The [2+2] Addition of Ethylene to Metal–Ligand Multiple Bonds: A Density Functional Study of Mo(E)OCl₂

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We have studied the [2+2] cycloaddition of ethylene to $Mo(E)OCl_2$ for E = S, Se, O, NH, PH, SiH_2, and CH_2 based on gradient-corrected density functional theory. The reactant Mo-$(E)OCl_2$ has for E = NH, PH, SiH_2, and CH_2 a preferred conformation with all atoms of the E ligand in the plane bisecting the Cl–Mo–Cl angle. The [2+2] cycloaddition takes place with ethylene approaching $Mo(E)OCl_2$ perpendicular to the plane bisecting the Cl–Mo–Cl angle. The reaction enthalpy follows the order (in kcal/mol) SiH_2 (−24.1) < CH_2 (−15.6) < PH (−7.4) < NH (−0.9) < S (5.9) < Se (6.2) < O (12.0) < Cl (13.0). The ligands with the less electronegative heteroatom give rise to the more exothermic reaction, as they have lone pairs of sufficiently high energy to donate charge to π^* of the incoming olefin and form a strong C–E bond. The activation energy for the addition follows the order (in kcal/mol) SiH_2 (2.3) < CH_2 (4.7) < PH (5.0) < S(16.6) < Se (16.6) < Cl (19.0) < NH (21.1) < O (25.8). Again, ligands with the less electronegative heteroatoms afford the lowest barrier for the addition since they have lone pairs that at an early stage of the reaction can interact, stabilizing with π^* of the incoming ethylene. The investigation affords a rationale for why [2+2] addition of olefin to M=E bonds is observed experimentally to be facile for E = SiH_2 and CH_2 but not for E = O.

1. Introduction

The $[2_\pi+2_\pi]$ cycloaddition of olefin to a metal–carbene double bond is well established as a viable reaction mechanism in olefin metathesis thanks to the pioneering work of Chauvin[1] and Schrock.[2] Theoretical calculations[3–7] have confirmed that the formally forbidden $[2_\pi+2_\pi]$ addition is surprisingly facile with a modest activation barrier.

The facile cycloaddition of ethylene to metal–carbene bonds led Sharpless[8a] and others to postulate that $[2_\pi+2_\pi]$ addition of olefin to other multiple-ligand bonds[9] might be feasible as well. In particular, Sharpless has suggested that the epoxidation and hydroxylation of olefins by the d^0 metal oxides $CrCl_2O_2$ and OsO_4, respectively, involve the initial formation of a four-centered metallaoxetane intermediate from a $[2_\pi+2_\pi]$ cycloaddition of olefin to a metal–oxygen bond. The $[2_\pi+2_\pi]$ cycloaddition of ethylene to metal–sulfur bonds[8b,c] in d^0 complexes has also been implied. The suggestion by Sharpless was further supported by early theoretical calculations.[10]

However, there is growing evidence from more recent theoretical calculations[11,12] as well as experimental work by Corey et al.[13] to indicate that $[2_\pi+2_\pi]$ cycloaddition of ethylene to metal–oxygen bonds in d^0 complexes is an unfavorable reaction.

We shall in the present investigation compare the $[2_\pi+2_\pi]$ cycloaddition of ethylene to the metal–carbene bond in $MoCl_2(O)CH_2$,

$$H_2C{=}CH_2 + MoCl_2(O)CH_2 \longrightarrow Cl_2(O)Mo{-}CH_2 \atop H_2C{-}CH_2 \qquad (1)$$
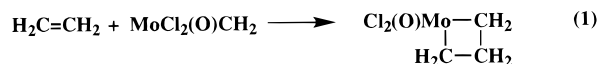
with the corrsponding process involving other multiple

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Table 1. Geometry Parameters and Bond Energies for the Reactant[b] $MoCl_2(O)E$

geometrical parameters[a,f]	ligand E							
	CH_2	SiH_2	NH	PH	O	S	Se	Cl[e]
Mo–E	1.89	2.35	1.77	2.27	1.71	2.14	2.27	2.27
∠Cl–Mo–O[c]	115	117	110	113	109	109	109	109
ΔH(Mo–E)[d]	104.8	57.8	115.0	72.7	153.5	106.7	93.6	81.2

[a] Distances in angstroms (Å) and angles in degrees. [b] Geometry corresponds to most stable conformation **2a** for E = CH_2, SiH_2, **3a** for E = NH, and **3b** for E = PH. [c] The angle Cl–Mo–O is the bisecting angle for the [2+2] addition of ethylene. [d] Bond formation enthalpies in kcal/mol with respect to $MoOCl_2$ and E in their ground states. Zero-point energy corrections and temperature contributions are not included. [e] For chlorine the calculations refer to $MoCl_2O_2$ and the bond energy is with respect to Cl and MoO_2Cl in their ground states. [f] In the specification of the parameters, E refers to C, Si, N, and P in the case of CH_2, SiH_2, NH, and PH, respectively.

metal–ligand bonds, M=E, in $MoCl_2(O)E$,

$$H_2C=CH_2 + MoCl_2(O)E \longrightarrow \begin{array}{c} Cl_2(O)Mo—E \\ | \quad | \\ H_2C—CH_2 \end{array} \qquad (2)$$
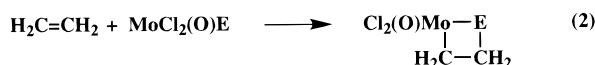
with the help of quantum mechanical calculations based on density functional theory (DFT).[14] This comparison should help to reveal the factors that determine whether the $[2_\pi+2_\pi]$ cycloaddition of ethylene to a M=E bond in d^0 complexes is facile. Representative ligands will include the chalcogenides E = O, S, and Se as well as E = SiH_2, NH, and PH. The reaction between the Mo–Cl bond in $MoCl_2O_2$ and ethylene was also considered in this study for comparison, although it is more correctly viewed as an insertion process rather than a cycloaddition.

