0.72	1.36/0.67	1.37/0.68
ρ	0.275/0.285	0.291	0.279	0.280	0.270	0.304	0.296
			ω (k)[e]				
MC	693 (3.0)	660 (2.7)	652 (2.7)	759 (3.6)	747 (3.5)	614 (2.4)	589 (2.2)
CH	3213 (5.7)/3350 (6.1)	3350 (6.1)	3140 (5.4)	3295 (5.9)	3137 (5.4)	3319 (6.0)	3203 (5.6)

[a] The properties described in this table were calculated by using the extended basis as the geometries obtained from basis A optimization. [b] These properties are derived from the AIM (atoms in molecules) analysis.[20] [c] The values R_M and R_C are the distances of the metal and C_α, respectively, from the position of the bond critical point. In all cases studied here the bond critical point is located along the bond axis, which is not always the case, e.g. in strained bonds.[19,20] [d] The charge density (in electrons $bohr^{-3}$) at the bond critical point is given by ρ. [e] The calculated stretching frequencies (ω, in cm^{-1}) and force constants (k, in mdyn $Å^{-1}$), in parentheses, were calculated by using the techniques described in: Boatz, J. A.; Gordon, M. S. *J. Phys. Chem.* 1989, *93*, 1819. This property is calculated at the same basis set as that used for the geometry optimization, i.e. basis A.

overlap population (BOP), and the charge density (ρ) at the bond critical point (bcp). The MC force constant and the charge density at the MC bond critical point (ρ_{MC}) both follow the order Z = SiH_3 > H > Me > F; the bond overlap population decreases according to $SiH_3 \approx$ H > Me > F. These data indicate that the MC bond is weakened by electron-withdrawing substituents on the alkylidene ligand and that the opposite is true for electron-releasing substituents, relative to H.

The same quantities (ρ_{CH}, BOP, and k_{CH}) can also be applied to the analysis of the CH bond of the substituted methylidene ligand. The NMR data on Mo and W complexes indicates that the two species in solution have markedly different C_α—H coupling constants (J_{CH}).[10a-d] For example, in the NMR spectrum of a silyl-substituted Mo alkylidene, $Mo(C(H)SiMe_3)(OAr)_2(NAr)$, there are two J_{CH} values: 145 and 117 Hz. A good gauge of the C_α—H_α interaction can be obtained from the CH coupling constant, since the differences in J_{CH} between the proposed rotamers is much larger than the differences in their other NMR properties (J_{MC}, J_{MH}, δ_{C_α}, or δ_{H_α}). From the k_{CH} data in Table V it appears as if the isomer with the larger J_{CH} is the anti rotamer and that with the smaller J_{CH} is the syn rotamer. For the silyl-substituted model complex $Mo(=C(H)SiH_3)(OH)_2(NH)$ the calculated CH force constant is 5% larger for the anti rotamer when compared to the syn rotamer (3295 and 3137 cm^{-1}). Even for the methylidene complex these same two quantities indicate that the H which is syn to the imido N is also stronger. The ρ_{CH} and BOP also imply a stronger bond in the anti rotamer than in the syn rotamer.

The syn and anti rotamers are close in energy. At the basis A level (with zero point energy and MP2 corrections included) the anti isomer is lower than the syn isomer by 1.9 and 0.2 kcal mol^{-1} for the silyl- and fluoro-substituted Mo alkylidenes, respectively. For the Mo ethylidene complex the syn isomer is favored, but only by 0.8 kcal mol^{-1} at the same level of theory. With such small differences in energy, and considering the approximations made in order to yield computationally tractable molecules, it is impossible to say with any degree of confidence which rotamer will be favored in the experimentally employed catalysts. All the four-coordinate, olefin metathesis catalysts that have been characterized by X-ray diffraction are found in the syn conformation. However, the NMR studies of Schrock and co-workers indicate that the interconversion of the syn and anti rotamer is facile at room temperature.[10a,b,n] Furthermore, the relative ease of interconversion of the two rotamers and the ability to observe two different isomers in solution implies that they are very close in energy.

A Boltzmann distribution calculation for the two isomers is very revealing. For an energy difference, ΔE, of 0.0 kcal mol^{-1}, one of course has a 50/50 mixture. For ΔE = 0.25, 0.50, 1.0, and 2.0 kcal mol^{-1}, the ratios become 60/40, 69/31, 87/13, and 98/2, respectively, at 300 K. This simple calculation clearly demonstrates the rapidity with which one isomer becomes increasingly preferred over another as their energies move only slightly away from degeneracy. In their study of four-coordinate Mo alkylidenes, Schrock et al. observe approximately 90–94% of the dominant species in those cases in which there are measurable amounts of each rotamer; this corresponds to energy differences on the order of 1–2 kcal mol^{-1}. In the case of $Mo(=C(H)SiMe_3)(NAr)(OAr)_2$–$C_6D_6$ solution, the distribution is more even, 65% for the high J_{CH} isomer and 35% for the low J_{CH} isomer.[10n] The theoretical results for $Mo(=C(H)SiH_3)(OH)_2(NH)$ suggest that the high J_{CH} isomer is the anti rotamer and that it is lower in energy. Combining these two pieces of data leads to the prediction that the anti isomer is lower in energy in solution for $Mo(C(H)SiMe_3)(OAr)_2(NAr)$.

IV. Summary and Conclusion

Several observations about the bonding and activity in high-valent, four-coordinate alkylidenes as olefin metathesis catalyst models are made in this paper, based on ab initio MO calculations.

With respect to the bonding in the new metathesis catalyst models, $M(OH)_2(XH)(CH_2)$, there are two main conclusions. The minimum energy structures arise as a result of the desire to maximize metal $d\pi$–ligand $p\pi$ bonding while competition among the ligands for the same $d\pi$ AO is minimized. When this balance is upset by rotating the alkylidene group about the MC bond axis, then the energy increases and significant reorganization of the ancillary ligands takes place in an attempt to maintain a maximum amount of MC π bonding. It is the ability of the ancillary ligand to distort in order to accommodate the carbene ligand which seems to control the height of the barrier.

The second important conclusion from this portion of the study deals with the relative MC bond polarity of $W(OH)_2(NH)(CH_2)$ versus $Mo(OH)_2(NH)(CH_2)$. It was observed that the WC bond is more polarized in a $M^+{=}C^-$ fashion for the W methylidene than is the MoC bond of the Mo methylidene analogue. The greater polarization correlates with greater metathesis activity exhibited by the W alkylidene metathesis catalysts when compared to Mo analogues.

The second part of this paper deals with the electronic structure of old metathesis catalyst models, $MCl_2(Y)(CH_2)$. The rotational barrier in the old catalysts is 2–3 times larger than in the new models. Additionally, the MC bond polarity is greater in the latter catalyst models. If, as suggested above, greater metathesis activity correlates with greater MC polarization, one would conclude that the old metathesis catalysts would be less active than new analogues.

Finally, the effects of substitution on the alkylidene ligand of a series of Mo alkylidenes was studied. It was found that electron-withdrawing ligands cause the MC bond length to increase while electron donors have the opposite effect. The corresponding trends in bond strength with the change in alkylidene substituent are predicted: electron donors strengthen the MC bond and vice versa. The calculated MC rotational barriers are in accord with experimentally observed enthalpies of activation for the NMR dynamic process. The rotamers, syn and anti, are very close in energy.

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