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Organometallic Analogues of the Diels–Alder Reaction: Molybdenum Dimer + Ethylene; Molybdenum Dimer + Butadiene

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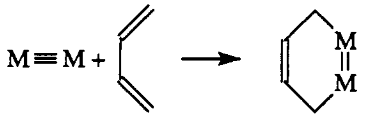
A theoretical study of the symmetry-concerted Diels–Alder analogue reactions of Mo_2 with 1,3-butadiene and ethylene is presented. Structure optimizations indicated elongation of the Mo—Mo and C=C bonds in the complexes. The optimized bond distances were found to be close to ones known in organomolybdenum complexes. The presented potential surfaces indicated, in agreement with symmetry-concerted models, that the Mo_2–Eth complex formation is thermally forbidden, as the reaction has to proceed in the excited state, but the Mo_2–But complex may be formed in the ground state with addition of thermal energy.

Introduction

Metal–metal multiple bonds provide versatile templates for the interaction with unsaturated organic molecules.[1] A rich coordination chemistry of Mo_2 and W_2 has already been noted with respect to carbon monoxide,[2] ethylene,[3] allene,[4] and butadiene.[5] A recent note[6] on the reaction of Cu_2 with ethylene in the gas phase once again raises the question[5] of a possible organometallic analogue of the Diels–Alder reaction:



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The multiple bonds in transition metal dimers offer a variety of low-lying electronic states which can interact with unsaturated organic compounds in a symmetry-concerted fashion. The Mo_2 dimer with its sextuple bond[7] is a perfect candidate for such a reaction. In this work we study the interactions of low-lying excited states of Mo_2 with ethylene and 1,3-butadiene.

Method and Computational Details

The presented calculations were performed using the SCF, CASSCF, and FOCI methods.[8] Geometry searches were done by quasi-Newton–Raphson procedures.[9,10] All of the calculations described here were made using relativistic effective core potentials (RECPs), which retained the outer 4s4p4d5s shells for Mo[11] and 2s2p shells for the carbon atom.[12] The basis set for Mo has been prepared from the LaJohn et al. collection[11] by decontracting the most diffuse Gaussians in a way which leads to a valence (3s3p2d) basis set. Other basis sets were also used for the test calculations for the Mo_2 dimer. The basis set for carbon was from of Pacios and Christiansen,[12] but we leave the most diffuse functions uncontracted. The carbon basis set was supplemented with six-component 3d Gaussian functions adopted from Dunning and Hay,[13] leading to a (2s2p1d) basis set. For hydrogen, van Duijneveldt's[14] (4s) basis set was employed. The calculations were performed using the Gamess package of codes.[15]

Calculations for Mo_2 Dimer

The geometry optimizations of ethylene–Mo_2 and butadiene–Mo_2 complexes depend strongly on the proper description of the Mo—Mo bond. The equilibrium geometry of Mo_2 is very sensitive to theoretical methods and basis sets employed. Mo_2 calculations serve also as a performance test for relativistic effective core potentials used in the current calculations. Spectroscopic studies[16] on the gas phase species lead to the equilibrium distance R_e = 1.928 Å for Mo_2, which is shorter than any other known Mo–Mo quadruple bond.[17] The predicted bond order in the Mo_2 dimer, based on the overlap population analysis, is 6[7,18] with two σ molecular orbitals and a δ orbital supplementing the well-known $\sigma_g^2\pi_u^4\delta_g^2$ quadruple bond. The available *ab initio* calculations gave bond distances between 1.87 and 2.1 Å, indicating difficulties with the proper reproduction of geometries.