2. Computational Details

All calculations were carried out using the Amsterdam Density Functional (ADF) package developed by Baerends[15] et al. and vectorized by Ravenek.[16] The numerical integration procedure applied for the calculations is that of te Velde and Baerends.[17] An uncontracted triple-ζ STO basis set was used for describing the 4s, 4p, 4d, 5s, and 5p orbitals of molybdenum. The oxygen (2s, 2p), nitrogen (2s, 2p), carbon (2s, 2p), sulfur (3s, 3p), phosphorus (3s, 3p), silicon (3s,3p), selenium (3d, 4s, 4p), chlorine (3s, 3p), and hydrogen (1s) atoms were also described by triple-ζ basis sets augmented with two extra polarization functions.[18,19] Electrons in the lower shells were treated within the frozen core approximation. A set of auxiliary s, p, d, f, and g functions, centered in all nuclei, was introduced in order to fit the molecular density and Coulomb potential in each SCF cycle.[20] All geometries and frequencies were evaluated at the local density approximation (LDA) level[21,22] augmented by Becke's nonlocal exhange[23] and Perdew's nonlocal correlation corrections.[24] Relativistic corrections

were taken into account by a quasi-relativistic method[25] (QR). The geometry optimization procedure was based on an analytical gradient scheme developed by Versluis[26] and Ziegler. The harmonic vibrational frequencies were computed from the force constants obtained by numerical differentiation of the energy gradients.[27] The application of this scheme, in comparison to other relativistic methods, has been discussed by Li[25b] et al. Transition-state stuctures were optimized according to the scheme by Banerjee[28] et al. and Baker[29] in the ADF implementation due to Fan[30] et al. All first-order saddle points were shown to have a Hessian matrix with a single negative eigenvalue.

The reactants $Mo(E)OCl_2$ are d^0 complexes with singlet ground states. The coordination about the metal is distorted tetrahedral in each case. All structures were optimized without symmetry constraints and were found to have C_s symmetry, except for the oxo complex, which had C_{2v} symmetry. The bond energies, BE(Mo–E), are not zero-point corrected, but this will not affect the observed trend. The zero-point correction might change the calculated bond energies by a few kcal/mol. The products $Mo(E)OCl_2–C_2H_4$ were optimized with no symmetry constraints; the only complex containing symmetry was for E = CH_2 which was C_s. The transition-state structures were obtained by a series of constrained geometry optimizations in which the Mo–C and E–C bonds were fixed and all other coordinates were optimized. The approximate stationary point from this procedure was then fully optimized as described above. No symmetry was found for any of the transition-state structures located in this study.

3. Results and Discussion

We shall in the following discuss the $[2_\pi+2_\pi]$ cycloaddition of ethylene to $MoCl_2(O)E$ (eq 2) for the chalcogenides E = O, S, and Se as well as E = SiH_2, NH, and PH. We begin the discussion with an analysis of the bonding and frontier orbitals in the reactant $MoCl_2(O)E$.

A. Mo(E)OCl₂. The optimized structures for $MoCl_2(O)E$ are given in Table 1. The chalcogenide series E = O, S, Se have a single stable conformation of C_s (E = S, Se) or C_{2v} (E = O) point-group symmetry, **1**. Two conformations were optimized for the polyatomic ligands E = CH_2 and SiH_2. The first of C_s symmetry has XH_2 (X = C, Si), **2a**, in the plane bisecting the Cl–Mo–Cl angle, whereas the second has XH_2 in a perpendicular plane, **2b**. We find for CH_2 and SiH_2 that the in-plane

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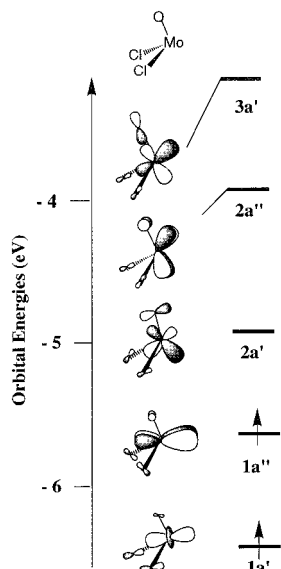(30) Fan, L.; Ziegler, T. *J. Chem. Phys.* **1990**, *92*, 46.

