DOI: 10.1002/chem.200601839

Cycloaddition Reactions of 16-Electron d^4 Metallocene Complexes with C_{60}: A Theoretical Study

Jeng-Horng Sheu and Ming-Der Su*[a]

Abstract: The potential-energy surfaces of the cycloaddition reaction $Cp_2M + C_{60} \rightarrow Cp_2M(C_{60})$ ($Cp = \eta^5\text{-}C_5H_5$; M = Cr, Mo, and W) were studied at the B3LYP/LANL2DZ level of theory. Two competing reaction pathways were found, which can be classified as [6,5] attack (path A) and [6,6] attack (path B). Given the same reaction conditions, the [6,6]-attack pathway for cycloaddition to C_{60} is more favorable than the [6,5]-attack pathway, both kinetically and thermodynamically. A qualitative model, based on the theory of Pross and Shaik, was used to develop an explanation for the reaction barrier heights. Thus, our theoretical findings suggest that the singlet–triplet splitting ΔE_{st} ($=E_{triplet}-E_{singlet}$) of the 16-electron d^4 Cp_2M and C_{60} species are a guide to predicting their reactivity towards cycloaddition. Our model results demonstrate that the propensity for cycloaddition to C_{60} increases in the order $Cp_2Cr < Cp_2Mo < Cp_2W$. We show that both electronic and geometric effects play a decisive role in determining the energy barriers and reaction enthalpies.

Keywords: cycloaddition · density functional calculations · fullerenes · metallocenes · reaction mechanisms

Introduction

Since macroscopic amounts of buckminsterfullerene (C_{60})[1] are becoming increasingly accessible through easier and more economical methods of synthesis,[2] its derivatives have become the current focus of research into possible or future roles for fullerenes, especially in biological and materials science.[3] With twelve five-membered rings, twenty six-membered rings, and thirty double bonds in contiguous conjugation, buckminsterfullerene has the potential for varied organometallic chemistry.[4] In fact, organometallic derivatives of C_{60} formed by addition reactions are highly attractive to chemists.[5] Many transition metal C_{60} complexes have been synthesized and structurally characterized.[6] The reason for the fast development of organometallic complexes of C_{60} is that they are expected to be new materials with intriguing properties.[7] Indeed, synthesis, characterization, and properties of various organometallic $\eta^n\text{-}C_{60}$ ($n = 1$–6) complexes have been the subject of recent studies.[8]

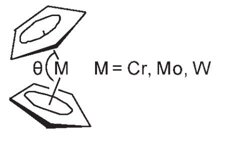
About a decade ago, Green et al. reported the first C_{60} derivatives of a metallocene, namely, $[Mo(\eta^5\text{-}C_5H_4R)_2(\eta^2\text{-}C_{60})]$ (R = H, *n*Bu).[9] They also proposed that such metallocenes may bond to C_{60} at one of its 30 equivalent double bonds, which occur at the fusion of two six-membered rings. However, to the best of our knowledge, no other experimental data for such reactions, or the species involved, have been reported in the literature. In addition, no theoretical study concerning the cycloaddition of metallocene complexes to C_{60} has appeared to date, let alone a systematic theoretical study of geometrical effects on the reactivity of such metallocene species.

It is these unsolved problems that inspired this study. What is the mechanism for the cycloaddition of metallocene species to C_{60}? What are the energies and structures of the transition states of the reactions? If a molybdocene can undergo C−C bond addition with C_{60}, would it be possible to extend this to other 16-electron d^4 metallocene-type complexes? If this is possible, which transition metal center bearing two cyclopentadienyl (Cp) ligands has the lowest activation energy, and therefore can undergo cycloaddition reaction with C_{60} fastest? As mentioned above, neither experimental nor theoretical studies have been performed on these systems to date.

We thus undertook a systematic investigation of metallocene additions to C_{60} in order to estimate the energetic feasibility of possible reaction pathways, and to assess the

---

[a] Dr. J.-H. Sheu, Prof. Dr. M.-D. Su
Department of Applied Chemistry
National Chiayi University
Chiayi 60004 (Taiwan)
E-mail: midesu@mail.ncyu.edu.tw



1

extent of involvement of the transition metal fragments. We investigated the addition of chromocene (Cp_2Cr), molybdocene (Cp_2Mo), and tungstocene (Cp_2W) to C_{60}. The most relevant geometrical parameter θ for these complexes is defined in **1** (i.e., the Cp-M-Cp angle; Cp = centroid of the Cp ring).

Through this theoretical study, we hope 1) to obtain a detailed understanding of C_{60} addition to 16-electron d^4 metallocenes, 2) to investigate the influence of the bending angle θ on the geometries and energies of the intermediates and transition states, 3) to elucidate the differences among the transition metals Cr, Mo, and W, and 4) to investigate the factors controlling the activation barrier. This study is intended to describe the most significant features of the potential-energy surface of the systems. As the first comprehensive examination of the systems, this paper should provide a firm basis for further study, both experimental and computational.

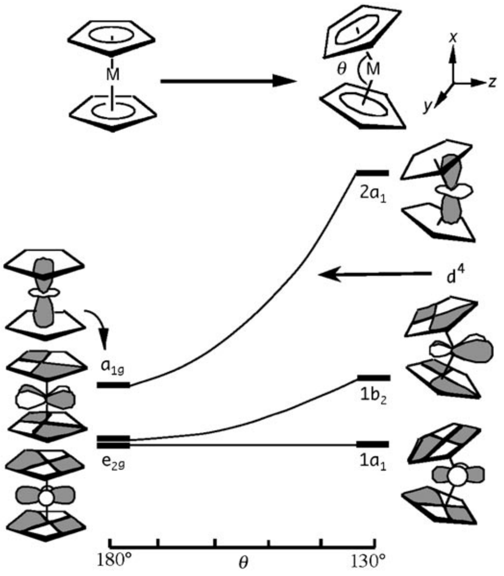


Figure 1. Walsh diagram for bending back of the Cp rings in the Cp_2M fragment.