We have optimized the geometry of Mo_2 by applying the SCF and MCSCF approaches. The calculations were performed with relativistic effective core potentials[11] which retained 14 electrons of the molybdenum atom ($4s^2 4p^6 4d^5 5s^1$) in the valence space. Several basis sets were prepared from the ones proposed by LaJohn et al.[11] by leaving the most diffuse exponents uncontracted according to the schemes given in Table 1. At both CASSCF

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Table 1. Theoretical and Experimental Bond Distances in Mo_2 (Å)

basis set	this work SCF	this work CASSCF	other theoretical	exptl
(5s5p4d) → [5s5p3d]	1.906	1.918		1.929[a]
(5s5p4d) → [3s3p2d]	1.903	1.923		
			1.87[b]	
			1.88[c]	
			1.97[d]	
			2.1[e]	

[a] Reference 16. [b] Reference 20; SCF with ECP. [c] Reference 21; SCF. [d] Reference 7; CI. [e] Reference 18; MCSCF.

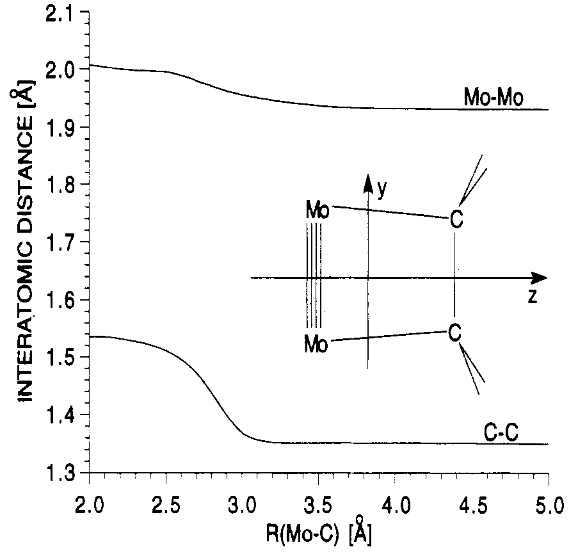

Figure 1. Mo—Mo and C—C bond distance variations for the symmetry-concerted reaction of Mo_2–Eth complex formation.

and CI stages, excitations from the 4s and 4p core orbitals were not allowed although these orbitals were allowed to relax. In the CASSCF calculations, twelve outermost electrons of Mo_2 were distributed in all possible ways among the active space of nine orbitals. This choice of active space corresponds to six highest occupied molecular orbitals and three lowest unoccupied orbitals. The active space consisted of two σ_g, two π_u, two π_g, and two δ_g orbitals and one σ_u orbital for Mo_2. Although this active space is sufficient to predict the potential minima, it is small for the computation of D_e of Mo_2. Twelve electrons were distributed in all possible ways among these orbitals. As seen from Table 1, the bond distances obtained using the CASSCF method with RECPs are in excellent agreement with experimental bond lengths. The SCF bond lengths obtained with the same basis are also reasonably close to the experimental value. The $\sigma_g^2\pi_u^4\delta_g^4\sigma_g^2$ leading configuration in the CASSCF near the equilibrium geometry is the same as the one predicted by others.[7,18]

Geometry Optimization of Mo_2–Ethylene and Mo_2–Butadiene Complexes

The geometry of the Mo_2–ethylene complex has been optimized assuming C_{2v} symmetry along the reaction pathway (Figure 1). The optimization has been performed at the SCF level. The C—C, Mo—Mo, and Mo—C bond distances at equilibrium are 1.53, 2.00, and 2.16 Å, respectively. The calculated C—C bond distance in the complex corresponds to a C—C single bond.[22] The Mo—Mo bond in the complex is 0.07 Å longer than the one in the Mo_2 dimer and corresponds to an average elongation of the bond after a single bond is broken. The calculated Mo—C distances are close to the bonds known from organometallic compounds containing molybdenum.[5] The optimized bond distances at the dissociation limit (C—C = 1.35 Å, Mo—Mo = 1.93 Å) are in agreement with the bond lengths found in ethylene[22] and the Mo_2 dimer.[16] The optimized structure of the Mo_2–Et complex has a dipole moment of 2.77 D, which is related to a significant charge transfer from the molybdenum atom to the carbon atoms amounting to 0.13 electron.