Figure 1. Frontier molecular orbitals for the MoCl2(O) fragment in the geometry of the reactant MoCl$_2$(O)E. Orbital energies are given in electronvolts.

conformation **2a** is favored over **2b** by 25.9 and 26.6 kcal/mol, respectively. Further, the out-of-plane conformation **2b** was found from frequency calculations to represent a transition state for the rotation of XH$_2$ around the Mo–X bond. The high barrier of rotation is in line with previous theoretical[5,6a,7] and experimental[2] studies on related d^0 alkylidene complexes of the type R(R′)C=Mo(OR″)$_2$. For E = NH and PH, we find again in-plane, **3a** and **3b**, as well as out-of-plane conformations, **3c**, with the latter representing a transition state for the rotation interconnecting the in-plane conformations **3a** and **3b**. For NH the cis-conformation, **3a**, with a Mo–N–H angle of 137° is favored over **3b** (Mo–N–H = 137°) by 7.0 kcal/mol, whereas the trans-conformation, **3b**, with a Mo–P–H angle of 82.1° is favored over **3a** (Mo–P–H = 96°) for PH by 2.1 kcal/mol.
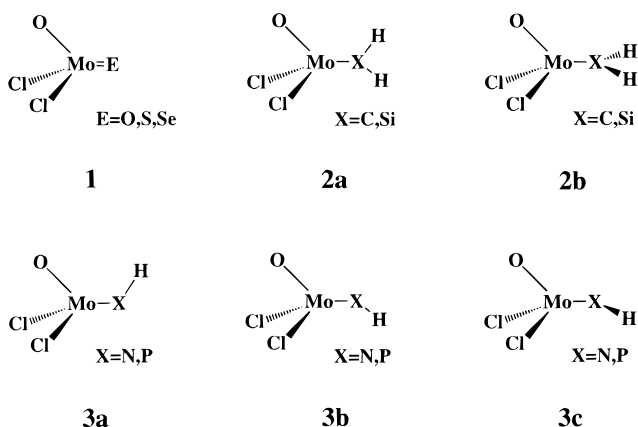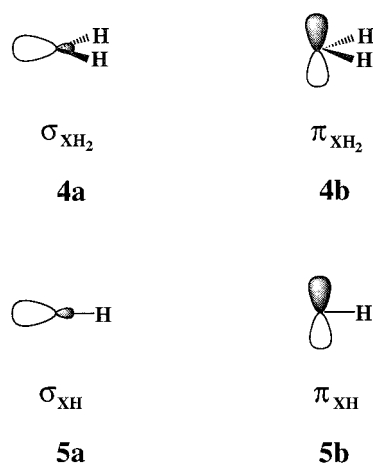

The conformational preference for the ligands E = CH$_2$, SiH$_2$, NH, and PH in MoCl$_2$(O)E as well as the reactivity and strength of the Mo=E bond can be understood by analyzing the frontier orbitals of E and MoCl$_2$(O) as well as their interactions in the combined MoCl$_2$(O)E complex. The MoCl$_2$(O) fragment with a d^2 electron count has a triplet ground state, and its highest occupied and lowest unoccupied frontier orbitals are displayed in Figure 1. The d-based orbitals of Figure 1

Figure 2. Frontier molecular orbital energies of the σ- and π-components for the ligands E = CH$_2$, NH, O, SiH$_2$, PH, S, Cl, and Se. Orbital energies are given in electronvolts.

rise in energy with increasing antibonding ligand interaction, where the oxygen σ and π ligands generally are more destabilizing than the corresponding chlorine components. The related orbital energies for the frontier orbitals of the E ligands are shown in Figure 2.

The frontier orbitals for XH$_2$ are σ_{XH2}, **4a**, and π_{XH2}, **4b**. They are both of lower energy than the d-based orbitals on MoCl$_2$(O), Figures 1 and 2. In the case of CH$_2$ the ground state is a triplet with the electronic configuration $(\sigma_{XH2})^1(\pi_{XH2})^1$, whereas SiH$_2$ has a singlet ground state with the configuration $(\sigma_{XH2})^2$. In both the in-plane, **2a**, and out-of-plane configuration, **2b**, of MoCl$_2$(O)E a σ-bond is readily established between σ_{XH2} and 1a′ of MoCl$_2$(O). For the in-plane conformation, **2a**, there is further a strong π-interaction between π_{XH2} and 1a″. The corresponding π-interaction in the out-of-plane conformation, **2b**, involves π_{XH2} and 2a′. It is less favorable than in **2a**, as 2a′ is of higher energy than 1a″, Figure 1. The in-plane conformation is as a consequence favored for E = CH$_2$ and SiH$_2$. Our explanation is based on the canonical fragment orbitals. A related rationale based on qualitative orbitals has been provided by Cundari[5] and Gordon. It should be noted that the energy gap between 1a″ and 2a′ of Figure 1, and thus the rotation barrier, can be readily changed by substituting either oxygen or chlorine with other auxiliary ligands.[2,5,7] The ΔH(Mo–XH$_2$) bond formation enthalpies are given in Table 1 as ΔH(Mo–CH$_2$) = −104.8 kcal/mol and ΔH(Mo–SiH$_2$) = −57.8 kcal/mol, respectively. The Mo–CH$_2$ bond is stronger because σ_{XH2} and π_{XH2} form better overlaps with the MoCl$_2$(O) fragment orbitals in the case of CH$_2$.