Computational Details

All geometries were fully optimized without imposing any symmetry constraints, although in some instances the resulting structures showed various elements of symmetry. Density functional theory (DFT) was employed with the three-parameter hybrid exchange functional of Becke[10] and the Lee, Yang, and Parr correlation functional,[11] commonly known as B3LYP. Calculations were carried out with relativistic effective core potentials on group 6 elements modeled with double-zeta (DZ) basis sets.[12] Thus, the model compounds $Cp_2M{\cdot}C_{60}$ have 540 (444 electrons) basis functions for M = Cr, Mo, and W. Moreover, the restricted B3LYP approach was used in this work to describe all the stationary points, except for the triplet states of the reactants, which were described by unrestricted wave functions. Hence, all the B3LYP calculations are denoted by B3LYP/LANL2DZ. Vibrational frequency calculations at the RHF/LANL2DZ level were used to characterize all the stationary points as either minima (no imaginary frequencies) or transition states (one imaginary frequency). Then these stationary points were further calculated at the B3LYP/LANL2DZ level by using the opt = readfc keyword. Due to the limitation of both available CPU time and memory size, the B3LYP zero-point energy (ZPE) could not be applied for all of the $CP_2M{\cdot}C_{60}$ systems in the present work, that is, because frequencies were not calculated for all species at the B3LYP/LANL2DZ level of theory, ZPE corrections were not performed. Nevertheless, the addition of these corrections would not change our conclusions. All the calculations were performed with the Gaussian 03 package of programs.[12]

Electronic Structure of Metallocenes

We analyzed the electronic structures of the d^4 C_{2v} Cp_2M. The frontier orbitals of the 16-electron Cp_2M fragment are known[13,14] and are shown in Figure 1. A block of three occupied levels, $1a_1$ (y^2-z^2), $1b_2$ (xy), and $2a_1$ (z^2) exist at low energy. These are primarily made up of metal d orbitals. Some metal $d_{y^2-z^2}$ and s character from $1a_1$ mixes into $2a_1$, so that the torus of d_{z^2} is hybridized away from the Cp ligands. Basically, the Dewar–Chatt–Duncanson model has been used to describe the bonding of a side-on coordinated π ligand to a transition metal fragment.[15] Based on this model, the bonding can be described in terms of donation of an electron from a filled π ligand orbital into a suitable vacant metal d orbital resulting in a σ-donation effect. Also, backdonation may occur from an occupied metal d orbital to a vacant π* ligand orbital leading to a π-backdonation effect. As a result, one may imagine that the major intersections between the frontier molecular orbitals of the d^4 C_{2v} Cp_2M fragment and those of C_{60} should be mainly on the $1b_2$ orbital of the transition metal fragment (see below).

Geometries and Energies of Metallocene+C_{60}

We present computational results for four regions on the potential-energy surfaces: 16-electron d^4 Cp_2M (M = Cr, Mo, and W) plus free C_{60} (Rea), the precursor complex (PC), the transition state (TS), and the cycloaddition product (Pro). The fully optimized geometries for these stationary points, calculated at the B3LYP/LANL2DZ level, are shown in Figures 2–5, respectively. To simplify comparison and emphasize trends, we also give the energies relative to the two reactant molecules, $Cp_2M + C_{60}$, in Table 1. Cartesian coordinates calculated for the stationary points at the B3LYP level are available as Supporting Information.

The 16-electron d^4 Cp_2M systems and C_{60}: Reactants Cp_2M (M = Cr, Mo, and W) were calculated both as low-spin (singlet) and as high-spin (triplet) species.[16] Unfortunately, to our knowledge, at present no experimental data for the Cp_2M and their derivatives are available for comparison. Nevertheless, it is clear from Figure 1 that in the triplet state

Table 1. Relative energies [kcal mol^{-1}] for singlet and triplet 16-electron d^4 Cp_2M fragments with C_{60} and for the process $Cp_2M + C_{60} \rightarrow$ precursor complex → transition state → cycloadduct.[a]

	ΔE_{st}[b]	ΔE_{cpx}[c]	ΔE_{act}[d]	ΔH[e]
Cp_2Cr				
[6,5] attack	−21.49	−0.8800	+28.58	+27.08
[6,6] attack	−21.49	−0.8800	+16.83	+10.80
Cp_2Mo				
[6,5] attack	−24.10	−10.78	−4.410	−21.25
[6,6] attack	−24.10	−10.78	−6.144	−39.96
Cp_2W				
[6,5] attack	−20.23	−5.942	−3.861	−29.94
[6,6] attack	−20.23	−5.942	−4.214	−49.92

[a] At the B3LYP/LANL2DZ level; see text. [b] Energy relative to the corresponding singlet state. A negative value means the triplet is the ground state. [c] Stabilization energy of the precursor complex relative to the corresponding reactants. [d] Activation energy of the transition state relative to the corresponding reactants. [e] Reaction enthalpy of the product relative to the corresponding reactants.

one electron is situated in the $2a_1$ orbital, in which antibonding interactions exist between the metal center and the Cp ring, whereas this orbital is empty in the singlet state. The distance r(M−X) between the metal atom and the center X of the Cp ring and the angle ∢(X-M-L) are therefore expected to be larger for the triplet state than for the singlet. This prediction agrees qualitatively with our B3LYP/LANL2DZ results in all cases, as shown in Figure 2. For instance, the B3LYP distances r(M−X) and bond angles ∢(X-M-L) are (1.911 Å, 178.9°), (1.950 Å, 149.6°), and (1.917 Å, 152.6°) for singlet Cp_2Cr, Cp_2Mo, and Cp_2W, respectively, and (1.877 Å, 178.7°), (2.028 Å, 177.1°), and (1.991 Å, 176.5°) for triplet Cp_2Cr, Cp_2Mo, and Cp_2W, respectively. In fact, as already shown in Figure 1, for a high-spin d^4 complex with configuration $(1a_1)^2(1b_2)^1(2a_1)^1$, the Walsh diagram predicts that a parallel-ring structure is preferred, which has been confirmed by some experimental observations,[17] for example, IR and UV matrix-isolation studies[17b] have shown Cp_2W to have a parallel sandwich structure with a $^3E_2$ ground state. Based on these results, it is thus expected that the singlet state of the d^4 Cp_2M system should be more bent than its triplet analogue. Again, this prediction is in accordance with our B3LYP/LANL2DZ results in all cases (Figure 2). The preference of singlet metallocenes for the bent structure is also consistent with the work of Green and Jardine.[18]

Moreover, the DFT calculations indicate that all the 16-electron d^4 Cp_2M fragments have a triplet ground state with the singlet–triplet splittings ΔE_{st} $(=E_{triplet}-E_{singlet})$ of −21.5, −24.1, and −20.2 kcal mol^{-1} for Cp_2Cr, Cp_2Mo, and Cp_2W, respectively. Again, the reason for this can be easily understood from Figure 1. In the bent, singlet state, the HOMO ($1b_2$) is destabilized as the bending angle θ decreases, the LUMO ($2a_1$) increases in energy, and the HOMO–LUMO gap in the bent d^4 Cp_2M complex widens. Thus, the energy gap between HOMO and LUMO for the d^4 Cp_2M singlet species is strongly dependent on the bending angle θ. We use the above results to explain the origin of barrier heights for their cycloaddition to C_{60} below.

