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DFT Study of the Geometry and Energy Order of the Low Singlet and Triplet States of [d^4-η^5-CpMo(CO)$_2$X] 16-Electron Complexes (X = Halogen, CN, H, and CH$_3$)

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DFT methods have been used to investigate the dependence of the geometry and energy order of the low energy states of [d^4-η^5-CpMo(CO)$_2$X] 16-electron complexes on X (X = halogen, CN, H and CH$_3$). The calculations use a double-ζ plus polarization valence basis set on all atoms and utilize relativistic ECPs on Mo and the heavier halogens. In every case two singlet and two triplet electronic states have been considered and minimized at the B3LYP level. For X = Cl, additional calculations were carried out at the BPW91, CCSD(T), and CASSCF levels. In the C_s point group, the singlet states are from the $(1a')^2(1a'')^2$ and $(1a')^2(2a')^2$ configurations of the valence d^4 electrons of the metal, and are denoted $^1A'$-a and $^1A'$-b, respectively. The triplet species are for the lowest $^3A''$ and $^3A'$ states from the $(1a')^2(2a')^1(1a'')^1$ and $(1a'')^2(1a')^1(2a')^1$ d^4 configurations. For all substituents, the geometry of both the singlet and triplet states is found to distort substantially from the uniform 3-leg piano-stool structural motif, a behavior that can be related to Jahn–Teller effects. When X is a halogen or a methyl, $^1A'$-b is predicted to be lower than $^1A'$-a, while the reverse order of these two singlet states is calculated for X = H and CN. For all substituents $^3A'$ is substantially higher than $^3A''$. In turn, the energy of $^3A''$ is calculated to be comparable to the lower singlet state of each complex. Attempts are made to rationalize some of these results using qualitative MO theory.

Introduction

η^5-Cyclpentadienyl complexes are among the important and most characteristic compounds in transition metal chemistry.[1] Among these, the 18-electron CpML$_4$ compounds of group 5 and 6 metals are known to react via the dissociative mechanism.[2,3] Knowledge of the geometry and electronic structure of the 16-electron intermediate implicated in this mechanism is fundamental to understanding the chemistry of these systems. There have been however only two classes of unsaturated d^4-CpML$_3$ compounds that could be characterized by conventional spectroscopic means. One class was developed by Malisch and co-workers using [CpM(CO)$_2$X] (M = Mo and W) in which X is an AY$_2$ type ligand such as P(NMe$_2$)$_2$ and As(t-Bu)$_2$.[4,5] Supported with crystal structures, the authors classified these complexes as having a double bond between M and AY$_2$, which would formally saturate the valence of the metal. The second class was designed by the Poli group, who employed more conventional ligands in novel synthetic routes that allowed isolation of several examples of [CpMoP$_2$X], where P is a phosphine and X = Cl[6,7] or OH.[8] Results from magnetic susceptibility measurements and variable-temperature NMR experiments

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were consistent with a triplet ground state in this class of complexes.[7] Calculations by the Poli group correctly reproduce this observation, and place the energy of the singlet state 5−10 kcal/mol higher, depending on the specific molecule and level of theory.[8]

Recently, the mechanism of the photochemical reactions of [CpM(CO)$_4$] complexes (M = V, Nb) in low temperature matrices has been the subject of several investigations.[9,10] To aid the analysis of transient intermediates observed in such experiments, Harris and co-workers used DFT methods to calculate the energy and vibrational modes of the low singlet and triplet states of [CpV(CO)$_3$].[11] The results predicted a triplet ground state for this molecule, and placed the singlet state 3 kcal/mol higher. Remarkably, the geometry of both the singlet and triplet states of [CpV(CO)$_3$] was noted to deviate substantially from the uniform pseudo-C_{3v} 3-leg piano stool motif. In addressing the origin of such distortions, we have recently reported calculations on [η^6-benzene-Nb-(CO)$_3$]$^+$ in which the symmetry properties of the C_{3v} point group could be utilized to demonstrate without ambiguity that these distortions pertain to Jahn−Teller effects originating in accessible ^{1}E′ and ^{3}E′ degenerate states in the undistorted motif.[12] More importantly, our study revealed that in the C_s point group two distinct closed shell singlet and two distinct triplet states in [benzene-Nb(CO)$_3$]$^+$ fall within a range of 5 kcal/mol. The same result was found for [CpNb(CO)$_3$]. Additional initial calculations on [CpMo-(CO)$_2$Cl] were then briefly presented to illustrate that changing the substituents in unsaturated CpML$_3$ can in fact reverse the order of the two singlet states. In light of these findings, Jensen and Poli have shown that in order to arrive at a qualitatively correct description of the CO and N$_2$ addition reactions to [CpMoP$_2$Cl], it is necessary to include more than one electronic state of each spin multiplicity.[13]