Table 2. Geometrical Parameters and Bond Energies for the Product[b] $Mo(E)OCl_2-C_2H_4$

geometrical parameters[a,c]	ligand E							
	CH_2	SiH_2	NH	PH	O	S	Se	Cl[e]
Mo−E	2.21	2.58	1.98	2.57	1.93	2.42	2.55	3.13
Mo−C	2.21	2.22	2.23	2.21	2.21	2.22	2.21	2.15
E−C	1.52	1.89	1.45	1.89	1.45	1.85	2.00	1.86
C−C	1.52	1.53	1.52	1.51	1.51	1.51	1.50	1.50
∠E−Mo−C	60	60	63	64	65	65	66	59
∠Mo−C−C−E	−29	−35	−2.6	−25	0.3	−20	−24	−40
Mo−O	1.70	1.70	1.71	1.70	1.70	1.70	1.70	1.72
ΔH(Mo−E)[d]	−15.6	−24.1	−0.9	−7.4	12.0	5.9	6.2	13.0

[a] Distances in angstroms (Å) and angles in degrees. [b] Geometry corresponds to most stable conformation **7a**. [c] In the specification of the parameters, E refers to C, Si, N, and P in the case of CH_2, SiH_2, NH, and PH, respectively. [d] Bond formation enthalpies in kcal/mol for the [2+2] addition with respect to $Mo(E)OCl_2$ and C_2H_4 in their ground states. Zero-point energy corrections and temperature contributions are not included. [e] For chlorine the bond energy is with respect to MoO_2Cl_2 and C_2H_4 in their ground states.

The two ligands NH and PH would in a linear conformation with Mo−X−H = 180° have one σ-interaction between 1a′ and σ_{XH}, **5a**, as well as two π-interactions involving the two π_{XH} orbitals, **5b**, and respectively 1a″ and 2a′. However the two ligands are seen to reduce the Mo−X−H angle by adopting an in-plane cis-conformation, **3a**, with Mo−X−H =137° in the case of NH and a corresponding trans-conformation, **3b**, for PH with Mo−X−H = 82°. The bending is for both ligands caused by the weaker π-interactions involving π_{XH} and 2a′ on the $MoCl_2$(O) fragment, Figure 2. In the case of PH the ligand rotates to Mo−P−H = 82° so that π_{XH} instead can be used in a σ-interaction with 1a′, **6a**. This interaction is stronger than the one involving σ_{XH} since π_{XH} is closer in energy to 1a′ than σ_{XH}, Figures 1 and 2. The acute Mo−P−H angle seems further to indicate a possible interaction between the P−H bond and the empty 2a′ orbital. The π-interaction involving π_{XH} and 2a′ is somewhat stronger for NH with the shorter Mo−X bond and the more compact π_{XH} orbital. The π-bond is as a consequence not completely destroyed by the bend to Mo−X−H =137°. This bend in addition allows for interactions between π_{XH} and 1a′, **6a**, as well as between σ_{XH} and 2a′, **6b**. The ΔH(Mo−XH) bond formation enthalpies are given in Table 1 as ΔH(Mo−NH) = −115.0 kcal/mol and ΔH(Mo−PH) = −72.7 kcal/mol, respectively. These bond strengths are quite comparable to the strengths of the corresponding Mo−CH_2 and Mo−SiH_2 bonds. The bending of the XH ligand observed here due to a weak π-interaction has also been found in $H_2X=XH_2$[31] and $M=XH_2$,[32] for higher carbon homologues (X = Sb, Pb).
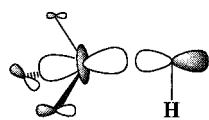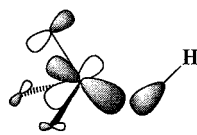
6a **6b**

The Mo−E bond in the chalcogenides complexes $MoCl_2$(O)E (E = O, S, Se) is again characterized by one σ- and two π-bonds, with the π-bond involving 2a′ being the weakest. We shall show later that the difference in strength in the two π-bonds strongly influences the way

in which ethylene adds to the Mo−E chalcogenide linkage. The ΔH(Mo−E) bond formation enthalpies are given in Table 1 as ΔH(Mo−O) = −153.5 kcal/mol, ΔH(Mo−S) = −106.7 kcal/mol, and ΔH(Mo−Se) = −93.6 kcal/mol, respectively. The trend is set by a decrease in the π-overlaps as well as the electronegativity of the chalcogenides through E = O, S, Se, as discussed in more detail by Gonzalez-Blanco et al.[33] We include as well for comparison the enthalphy of formation of one Mo−Cl bond in $MoCl_2O_2$ from $MoClO_2$ and Cl as ΔH(Mo−Cl) = −81.2 kcal/mol, Table 1.

B. Cycloaddition Products. The [2+2] cycloaddition of ethylene to the Mo=E bond in $Mo(E)OCl_2$ can take place along two paths bisecting either the Cl−Mo−O angle, **7a**, or the Cl−Mo−Cl angle, **7b**. Our calculations show that the product **7a** from the approach bisecting the Cl−Mo−O angle is the more stable for all E. The $Mo(E)OCl_2$ complexes studied here are representative of the more general class $M(E)(X)L_2$ where X is a second multiply bonded ligand and L is a singly bonded ligand (halide, alkyl, or alkoxide). Studies[6a,7,12a,b] to date have shown that the products analogous to **7a** with the incoming ethylene bisecting the L−M−X angle are the more stable.
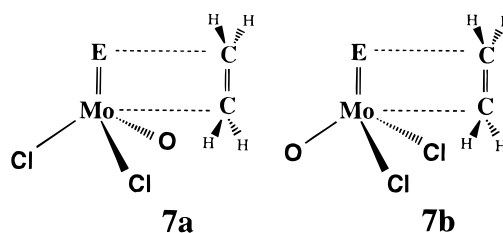
7a **7b**

The [2+2] cycloaddition products, **7a**, have a square pyramidal coordination around the molybdenum atom with the remaining Mo=O bond in the apical position. Geometrical parameters for the optimized products are given in Table 2, and structures of **7a** are displayed in Figure 3 for E = CH_2 and NH. The Mo−C−C−E ring is seen to be puckered with a ring twist defined by the dihedral angle Mo−C−C−E. Puckering of the ring alleviates the steric repulsion between the two CH_2 units of the incoming ethylene by twisting them from an eclipsed conformation toward a staggered conformation. The ring twist for E = CH_2, SiH_2, PH, S, and Se amounts to between 35° (E = SiH_2) and 20° (E = S).