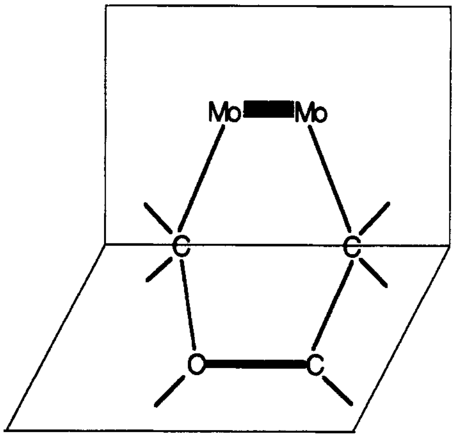

Figure 2. Optimized structure of the Mo_2–butadiene complex. The Mo—Mo, Mo—C, C—C, and C=C distances in the complex are 2.12, 2.34, 1.39, and 1.47 Å, respectively. The optimized angle between the two planes is 79.9°. The Mo—Mo, Mo—C, and C—C bond distances of the Mo_2–ethylene complex are 2.00, 2.16, and 1.53 Å, respectively.

The optimization of the Mo_2–butadiene complex has been performed for the equilibrium geometry assuming the C_s symmetry. Butadiene and Mo_2 lie in two planes, with outer carbons of butadiene lying at the intersection of planes (see Figure 2). The optimized angle between the two planes is 79.9°. The Mo—Mo distance in the Mo_2–But complex (2.12 Å) is similar to that of the Mo–Mo quadruple bonds.[21] Bonds in butadiene skeleton have been relaxed compared to those in the free butadiene molecule and are 1.39 Å for the newly created double bond and 1.47 Å for single bonds. The calculated Mo—C bond distance of 2.34 Å compares well with the bonds found in organomolybdenum compounds.[8] The Mo_2–But complex is not as rigid as Mo_2–Eth, and the strain in a newly formed six-member ring is much smaller than that in a four-member ring of the Mo_2–Eth complex. As will be shown later, these geometrical differences affect the energetics of the symmetry-concerted reactions leading to the formation of studied organometallic compounds.

The CASSCF computations of the Mo_2 + butadiene reaction included four a′ orbitals and two a″ orbitals in C_s symmetry. The six active electrons were distributed in all possible ways among these orbitals. The first-order configuration interaction (FOCI) method included all configurations in the CASSCF plus configurations obtained by distributing one electron in the orthogonal external space in all possible ways, simultaneously distributing the remaining five electrons in the CASSCF internal space.

Interactions of Mo_2 with Ethylene

In analogy to the dimerization of ethylene, ethylene–Mo_2 cyclization can be regarded as a reaction which preserves the C_{2v} symmetry. The Mo_2 dimer has a number of low-lying closed-shell states which may interact with the ground state of ethylene (X^1A_g). The stable complex is formed by the $\pi_u^4\sigma_g^2\delta_g^2\sigma_g^2\sigma_u^2$ valence configuration of Mo_2, which is higher in energy. The ground state SCF potential curve has a significant barrier of 31.0 kcal/mol, formed due to an avoided crossing at a Mo—C distance of 2.7 Å. A simple model such as the closed-shell SCF approach

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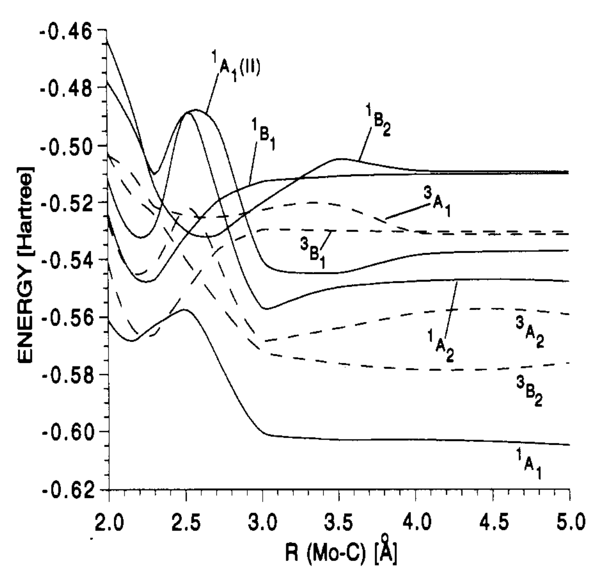

Figure 3. CASSCF potential surfaces for the C_{2v}-concerted reaction of Mo_2 with ethylene. 1 hartree = 27.211 eV = 635.6 kcal/mol.

shows that potential surfaces between 2.0 and 3.0 Å have very complicated structures with a large number of avoided crossings.