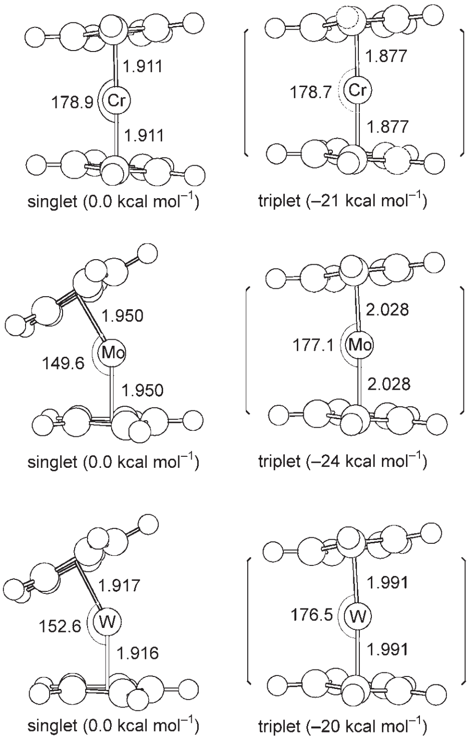


Figure 2. B3LYP/LANL2DZ optimized geometries [Å, °] of the reactants (singlet and triplet) of Cp_2Cr, Cp_2Mo, and Cp_2W.

Adoption of triplet ground states by the metallocene reactants implies that they might add to a C=C bond of C_{60} by a diradical-type mechanism. Furthermore, it is well established that whenever a reactant contains a heavy atom, which is not necessarily directly involved in the reaction, strong spin–orbit coupling (SOC) may occur.[19,20] Thus, a triplet reactant, via the agency of the heavy atom, can undergo a spin-inversion process to the singlet state and thence proceed along the singlet reaction pathway. Additionally, our B3LYP results (Table 1) also indicate that reactants with a triplet ground state would have a small excitation energy to the first singlet state ($\Delta E_{st} = -24$ to -20 kcal mol^{-1} at the B3LYP level of theory). Accordingly, since the Cp_2M (M = Cr, Mo, and W) species have small ΔE_{st} and a heavy transition metal is involved, SOC is expected to be substantial, and would obscure distinctions between singlet and triplet. Therefore, the cycloaddition of d^4 Cp_2M to C_{60} may proceed on the singlet surface, even if the reactants start from the triplet state. We thus focus on the singlet surface from now on.

On the other hand, although every carbon atom in C_{60} is chemically equivalent, buckminsterfullerene has two different types of C−C bonds.[6b,21] One type occurs at the six–six ring-fusion sites ([6,6] bond), and the other at the six–five ring-fusion sites ([6,5] bond). There are no five–five ring-fusion sites. Thus, two derivatives of C_{60} could, in principle, be obtained by addition of transition metal complexes to buckminsterfullerene (see below). We thus performed a geometry optimization on the free buckminsterfullerene molecule under I_h symmetry constraints. The computed values of 1.404 and 1.464 Å for the [6,6] and [6,5] bonds, respectively, are very close to the experimental values of 1.401 and 1.458 Å from electron diffraction[17a] and 1.391 and 1.455 Å from neutron powder diffraction.[17b] Because of the good agreement between DFT (B3LYP) and experimental data of buckminsterfullerene, we are confident that the computational methods used in this study are reliable.

The precursor complex: As shown in Figures 3–5, all precursor complexes (PC-Cr, PC-Mo, and PC-W) have very similar $Cp_2M–C_{60}$ bonding characteristics. The buckminsterfullerene ligand is coordinated to the transition metal atom in an η^2 fashion via two M−C σ bonds. The distance between the transition metal atom and the two Cp rings in the metallocene moiety is elongated (1.917, 1.972, and 2.028 Å for Cp_2Cr, Cp_2Mo, and Cp_2W, respectively, compared to 1.795, 1.950, and 1.917 Å in the corresponding free metallocenes). The M−C distance to C_{60} in the precursor complexes PC-Cr, PC-Mo, and PC-W is 4.523, 3.834, 4.587 Å, respectively. As shown in Table 1, in the first step the reactants yield a precursor complex with stabilization energies of 11 and 5.9 $kcal\,mol^{-1}$ at the B3LYP/LANL2DZ level for PC-Mo and PC-W, respectively, which are much larger than that of PC-Cr (0.88 $kcal\,mol^{-1}$). Large M−C distances correlate with low values of the intermediate stabilization energy. Due to such low stabilization energies, it seems that experimental detection of intermediates formed in the gas phase at room temperature is quite challenging.

The transition state: The TS geometries for the additions of d^4 Cp_2M (M = Cr, Mo, and W) to buckminsterfullerene are given in Figures 3–5, respectively. Since C_{60} has two different types of chemical bonds, the approaching metallocene may attack either. Thus, it rearranges either into a [6,5] cycloadduct via [6,5] attack (path A) or into a [6,6] cycloproduct via [6,6] attack (path B).

For path A, we located transition states [6,5]-TS-Cr, [6,5]-TS-Mo, and [6,5]-TS-W at the B3LYP/LANL2DZ level of theory, along with the imaginary frequency eigenvector (see Figures 3–5). These reactions appear to be concerted; we were able to locate only one TS for each reaction, and have confirmed that it is a true TS on the basis of frequency analysis. The RHF/LANL2DZ frequency calculations for the transition states [6,5]-TS-Cr, [6,5]-TS-Mo, and [6,5]-TS-W give single imaginary frequencies of 165i, 152i, and 260i cm^{-1}, respectively. As shown in Figures 3–5, the major component of the [6,5]-TS vibrational mode is located at the transition metal and two connected carbon atoms.

For path B, the TS geometries for [6,6] attack are depicted in Figures 3–5, respectively. All these TSs have one imaginary frequency and are true first-order saddle points. Our RHF/LANL2DZ calculations gave frequencies of 173i, 236i, and 270i cm^{-1} for [6,6]-TS-Cr, [6,6]-TS-Mo, and [6,6]-TS-W, respectively. As shown in Figures 3–5, the main component of the [6,6]-TS vibrational mode corresponds to displacement of the metallocene towards a double bond in C_{60} with formation of a three-membered cycloadduct.