(31) (a) Jacobsen, H.; Ziegler, T. *J. Am. Chem. Soc.* **1994**, *116*, 3667−3679. (b) Malrieu, J.-P.; Tranquier, G. *J. Am. Chem. Soc.* **1989**, *111*, 5916.

(32) (a) Jacobsen, H.; Ziegler, T. *Inorg. Chem.* **1996**, *35*, 773. (b) Jacobsen, H.; Ziegler, T. *Comments Inorg. Chem.* **1995**, *5*, 301. (c) Márquez, A.; Fernández Sanz, J. *J. Am. Chem. Soc.* **1992**, *114*, 2903.

(33) Gonzalez-Blanco, O.; Branchadell, V.; Monteyne, K.; Ziegler, T. *Inorg. Chem.* **1998**, *37*, 1744.
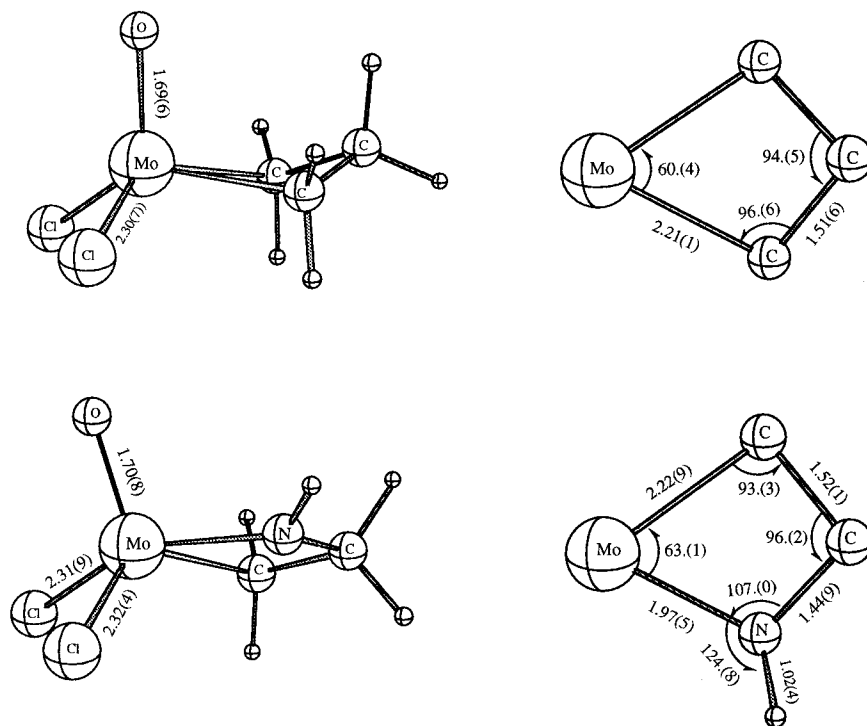
Figure 3. Optimized geometries of the cycloaddition product **7a** for the ligands E = CH$_2$ and NH. Bond lengths are in angstroms (Å), and bond angles are in degrees.
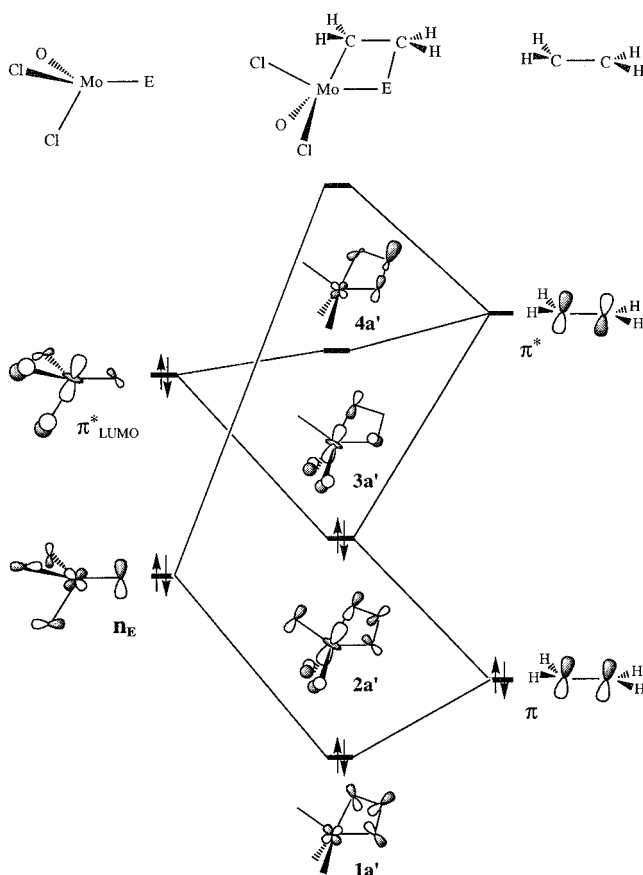

Figure 4. Orbital interaction diagram for the formation of the metallacycle product. The Mo−C and E−C bond formation involves the frontier molecular orbitals n$_E$ and $\pi^*$$_{LUMO}$ of the reactant MoCl$_2$(O)E and the π and π^* of the incoming ethylene.