The potential energy surfaces for the interactions of Mo_2 with ethylene and butadiene were studied within the CASSCF formalism. As noted above, the active space is sufficiently flexible to yield reasonable spectroscopic constants near the minima. While the dissociation energies tend to depend more heavily on higher-order correlation effects, qualitative description of such large-scale systems is possible within the CASSCF approach. This was already demonstrated in a recent study on the Pt + CO system.[23] However, in the current study, the more accurate FOCI method, which includes higher-order correlation effects, was used for semiquantitative estimation of the dissociation energies. It should also be noted that the computations of the dissociation energies of the Mo_2–Eth and Mo_2–But complexes are easier and less intensive compared to computing the D_e of Mo_2.

The CASSCF computations of the Eth–Mo_2 system were made in C_{2v} symmetry. The active space consisted of six orbitals (three HOMOs and three unoccupied orbitals) which spanned three a_1 orbitals, two b_1 orbitals, and one b_2 orbital in the C_{2v} group. Six active electrons were distributed in all possible ways among these orbitals. The FOCI computations included all CASSCF configurations plus those configurations obtained by distributing five electrons in the internal space and one electron in the orthogonal external space in all possible ways.

Potential Energy Surfaces for the Interactions of Mo_2 with Ethylene and 1,3-Butadiene

The low-lying electronic states for the symmetry-concerted reaction (C_{2v}) of Mo_2 with ethylene are shown in Figure 3. Due to strong interactions between the electronic states, the potential energy surfaces are often irregular. Similar to those of the diabatic SCF model, the curves change their characteristic around a Mo—C distance of 2.7 Å. The CASSCF ground state curve ($^1A_1$) changes its character along the dissociation pathway, and the valence configuration of $a_1^2b_2^2b_1^2a_1^2$ near the equilibium geometry is replaced by a $a_1^2b_1^2a_1^2a_1^2$ near the dissociation limit. The lowest excited state of $^1A_1$ symmetry also corresponds to a closed-shell configuration. The nature of the state is very similar to that of the ground state; namely, different configurations contribute to it at the equilibrium geometry ($a_1^2b_2^2a_1^2b_2^2$) and the dissociation limit ($a_1^2b_2^2a_1^2a_1^2$) in the CASSCF wave function. The configurations contributing to the ground and lowest excited states are different, however. The complicated structure of both these curves is due to interactions with higher states. The energy barrier for the ground state reaction is 6 kcal/mol when calculated within the CASSCF model. Calculations with the first-order configuration interaction (FOCI) formalism lead to a barrier of 28.6 kcal/mol. The energies of the dissociation products, however, lie much lower than the energy minimum of the complex, and the dissociation energy is −22.97 kcal/mol (CASSCF) or −17.64 kcal/mol (FOCI). The reaction is thermally forbidden. The reaction is photochemically allowed and may proceed in many different excited electronic states which lead to the bonding structure. The $^3B_1$ state leads to a structure geometrically and energetically very close to the ground state.

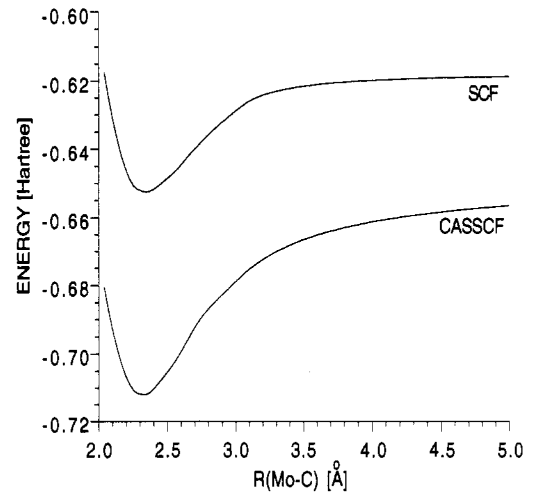

Figure 4. CASSCF and SCF ground state potential surfaces of the Mo_2 and 1,3-butadiene reaction. 1 hartree = 27.211 eV.