The factors that control the structure and energy of the low states in d^4 CpML$_3$ remain largely unexplored. A computational investigation by Poli of substituents in [CpMoP$_2$X] focused on identifying factors that may influence the gap between the lower energy species of each spin state.[14] In the present work we use DFT methods to study the [CpMo(CO)$_2$X] system with X = halogen, CN, H, and Me in greater details. A role for these compounds has been proposed in the thermal[2,3] and photochemical[15] reactions of CpMo(CO)$_3$X, but they have not been isolated or characterized. We first consider [CpMo(CO)$_2$Cl] to define the four electronic states of interest and to describe their structural details. We then calculate the dependence of these states on the identity of X, and try to interpret some of the results using qualitative MO theory.

Computational Details

All calculations were carried out using Gaussian 98.[16] The 6-31G** basis set was used on the lighter atoms.[17] The heavier atoms carried the Hay-Wadt ECPs, and the double-ζ basis set supplied with them (LANL2DZ),[18] along with a set of 10f polarization functions on Mo with exponent = 0.4, and a set of 6d functions on the halogens of exponents 0.75 (Cl), 0.39 (Br), and 0.27 (I).[19] The singlet and triplet states were calculated using the restricted and unrestricted B3LYP methods, respectively.[20] Stationary points were located in the C_s point group and characterized by normal mode analysis. Two orientations of the Cp ring were considered in imposing the C_s constraint. These were found to have comparable energies, but one was a minimum and one a transition state for Cp rotation. We report results only for the minima. Complexes showing imaginary frequencies other than Cp rotation are discussed in the text, and these were recalculated in C_1. For X = Cl, additional energies were calculated at the BPW91,[21] CCSD-(T),[22] and CASSCF[23] levels of theory and the basis set specified before.

Results and Discussion

The Low Energy States of [η^5-CpMo(CO)$_2$Cl]. In the C_s point group of [d^4-CpMo(CO)$_2$X], Mo(II) would have two a′ and one a″ formally nonbonding d-type MOs. With the single determinant method used in the present study it is possible to use these MOs to calculate two singlet and two triplet states by varying their d^4 electron occupancy. The singlet states are obtained from the closed shell (1a′)^2(1a″)^2 and (1a′)^2(2a′)^2 d^4 configurations, which we denote ^{1}A′-a and ^{1}A′-b, respectively. The triplet states are differentiated by

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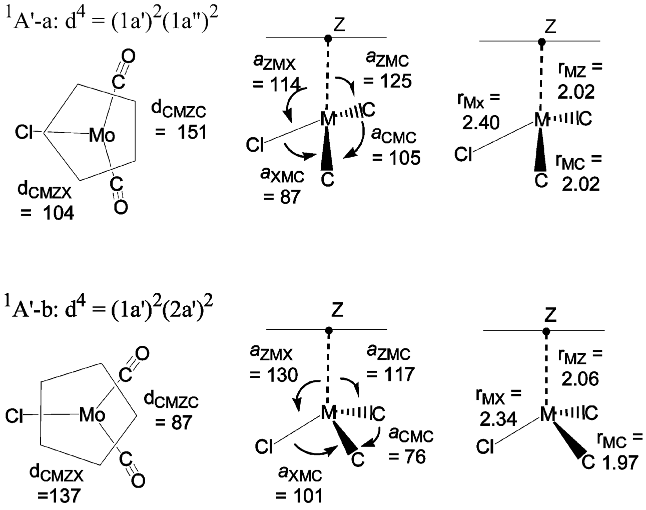

Figure 1. Geometry of the two closed shell singlet states of [CpMo(CO)$_2$Cl] defined by the specified d^4 configurations.

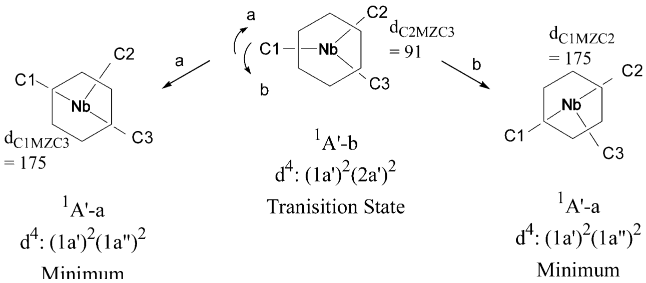

Figure 2. Dihedral angles in the two singlet states of [benzene-Nb(CO)$_3$]$^+$ (from ref 12).

the (1a″)^2(1a′)^1(2a′)^1 or (1a′)^2(1a″)^1(2a′)^1 configurations, which yield ^{3}A″ and ^{3}A′ states, respectively. The open shell singlet states from the latter configurations are expected to be higher in energy than the triplet states, and no attempt has been made to evaluate them.