Table 3. Change^{a,b} in Occupation Numbers^c for Frontier Fragment Orbitals in the Product Mo(E)OCl$_2$−C$_2$H$_4$

orbital	ligand E						
	CH$_2$	SiH$_2$	NH	PH	O	S	Se
π^*	0.96	1.02	0.88	0.93	0.76	0.87	0.90
π	−0.85	−0.75	−0.91	−0.80	−0.95	−0.85	−0.79
$\pi^*$$_{LUMO}$	0.27	0.86	0.49	0.73	0.57	0.76	0.86
n$_E$	−0.90	−0.89	−0.61	−1.00	−0.45	−0.46	−0.51

^{a} The orbitals π^* on ethylene and $\pi^*$$_{LUMO}$ on the MoCl$_2$O(E) complex are empty in the free fragments. The entries for these orbitals indicate the amount of electron occupation gained in the combined Mo(E)OCl$_2$−C$_2$H$_4$ complex. ^{b} The orbitals π on ethylene and n$_E$ on the MoCl$_2$O(E) complex are occupied in the free fragments. The entries indicate the amount of electron occupation lost in the combined Mo(E)OCl$_2$−C$_2$H$_4$ complex. ^{c} The gains (positive) and losses (negative) might not add up due to the involvement of other orbitals.

angles of 0.3° and 2.6°, respectively, Table 2. The puckering of the ring is done at the expense of reducing the metal−E π-interaction in the plane perpendicular to that ring. For E = O, NH with the best π-overlaps the reduction in the Mo−E π-interaction is too costly.

The formation of the metallacycle, **7a**, from the [2+2] addition involves essentially the occupied π and unoccupied π^* orbitals on ethylene as well as the occupied lone pair orbital n$_E$ on E and the antibonding Mo−E LUMO $\pi^*$$_{LUMO}$. These orbitals are shown schematically in Figure 4. The outcome of the interactions between these orbitals is the two occupied orbitals 1a′, 2a′ as well as the two virtual orbitals 3a′, 4a′, Figure 4. Here 1a′ and 2a′ represent the E−C and Mo−E bonds, respectively, whereas 3a′ and 4a′ are the corresponding antibonding combinations. In the formation of the metallacycle, **7a**, charge is donated from the n$_E$ lone pair orbital on the MoCl$_2$(O)E fragment to the π^* orbital of ethylene as well as from the π orbital on ethylene to the $\pi^*$$_{LUMO}$ orbital of MoCl$_2$(O)E, Table 3.

The two most electronegative ligands E = O and NH are seen to maintain a planar ring structure with twist
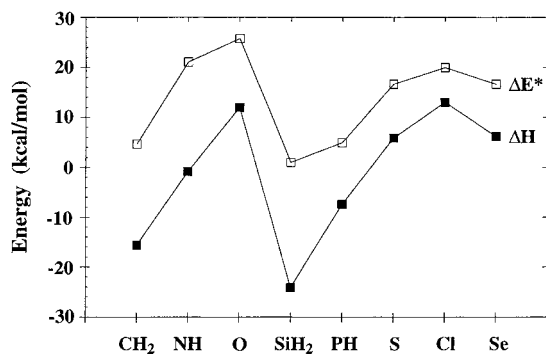
Figure 5. Activation barriers ΔE^* and reaction enthalpies ΔH for the [2+2] addition of ethylene to the Mo=E bond in the series of reactants $MoCl_2(O)E$ for E = CH_2, NH, O, SiH_2, PH, S, Cl, and Se.
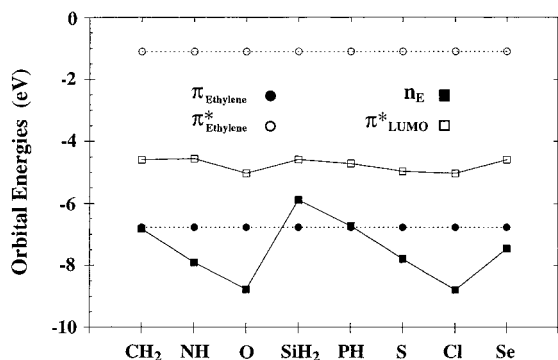

Figure 6. Frontier molecular orbital energies for the reactants $MoCl_2(O)E$ and ethylene. Metallacycle formation involves the n_E and π^*_{LUMO} of the reactant $MoCl_2(O)E$ and the π and π^* of the ethylene. Orbital energies are given in electronvolts.