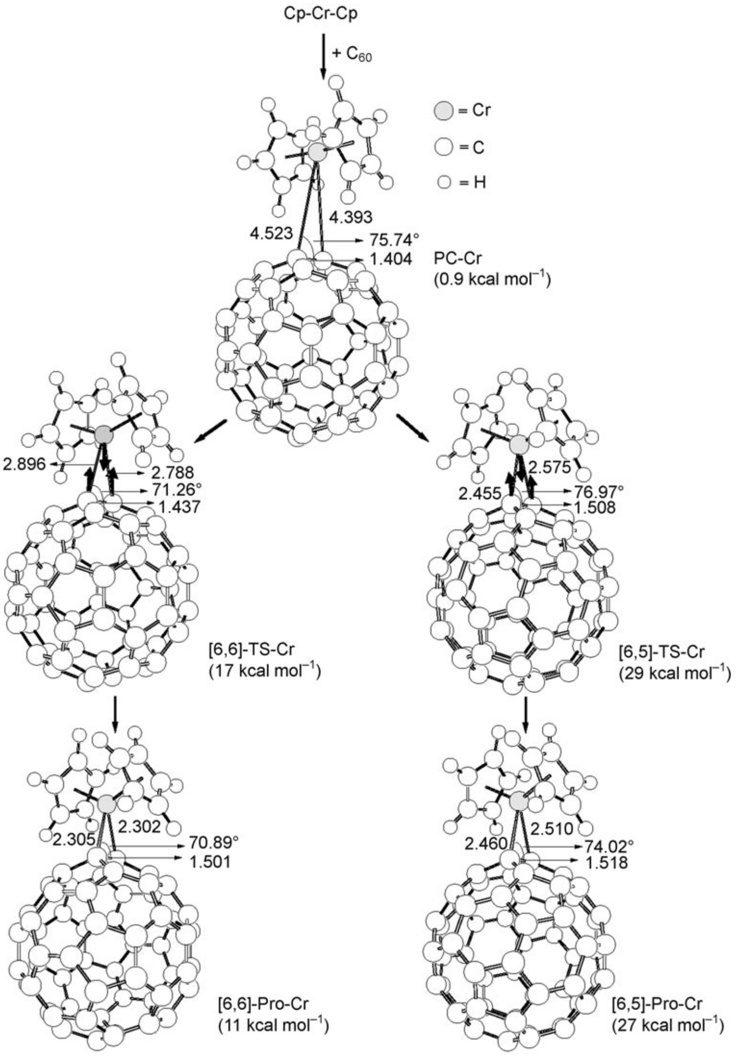


Figure 3. B3LYP/LANL2DZ optimized geometries [Å,°] of the precursor complex, transition states, and products for Cp_2Cr. The bold arrows indicate the main atomic motions in the transition-state eigenvector.

Of the two possible routes for C_{60} cycloaddition reactions with Cp_2M, the most promising is path B ([6,6] attack), which has a lower activation energy than path A ([6,5] attack). For example, the barrier heights of paths A and B show the following trend: [6,6]-TS-Cr (16 $kcal\,mol^{-1}$) < [6,5]-TS-Cr (28 $kcal\,mol^{-1}$), [6,6]-TS-Mo (4.6 $kcal\,mol^{-1}$) < [6,5]-TS-Mo (6.4 $kcal\,mol^{-1}$), and [6,6]-TS-W (1.7 $kcal\,mol^{-1}$) < [6,5]-TS-W (2.1 $kcal\,mol^{-1}$). Accordingly, our model calculations strongly indicate that cycloadditions of metallocenes to C_{60} should produce a majority of the [6,6] cycloadduct via [6,6] attack, with some [6,5] cycloproduct via [6,5] attack.

Furthermore, it is clear from Table 1 and Figures 3–5 that the calculated activation energies for cycloadditions is substantially lower for W than for Cr and Mo. For instance, at the B3LYP level of theory, the barrier height for metallocene addition increases in the order: [6,6]-TS-Cr (16) > [6,6]-

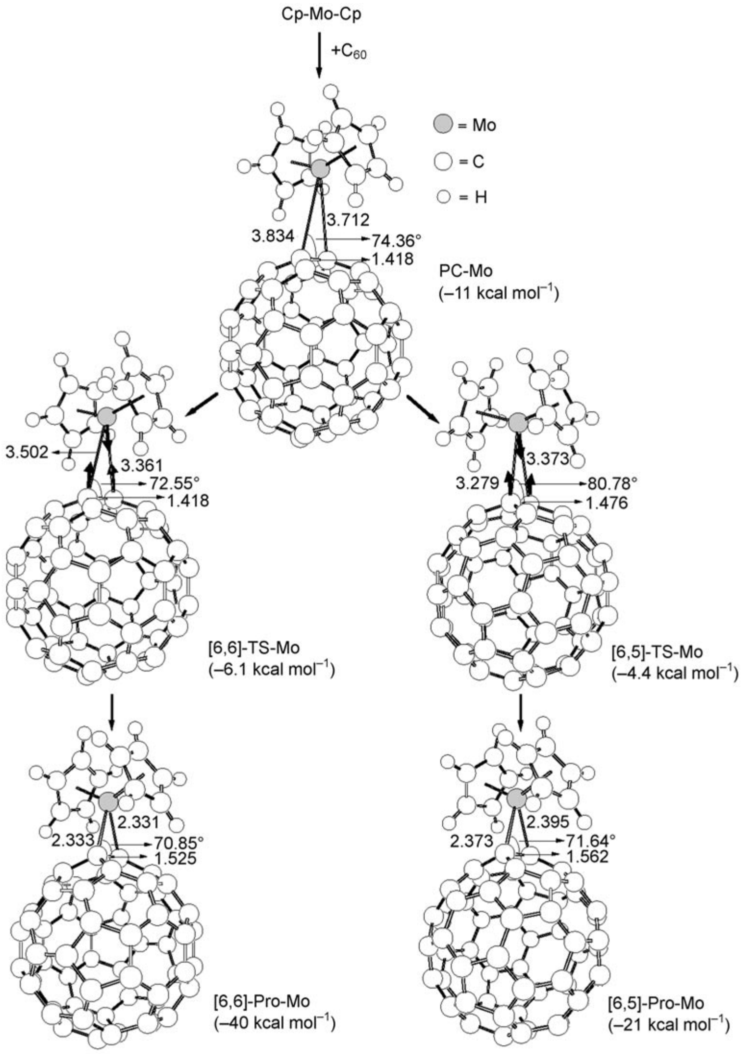


Figure 4. B3LYP/LANL2DZ optimized geometries [Å, °] of the precursor complex, transition states, and products of Cp_2Mo case. The bold arrows indicate the main atomic motions in the transition-state eigenvector.