The $^1B_1$ state is qualitatively similar but higher in energy. The lowest $^3B_2$ excited state is repulsive (Figure 3). As seen from Figure 3, excited states of Mo_2 + ethylene such as $^1A_1$(II) and $^1A_2$ exhibit prior to the formation of a second long-range minimum or dissociation. The first set of minima in $^1A_2$, $^3B_1$, $^1B_1$, and $^3A_2$ are qualitatively similar to the $^1A_1$ state's minimum. Most of the electronic states shown in Figure 3 exhibit barriers to dissociation; while some of the excited states are considerably higher in energy, the $^3B_1$ state is certainly not very far from the $^1A_1$ state, which is believed to be the ground state.

The reaction of Mo_2 with 1,3-butadiene has been studied for the ground state only. Since we optimized the geometry for the equilibrium structure only, the complex was dissociated by keeping Mo_2 and butadiene geometries unchanged. In contrast to the ground state potential curve of the Mo_2–Eth complex, the MO_2 + butadiene complex curve (Figure 4) has a regular shape without any energy barrier. At the CASSCF level, the dissociation energy is 34.9 kcal/mol. The dissociation energy calculated using the FOCI method amounts to 50.3 kcal/mol. Compared to the CASSCF, the FOCI method includes more electron correlation effects. We expect the FOCI D_e to increase further if more electron correlation effects are included. Note that the equilibrium geometry of the complex is fully optimized while the geometries of the dissociated fragments were not fully optimized. Thus, D_e would be overestimated by a few kcal/mol, which however would be offset by the electron correlation effects.

A previous study[26] employed the same basis set for Mo and the CASSCF/CI technique to compute the properties of MoH and MoH^+. The $D_0^0(MoH^+)$ obtained using the theoretical method is 41.0 kcal/mol, in almost exact agreement with the D_0 value of 41 ± 3 kcal/mol reported by Schilling et al.[27] Due to the similarity of the Mo—H and Mo—C σ bonds, we expect the Mo—C σ bonds in the Mo–butadiene and Mo–Eth complexes to

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be computed with good accuracies. The complex formation reaction is thermally allowed.

The computed potential energy surfaces reveal significant differences between interactions of Mo_2 with ethylene and butadiene. The Mo_2–Eth reaction is thermally forbidden and the complex is formed in the excited states, while the formation of Mo_2–But proceeds in the ground state potential energy surface spontaneously. These results are in agreement with a simple model of symmetry-concerted reactions[25,26] based on symmetry considerations of molecular orbitals, in analogy to the Diels-Alder reaction between olefins.

Conclusion

Geometry optimizations of complexes between Mo_2 and ethylene and 1,3-butadiene lead to structures with elongaed Mo—Mo bonds similar to the one found in organometallic compounds containing molybdenum. The C—C bond distances change due to the rearrangement of π electrons. Calculated bond distances agree well with chemical intuitions. The C—C bond in the Mo_2–Eth complex became close to a C—C single bond. The butadiene ring gains one double bond in the C(2) position. The predicted Mo—C bond distance agrees with known distances in organometallic compounds composed of Mo.

Potential energy curves for the concerted reactions are very complicated due to many low-lying excited states of Mo_2. The formation of the Mo_2–Et complex is thermally forbidden in the $^1A_1$ ground state due to a significant barrier found in the potential energy surface. The reaction may however proceed in the excited state and requires irradiation of substrates to access many of the possible excited states leading to a stable complex. The $^1A_1$ ground state curve of Mo_2–But has no energy barrier and leads to a stable complex, thus the reaction is thermally allowed. The possible scenario of complex formation reactions deduced from the potential energies agrees with the model of symmetry-concerted reactions in full analogy to the Diels–Alder reaction between olefins.[24,25]

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