The feasibility of the cycloaddition varies considerable with the ligand E. Thus, the addition is increasingly exothermic for E = PH, CH_2, and SiH_2 and increasingly endothermic for E = S, Se, O, whereas NH gives rise to a thermoneutral process, Figure 5 and Table 2. The trends in the calculated reaction enthalpies, ΔH of Figure 5, follow to some extent the energy of the n_E orbital of $MoCl_2(O)E$, Figure 6, which again correlates with the energy of the π orbitals of the E ligand, Figure 2, and the electronegativity of the central atom on E.
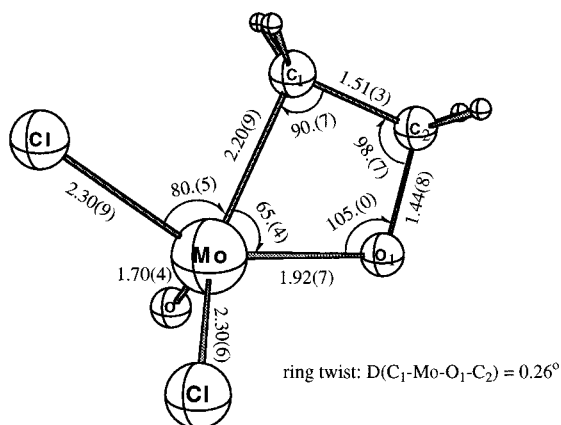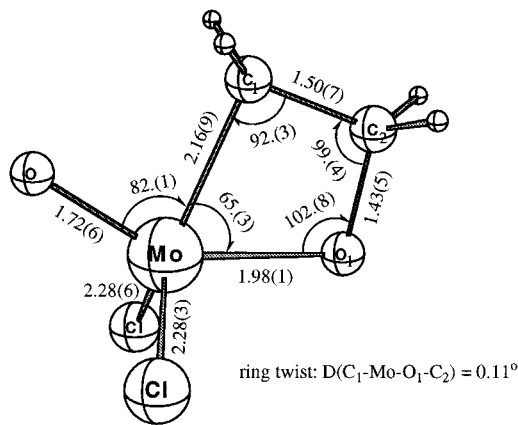
The ligands E = PH, CH_2, and SiH_2 have π orbitals, Figure 2, and n_E orbitals, Figure 6, of increasingly high energy as the electronegativity of the central atom on E decreases. The generally high energy of n_E facilitates the required donation of charge to π^*, Table 3, and gives rise to an exothermic reaction, where the exothermicity increases with the energy of n_E. On the other hand, E = Se, S, and O have π orbitals, Figure 2, and n_E orbitals, Figure 6, of relatively low energy because of their high electronegativity, especially in the case of oxygen. The general endothermicity of the addition to the Mo=E bond for E = Se, S, and O can be rationalized from the fact that the required donation of charge in the [2+2] addition from n_E to π^*, Figure 4, is less favorable for this class of electronegative ligands, Table 3. This is especially the case for E = O, where the addition process is calculated to be exothermic by 12 kcal/mol. Thus, it is apparent that a feasible addition of ethylene to a M= E bond requires an n_E orbital of relatively high energy.

The isomer **7b** does not represent a minimum on the potential energy surface for E = CH_2, SiH_2, NH, and PH. This is in line with the fact that the out-of-plane conformations, **2b** and **3c**, are transition states for the reactant $MoCl_2(O)E$. For the chalcogens, conformation **7b** was found to be 6−8 kcal/mol higher in energy than the corresponding isomer **7a**. The two conformations are shown for E = O in Figure 7. In conformation **7b** the two M−O bonds are in the same plane, which results in the occupied oxygen π orbitals competing for the same empty d orbitals for stabilizing interactions. In conformation **7a** the two Mo−O bonds are in perpendicular planes, which allows for different empty d orbitals to supply the stabilizing interactions with the occupied oxygen π orbitals. As a result, the Mo−O bonds in **7a** are shorter than in **7b**, and the former conformation is more stable.

We include as well for comparison the [2+2] addition of ethylene to the Mo−Cl bond in $MoCl_2O_2$. This reaction is better represented as an insertion of ethylene into the Mo−Cl bond, as this bond is completely broken in the product, Table 2. The reaction is endothermic with an enthalpy of 13.0 kcal/mol.

C. Cycloaddition Transition States and Activation Energies. It follows from Figure 5 that the energy

7a

7b

Figure 7. Optimized geometries for the metallacycle products arising from ethylene addition to $MoCl_2(O)E$ for E = O via the Cl−Mo−O angle **7a** and the Cl−Mo−Cl angle **7b**. Bond lengths are in angstroms (Å), and bond angles are in degrees.

Table 4. Geometrical Parameters and Bond Energies for Transition States:^{b} Mo(E)OCl$_2$−C$_2$H$_4$^{e}

geometrical parameters^{a,c}	ligand E							
	CH$_2$	SiH$_2$	NH	PH	O	S	Se	Cl^e
Mo−E	1.91(5)	2.36(0)	1.87(0)	2.28(9)	1.91(0)	2.28(8)	2.43(7)	2.58(8)
Mo−C	3.09(0)	3.11(2)	2.25(1)	2.90(7)	2.20(0)	2.18(6)	2.19(6)	2.48(2)
E−C	3.20(2)	3.41(9)	1.84(3)	3.26(5)	1.57(7)	2.02(0)	2.14(2)	2.41(8)
C−C	1.34(5)	1.34(6)	1.46(2)	1.34(9)	1.50(0)	1.48(8)	1.48(6)	1.40(4)
∠E−Mo−C	99.(8)	99.(0)	83.(5)	99.(4)	70.(0)	80.(0)	78.(7)	72.(0)
∠Mo−C−C−E	9.(9)	11.(7)	4.(7)	19.(0)	3.(7)	−25.(4)	−23.(4)	5.(3)
Mo−O	1.71(7)	1.70(2)	1.71(4)	1.70(4)	1.71(0)	1.70(4)	1.70(4)	1.71(6)
ΔH^{d,e}	4.7	2.3	21.1	5.0	25.8	16.6	16.6	19.0