TS-Mo (4.6) > [6,6]-TS-W (1.7 $kcal\,mol^{-1}$) and [6,5]-TS-Cr (28) > [6,5]-TS-Mo (6.4) > [6,5]-TS-W (2.1 $kcal\,mol^{-1}$). Accordingly, our calculations suggest that the most favorable reaction is C_{60} cycloaddition with d^4 Cp_2W.

In the [6,5]-TS in Figures 3–5, the forming M–C bond is stretched on average by 1.2, 40, and 45% in [6,5]-TS-Cr, [6,5]-TS-Mo, and [6,5]-TS-W, respectively, relative to its corresponding three-membered cycloadduct. Similarly, the forming M–C bond is stretched on average by 23, 47, and 53% relative to its equilibrium value for [6,6]-TS-Cr, [6,6]-TS-Mo, and [6,6]-TS-W, respectively; that is, the barrier is encountered earlier in the reactions with Cp_2Mo and Cp_2W than in the reaction with Cp_2Cr. Additionally, these values also suggest that the structures of the [6,6]-TS are more reactantlike, whereas those of the [6,5]-TS are more productlike. Taken together, a metallocene with a more massive but less electronegative central atom reaches the TS relatively early, whereas a metallocene with a less massive and more electronegative central atom arrives relatively late. The former is therefore predicted to undergo a more exothermic addition, which is borne out by our DFT calculations (see below).

Furthermore, as shown in Table 1 and Figures 3–5, the energies of the transition states for [6,5] attack and [6,6] attack lie below those of the corresponding reactants only in the cases of molybdenum and tungsten. This strongly implies that a d^4 metallocene will undergo cycloaddition to C_{60} in a concerted manner, especially for Cp_2Mo and Cp_2W, and thus the stereochemistry of their final three-membered cycloproducts should be preserved. As there are no relevant experimental and theoretical data on such systems, the above conclusion is a prediction.

The cycloadducts: The optimized structures of products [6,5]-Pro-Cr, [6,6]-Pro-Cr, [6,5]-Pro-Mo, [6,6]-Pro-Mo, [6,5]-Pro-W, and [6,6]-Pro-W are shown in Figures 3–5. Calculated reaction enthalpies for cycloaddition are summarized in Table 1.

The order of reaction enthalpy for the cycloaddition of C_{60} to a metallocene follows a similar trend to that of the activation energy. For example, the enthalpy for [6,5] attack decreases in the order [6,5]-Pro-Cr (+27.1 $kcal\,mol^{-1}$) > [6,5]-Pro-Mo (−21.3 $kcal\,mol^{-1}$) > [6,5]-Pro-W (−29.9 $kcal\,mol^{-1}$). Similarly, for [6,6] attack the reaction enthalpy decreases in the order [6,6]-Pro-Cr (−10.8 $kcal\,mol^{-1}$) > [6,6]-Pro-Mo (−40.0 $kcal\,mol^{-1}$) > [6,6]-Pro-W (−49.9 $kcal\,mol^{-1}$). Three intriguing points follow from the above. Firstly, our computational results suggest that the reaction enthalpy of [6,6] attack should be more exothermic than that of [6,5] attack. Secondly, from both a kinetic and a thermodynamic viewpoint, the chemical reactivity for C_{60} cycloadditions increases in the order: $Cp_2Cr < Cp_2Mo < Cp_2W$. Thirdly, the energies of [6,6]-Pro-Cr and [6,5]-Pro-Cr are above those of their corresponding starting materials. In consequence, we expect Cp_2Cr to be much more stable with respect to cycloaddition to a buckminsterfullerene than either Cp_2Mo or Cp_2W.

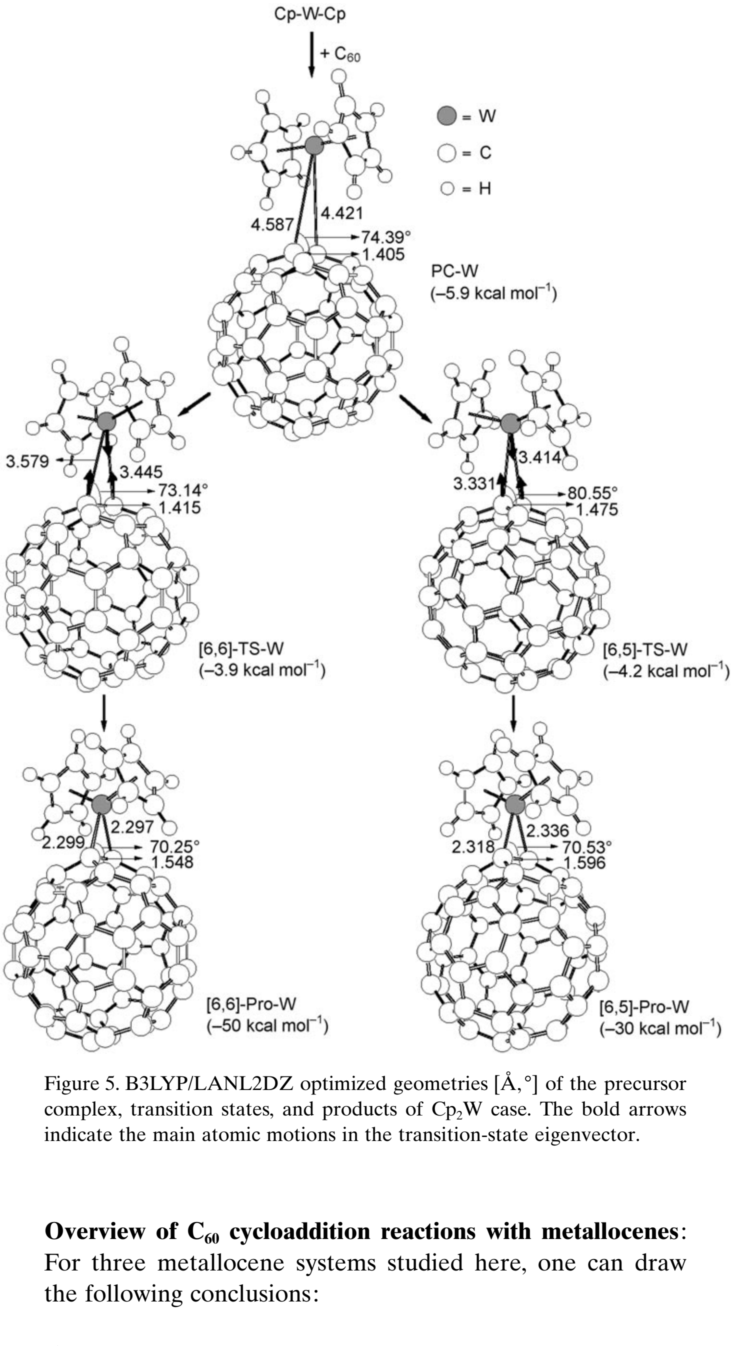


Figure 5. B3LYP/LANL2DZ optimized geometries [Å,°] of the precursor complex, transition states, and products of Cp_2W case. The bold arrows indicate the main atomic motions in the transition-state eigenvector.