^{a} Distances in angstroms (Å) and angles in degrees. ^{b} Geometry corresponds to ethylene addition along path **7a**. ^{c} In the specification of the parameters, E refers to C, Si, N, and P in the case of CH$_2$, SiH$_2$, NH, and PH, respectively. ^{d} Enthalpy of activation in kcal/mol for the formation of the metallacycle, with respect to Mo(E)OCl$_2$ and C$_2$H$_4$ in their ground states. Zero-point energy corrections and temperature contributions are not included. ^{e} For chlorine the enthalpy is with respect to MoO$_2$Cl$_2$ and C$_2$H$_4$ in their ground states.

of activation, ΔE^*, for the cycloaddition of ethylene to the M=E bond of MoCl$_2$(O)E follows roughly the same trend as the heat of reaction, ΔH, with respect to the electronegativity of the ligand E. Thus for E = SiH$_2$, CH$_2$, and PH we find modest barriers of 2.3, 4.7, and 5.0 kcal/mol, respectively, Table 4. On the other hand for E = S, Se, NH, and O the calculated barriers of 16.6, 16.6, 21.1, and 25.8 kcal/mol, respectively, are much higher.

For E = SiH$_2$, CH$_2$, and PH where the cycloaddition addition is exothermic with a low barrier, we find as expected early transition states with Mo−C distances of 3.11, 3.09, and 2.90 Å, respectively, Table 4. For E = S, Se, NH, and O where the cycloaddition addition is endothermic (E = S, Se, O) or thermoneutral (E = NH) with high barriers, we find as expected more productlike transition states with Mo−C distances of 2.18, 2.19, 2.25, and 2.20 Å, respectively.

As the reaction system approaches the transition state, the occupied π orbital of ethylene and the n$_E$ orbital of MoCl$_2$(O)E will interact to form in-phase and out-of-phase combinations. The latter, **8a**, will destabilze the reaction system and contribute substantially to the barrier. The repulsive reaction in **8a** can be reduced by an admixture of the π^* orbital of ethylene through interactions with n$_E$, **8b**. The extent of the admixture as well as the reduction in the potential barrier caused by **8a** will decrease with an energy gap between π^* and n$_E$ according to general considerations based on perturbation theory. Thus, it is understandable that the cycloaddition for E = SiH$_2$, CH$_2$, and PH will have a modest energy barrier as the n$_E$ orbital is high in energy and the π^* to n$_E$ energy gap relatively small, Figure 6. On the other hand, the lower energy of n$_E$ in MoCl$_2$-(O)E for E = S, Se, O, and NH will result in higher barriers for the addition, Table 4 and Figure 6.

8a   **8b**
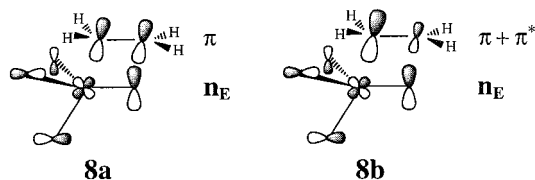
4. Concluding Remarks

The [2+2] cycloaddition of olefin to a M=E multiple bond is a contested area in organometallic chemistry. Addition of olefin to metal−carbene bonds has been firmly established by experimental and theoretical studies as a [2+2] cycloaddition. However, it has never been possible conclusively to demonstrate the occurrence of a similar olefin addition to M=O or M=S bonds, although reaction steps of this type have been invoked frequently. We have carried out a systematic study of the [2+2] cycloaddition of ethylene to the M=E bond in MoCl$_2$(O)E for E = S, Se, O, NH, PH, SiH$_2$, and CH$_2$. Our objective has been to identify the key factors of importance for the reaction enthalpy and activation barrier of the addition reaction as well as the way in which these factors are influenced by the nature of E.

Our systematic investigation has shown that the feasibility of the [2+2] addition depends on the electronegativity of the heteroatom on the ligand E. The ligands with the less electronegative heteroatom give rise to exothermic reactions, (in kcal/mol) SiH$_2$ (−24.1) < CH$_2$ (−15.6) < PH (−7.4), as they have lone pairs of sufficiently high energy to donate charge to π^* of the incoming olefin and form a strong C−E bond. On the other hand, the addition is endothermic for the more electronegative ligands, S (5.9) < Se (6.2) < O (12.0) < Cl (13.0), as their lone pairs are of too low energy to effectively donate charge to π^* of the incoming olefin. The activation energy for the addition follows the order (in kcal/mol) SiH$_2$ (2.3) < CH$_2$ (4.7) < PH (5.0) < S(16.6) < Se (16.6) < Cl (19.0) < NH (21.1) < O (25.8). Again, ligands with the less electronegative heteroatoms afford the lowest barrier for the addition since they have lone pairs which at an early stage of the reaction can interact with the stabilizing π^* of the incoming ethylene.

This is the first theoretical investigation of the [2+2] cycloaddition of ethylene to the M=E bond in which the influence of the ligand E has been considered in a systematic way. Our study affords a rationale for why [2+2] cycloaddition of olefin to metal−carbene bonds is facile whereas the corresponding addition to an M=O bond is much less favorable. We conclude on the basis of our analysis that the [2+2] cycloaddition of ethylene to the M=O bond of d^0 metal complexes is unlikely to be operative in all but a few cases, if at all.