Overview of C_{60} cycloaddition reactions with metallocenes: For three metallocene systems studied here, one can draw the following conclusions:

1) Based on the present theoretical calculations, a precursor complex for the cycloaddition of C_{60} to a metallocene will be difficult to observe.
2) The barriers for cycloaddition of both Cp_2Mo and Cp_2W to C_{60} are low. This strongly implies that both cycloadditions with C_{60} should be facile processes at room temperature.
3) For a given metallocene species, the activation barrier for [6,6] attack is smaller than that for [6,5] attack, that is, the former is kinetically more favorable than the latter. Accordingly, the yield of the product of [6,6] attack should be much larger than that of [6,5] attack.
4) Cycloaddition of C_{60} to metallocenes should produce a three-membered cycloadduct in a single step (i.e., in a concerted manner) stereospecifically. Such cycloaddition reactions favor products with stereoretention.
5) Given identical reaction conditions, [6,6] attack should be more exothermic than [6,5] attack. Consequently, the production of $Cp_2M(C_{60})$ compounds from on former pathway is thermodynamically favored.
6) Electronic and steric factors should play an important role in determining the chemical reactivity of metallocenes with C_{60} from both a kinetic and thermodynamic viewpoint.

In short, considering both activation barriers and reaction enthalpies calculated here, we conclude that the order of metallocene reactivity is $Cp_2Cr < Cp_2Mo < Cp_2W$.

The configuration mixing model: A tool for interpreting the relative reactivity of the reactants is provided by the configuration mixing (CM) model, which is based on the work of Pross and Shaik.[23,24] According to their conclusions, the energy barriers governing processes, as well as the reaction enthalpies, should be proportional to the singlet/triplet energy gaps for both metallocene and C_{60}, that is, ΔE_{st} ($= E_{triplet} - E_{singlet}$ for Cp_2M) $+ \Delta E_{\pi\pi^*}$ ($= E_{triplet} - E_{singlet}$ for C_{60}). We therefore conclude that both the order of the singlet and triplet states and their energy separation are responsible for the existence and the height of the energy barrier.[23,24] Bearing these analyses in mind, we now explain the origin of the following observed trends:

The W reaction is more favorable than the Cr and Mo reactions in the cycloaddition of C_{60} to metallocene The reason for this can be traced back to the singlet–triplet gap (ΔE_{st}) of a 16-electron d^4 Cp_2M. According to the available experiments,[25] both Cr and Mo atoms have a septet d^5s^1 ground state with high excitation energies of 22.1 and 31.4 kcal mol^{-1}, respectively, to the quintet d^4s^2 state. On the other hand, the ground state of the W atom is quintet d^4s^2, which has a relatively low excitation energy of 8.44 kcal mol^{-1} to the septet d^5s^1 state. This strongly implies that W prefers to remain in a high-spin state, whereas both Cr and Mo favor low-spin states. Indeed, if the bending angle θ in **1** is fixed at 145.0° and the other geometrical parameters are fully optimized, then our B3LYP/LANL2DZ results indicate that ΔE_{st} is -18.2, -20.7, and -22.4 for Cp_2Cr, Cp_2Mo, and Cp_2W, respectively, that is, ΔE_{st} of the W complex is less than those of the analogous Cr and Mo complexes. This suggests that cycloaddition of C_{60} to a metallocene should be easier and more exothermic for the W system than for either its Cr or Mo counterpart. This is what is observed in the 16-electron d^4 Cp_2M (M = Cr, Mo, and W) systems in the present work. Accordingly, our theoretical findings are in good accordance with the CM model.

Given identical reaction conditions, the [6,6]-attack path is more favorable than the [6,5]-attack path, both kinetically and thermodynamically. The driving force for this can be traced to ΔE_{st} of C_{60}. According to the CM model, a smaller ΔE_{st} for the fused two-ring system results in a lower barrier height and a larger exothermicity. Since C_{60} is too large and complicated for calculation, we chose $C_{10}H_8$ (naphthalene) and $C_9H_7^{-1}$ to mimic the fusion of two six-membered rings and a six- and a five-membered ring, respectively. Our B3LYP/LANL2DZ calculations gave ΔE_{st} of 59.0 and $55.4\,kcal\,mol^{-1}$ for $C_{10}H_8$ and $C_9H_7^{-1}$, respectively. This correlates well with the trend in both barrier heights and reaction enthalpies for [6,6] and [6,5] attack.

Conclusion

The CM approach gives extra insights into this relatively poorly understood area of mechanistic studies. Regardless of whether the metallocene or buckminsterfullerene is considered, knowledge of the singlet–triplet splitting is of great importance in understanding their reactivity, since it can affect the driving force for cycloadditions.

Although the relative reactivity of 16-electron d^4 metallocenes is determined by the entire potential-energy surface, the concept of the CM model, which focuses on the singlet–triplet splitting in the reactants, allows one to assess quickly the relative reactivity of a variety of metallocenes without specific knowledge of the actual energies of the interactions involved. Therefore, the energetic separation between the lowest singlet and triplet electronic states of a metallocene is perhaps the most critical parameter required for prediction of its reactivity. In spite of its simplicity, our approach can provide chemists with important insights into the factors controlling the activation energies for cycloaddition reactions to C_{60}, and thus permit them to predict the reactivity of some unknown substituted metallocenes. The predictions may be useful as a diagnostic tool in future synthetic studies and for indicating problems that merit further study by both theory and experiment. We hope that the present work will stimulate further research into this subject.

Acknowledgements

The authors are grateful to the National Center for High-Performance Computing of Taiwan for generous amounts of computing time. They also thank the National Science Council of Taiwan for financial support.

---

[1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **1985**, *318*, 354.

[2] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, *Nature* **1990**, *347*, 354; W. Krätschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, *Chem. Phys. Lett.* **1990**, *170*. 167.

[3] For a recent review on methanofullerenes, see: F. Diederich, L. Isaacs, D. Philp, *J. Chem. Soc. Rev.* **1994**, 243–255; for a recent report on possible biotechnological application of C_{60}, see: C. Wrotnowski, *Genet. Eng. News* **1994**, 36; for recent advances in C_{60} biological effects, see: a) W. Z. Li, K. X. Qian, W. D. Huang, X. X. Zhang, W. X. Chen, *Chin. Phys. Lett.* **1994**, *11*, 207–210; b) A. S. Boutorine, H. Tokuyama, M. Takasugi, H. Isobe, E. Nakamura, C. Helene, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2462–2465; c) A. W. Jensen, S. R. Wilson, D. I. Schuster, *Bioorg. Med. Chem.* **1996**, *4*, 767.

[4] For recent reviews, see: a) J. M. Hawkins, *Acc. Chem. Res.* **1992**, *25*, 150; b) P. J. Fagan, J. C. Calabrese, B. Malone, *Acc. Chem. Res.* **1992**, *25*, 134; c) A. Balch, M. M. Olmstead, *Chem. Rev.* **1998**, *98*, 2123; d) K. Kee, H. Song, J. T. Park, *Acc. Chem. Res.* **2003**, *36*, 78.

[5] a) A. H. H. Stephens, M. L. H. Green, *Adv. Inorg. Chem.* **1997**, *44*, 1; b) M. L. H. Green, A. H. H. Stephens, *Chem. Commun.* **1997**, 793; c) A. N. Chernega, M. L. H. Green, J. Haggit, A. H. H. Stephens, *J. Chem. Soc. Dalton Trans.* **1998**, 755.

[6] a) P. J. Fagan, J. C. Calabrese, B. Malone, *Science* **1991**, *252*, 1160; b) J. M. Hawkins, A. Meyer, T. A. Lewis, S. Loren, F. J. Hollander, *Science* **1991**, *252*, 312; c) A. L. Balch, V. J. Catalano, J. W. Lee, *Inorg. Chem.* **1991**, *30*, 3980; d) P. J. Fagan, J. C. Calabrese, B. Malone, *J. Am. Chem. Soc.* **1991**, *113*, 9408; e) A. L. Balch, V. J. Catalano, J. W. Lee, M. M. Olmstead, *J. Am. Chem. Soc.* **1992**, *114*, 5455; f) J. M. Hawkins, A. Meyer, T. A. Lewis, S. Loren, F. J. Hollander, *Science* **1991**, *252*, 312; g) A. L. Balch, J. W. Lee, B. C. Noll, M. M. Olmstead, *J. Am. Chem. Soc.* **1992**, *114*, 10984; h) V. V. Bashilov, P. V. Petrovskii, V. I. Sokolov, S. V. Lindeman, I. A. Guzey, Y. T. Struchkov, *Organometallics* **1993**, *12*, 991; i) A. L. Balch, J. W. Lee, B. C. Noll, M. M. Olmstead, *Inorg. Chem.* **1993**, *32*, 3577; j) I. P. Mavunkal, Y. Chi, S.-M. Peng, G.-H. Lee, *Organometallics* **1995**, *14*, 4454; k) K. Lee, H.-F. Hsu, J. R. Shapley, *Organometallics* **1997**, *16*, 3876; l) M. Sawamura, Y. Kuninonu, E. Nakamura, *J. Am. Chem. Soc.* **2000**, *122*, 12407; m) T. T. Park, H. Song, K. Lee, C. H. Lee, J. T Park, H. Y. Chang, M.-G. Choi, *Angew. Chem.* **2001**, *113*, 1548; *Angew. Chem. Int. Ed.* **2001**, *40*, 1500; n) M. Sawamura, Y. Kuninonu, M. Taganoh, Y. Matsuo, M. Yamanaka, E. Nakamura, *J. Am. Chem. Soc.* **2002**, *124*, 9354; o) Y. Matsuo, Y. Mitani, Y.-W. Zhong, E. Nakamura, *Organometallics* **2006**, *25*, 2826.

[7] For instance, see: a) N. Koga, K. Morokuma, *Chem. Phys. Lett.* **1993**, *202*, 330; b) J. Rogers, D. S. Marynick, *Chem. Phys. Lett.* **1993**, *205*, 197; c) D. L. Lichtenberger, L. L. Wright, N. E. Gruhn, M. E. Rempe, *Synth. Met.* **1993**, *59*, 353; d) H. Fujimoto, Y. Nakao, K. Fukui, *J. Mol. Struct.* **1993**, *300*, 425; e) J. A. López, C. Mealli, *J. Organomet. Chem.* **1994**, *478*, 161; f) D. L. Lichtenberger, L. L. Wright, N. E. Gruhn, M. E. Rempe, *J. Organomet. Chem.* **1994**, *478*, 213; g) C. Bo, M. Costas, J. M. Poblet, *J. Phys. Chem.* **1995**, *99*, 5914; h) F. Nunzi, A. Sgamellotti, N. Re, C. Floriani, *Organometallics* **2000**, *19*, 1628; i) L.-C. Song, J.-T. Liu, Q.-M. Hu, L.-H. Weng, *Organometallics* **2000**, *19*, 1643; j) E. D. Jemmis, M. Manoharan, P. K. Sharma, *Organometallics* **2000**, *19*, 1879; k) L.-C. Song, J.-T. Liu, Q.-M. Hu, G.-F. Wang, P. Zanello, M. Fontani, *Organometallics* **2000**, *19*, 5342; l) A. J. Babcock, J. Li, K. Lee, J. R. Shapley, *Organometallics* **2002**, *21*, 3940; m) Y. Kameno, A. Ikeda, Y. Nakao, H. Sato, S. Sakaki, *J. Phys. Chem. A* **2005**, *109*, 8055.

[8] For instance, see: a) J. M. Hawkins, T. A. Lewis, S. D. Loren, A. Meyer, J. R. Heath, Y. Shibato, R. J. Saykally, *J. Org. Chem.* **1990**, *55*, 6250; b) R. S. Koefod, M. F. Hudgens, J. R. Shapley, *J. Am. Chem. Soc.* **1991**, *113*, 8957; c) S. Schreiner, T. N. Gallaher, H. K. Parsons, *Inorg. Chem.* **1994**, *33*, 3021; d) J. T. Park, J.-J. Cho, H. Song, *J. Chem. Soc. Chem. Commun.* **1995**, 15; e) M. Sawamura, H. Iikura, E. Nakamura, *J. Am. Chem. Soc.* **1996**, *118*, 12850; f) M. Sawamura, H. Iikura, A. Hirai, E. Nakamura, *J. Am. Chem. Soc.* **1998**, *120*, 8285; g) M. Sawamura, H. Iikura, A. Hirai, E. Nakamura, *J. Am. Chem. Soc.* **1998**, *120*, 8285; h) J. T. Park, H. Song, J.-J. Cho, M.-K. Chung, J.-H. Lee, I.-H. Suh, *Organometallics* **1998**, *17*, 227; i) M. Sawamura, M. Toganoh, Y. Kuninobu, S. Kato, E. Nakamura, *Chem. Lett.* **2000**, *29*, 270; j) M. Sawamura, H. Iikura, T. Ohama, U. E. Hackler, E. Nakamura, *J. Organomet. Chem.* **2000**, *599*, 32; k) E. Nakamura, M. Sawamura, *Pure Appl. Chem.* **2001**, *73*, 355; l) M. Sawamura, M. Toganoh, Y. Kuninobu, S. Kato, E. Nakamura, *Chem. Lett.* **2000**, 270; m) M. Sawamura, H. Iikura, T. Ohama, U. E. Hackler, E. Nakamura, *J. Organomet. Chem.* **2000**, *599*, 32; n) M. Sawamura, M. Toganoh, K. Suzuki, A. Hirai, H. Iikura, E. Nakamura, *Org. Lett.* **2000**, *2*, 1919; o) M. Sawamura, Y. Kuninobu, E. Nakamura, *J. Am. Chem. Soc.* **2000**, *122*, 12407; p) P. Zanello, F. Laschi, A. Cinquantini, M. Fontani, K. Tang, X. Jin, L. Li, *Eur. J. Inorg. Chem.* **2000**, 1345; q) E. Nakamura, M. Sawamura, *Pure Appl. Chem.* **2001**, *73*, 355; r) M. Sawamura, M. Toganoh, H. Iikura, Y. Matsuo, A. Hirai, E. Nakamura, *J. Mater. Chem.* **2002**, *12*, 2109; s) K. Lee, H. Song, B. Kim, J. T. Park, S. Park, M.-G. Choi, *J. Am.*

Chem. Soc. **2002**, *124*, 2872; t) M. Sawamura, Y. Kuninobu, M. Toganoh, Y. Matsuo, M. Yamanaka, E. Nakamura, *J. Am. Chem. Soc.* **2002**, *124*, 9354; u) M. Toganoh, Y. Matsuo, E. Nakamura, *J. Am. Chem. Soc.* **2003**, *125*, 13974; v) Y. Matsuo, E. Nakamura, *Organometallics* **2003**, *22*, 2554; w) M. Toganoh, Y. Matsuo, E. Nakamura, *J. Organomet. Chem.* **2003**, *683*, 295; x) Y. Kuninobu, Y. Matsuo, M. Toganoh, M. Sawamura, E. Nakamura, *Organometallics* **2004**, *23*, 3259.

[9] R. E. Douthwaite, M. L. H. Green, A. H. H. Stephens, J. F. C. Turner, *J. Chem. Soc. Chem. Commun.* **1993**, 1522.

[10] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372; c) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[11] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372; c) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[12] Gaussian 03 (Revision C.02), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

[13] a) J. W. Lauher, R. Hoffmann, *J. Am. Chem. Soc.* **1976**, 98, 1729; b) T. A. Albright, J. K. Burdett, M. H. Whangbo, *Orbital Interaction in Chemistry*, Wiley, New York, **1985**, p. 394.

[14] a) T. Ziegler, W. Cheng, E. J. Baerends, W. Ravenek, *Inorg. Chem.* **1988**, *27*, 3458; b) M.-D. Su, S.-Y. Chu, *J. Phy. Chem. A* **2001**, *105*, 3591.

[15] a) M. J. S. Dewar, *Bull. Soc. Chem. (Fr.)* **1951**, *18*, C71; b) J. Chatt, L. A. Ducanson, *J. Chem. Soc.* **1953**, 2939; c) T. A. Albright, J. K. Burdett, M. H. Whangbo, *Orbital Interaction in Chemistry*, Wiley, New York, **1985**, pp. 355.

[16] J. Chetwynd-Talbot, P. Grebenik, R. Perutz, *Inorg. Chem.* **1982**, *21*, 3647.

[17] a) M. Grebenik, A. J. Downs, M. L. H. Green, R. N. Perutz, *J. Soc. Chem. Chem. Commun.* **1979**, 742; b) J. Chetwynd-Talbot, P. Grebnik, R. N. Perutz, *Inorg. Chem.* **1982**, *21*, 3647; c) P. A. Cox, P. Grebenik, R. N. Perutz, M. D. Robinson, R. Grinter, D. R. Stern, *Inorg. Chem.* **1983**, *22*, 3614.

[18] J. Green, C. N. Jardine, *J. Chem. Soc. Dalton Trans.* **1998**, 1057.

[19] a) S. P. McGlynn, T. Azumi, M. Kinoshita, The Triplet State, Prentice-Hall, New York, **1969**, pp. 190–198; b) M. A. El-Sayed, *J. Chem. Phys.* **1963**, *36*, 2834; c) M. A. El-Sayed, *Acc. Chem. Res.* **1968**, *1*, 8.

[20] a) M.-D. Su, *Chem. Phys. Lett.* **1995**, *237*, 317; b) M.-D. Su, *J. Org. Chem.* **1995**, *60*, 6621; c) M.-D. Su, *J. Phys. Chem.* **1996**, *100*, 4339; d) M.-D. Su, *Chem. Phys.* **1996**, *205*, 277; e) M.-D. Su, *J. Org. Chem.* **1996**, *61*, 3080.

[21] a) W. I. F. David, R. M. Ibberson, J. C. Matthewman, K. Prassides, T. J. S. Dennis, H. W. Hare, R. Taylor, D. R. M. Walton, *Nature* **1991**, *353*, 147; b) K. Hedberg, L. Hedberg, D. S. Bethune, C. A. Brown, H. C. Dorn, R. D. Johnson, M. de Vries, *Science* **1991**, *254*, 410.

[22] G. S. Hammond, *J. Am. Chem. Soc.* **1954**, *77*, 334.

[23] For details, see: a) S. Shaik, H. B. Schlegel, S. Wolfe in *Theoretical Aspects of Physical Organic Chemistry*, Wiley, New York, **1992**; b) A. Pross in *Theoretical and Physical Principles of Organic Reactivity*, Wiley, New York, **1995**; c) S. Shaik, *Prog. Phys. Org. Chem.* **1985**, *15*, 197.

[24] a) The first paper on the CM model: S. Shaik, *J. Am. Chem. Soc.* **1981**, *103*, 3692; b) updated review of the CM model: S. Shaik, A. Shurki, *Angew. Chem.* **1999**, *111*, 616; *Angew. Chem. Int. Ed.* **1999**, *38*, 586.

[25] C. E. Moore, *Atomic Energy Levels, Vol. III*, NBS, Washington, DC, **1971**..

Received: December 21, 2006