The minimized structural parameters of ^{1}A′-a and ^{1}A′-b are compared in Figure 1 for X = Cl.[24] The results show that in both species the geometry deviates significantly from the idealized 3-leg piano-stool motif. This is most apparent in the dihedral between the two carbonyls (d_{CMZC}), which is 151° in ^{1}A′-a and 87° in ^{1}A′-b. Such values may be understood as distortions taking place in opposite directions from 120° expected for a symmetrical arrangement of Cl and the two COs. Variations in the other angular parameters are also suggestive of opposite distortions relative to a reference point. In ^{1}A′-a for example the two COs are more bent than Cl ($a_{\mathrm{ZMC}} = 125°$, $a_{\mathrm{ZMX}} = 114°$), whereas in ^{1}A′-b the reverse is the case ($a_{\mathrm{ZMC}} = 117°$, $a_{\mathrm{ZMX}} = 137°$). Similarly, the angle between the two carbonyls is wide in ^{1}A′-a ($a_{\mathrm{CMC}} = 105°$) but narrow in ^{1}A′-b ($a_{\mathrm{CMC}} = 76°$).

The distortions described in Figure 1 are similar to those found for the low singlet states of [benzene-Nb(CO)$_3$]$^+$ (Figure 2). In the latter molecule, structural distortions follow from a first-order Jahn–Teller effect applicable to the ^{1}E′ state resulting from the (e)^2(a$_1$)^2 d^4 configuration in the symmetrical C_{3v} geometry. The JT theorem predicts that such an electronically degenerate state would couple with a degenerate vibrational mode, and the energy would be lowered by distortion in either of two opposite directions, one leading to a minimum and one to a transition state connecting two equivalent minima.[25] In [benzene-Nb(CO)$_3$]$^+$,[12] ^{1}A′-a is the minimum and ^{1}A′-b is the transition state connecting two ^{1}A′-a geometries in a process having an activation energy of 4.5 kcal/mol. Clearly, although [CpMo(CO)$_2$Cl] does not have degenerate electronic states due to the presence of heterosubstituents (CO and Cl), the similar geometries in Figures 2 and 3 show that JT-type effects continue to dictate the structural details of the low singlet states in [CpMo(CO)$_2$Cl]. Unlike [benzene-Nb(CO)$_3$]$^+$, however, both ^{1}A′-a and ^{1}A′-b in [CpMo(CO)$_2$Cl] are minima, and ^{1}A′-a is 19 kcal/mol higher in energy than ^{1}A′-b.

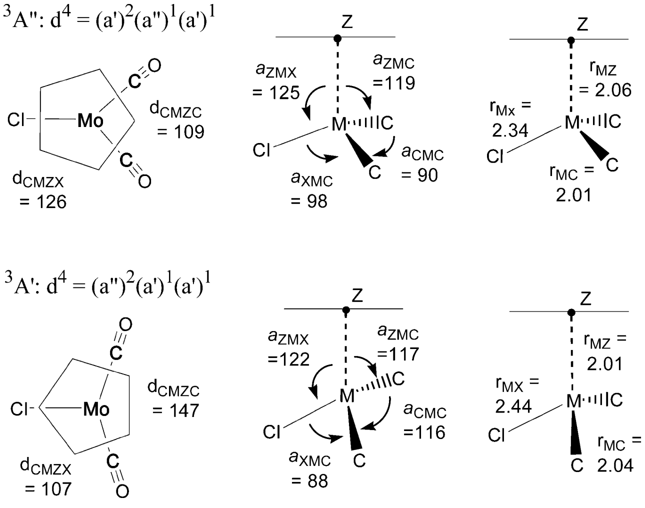

Figure 3. Geometry of the two triplet states of [CpMo(CO)$_2$Cl] defined by the specified d^4 configurations.

Structural differences related to those described above are also present in the two triplet states of [CpMo(CO)$_2$Cl] (Figure 3), although their magnitudes are not as large. Specifically, the dihedral between the two COs is wider than 120° in ^{3}A′ and is significantly narrower in ^{3}A″ (d_{CMZC} = 147° and 109°, respectively). Such differences are signatures of an underlying JT effect. As before, the nature of this effect can be clarified using [benzene-Nb(CO)$_3$]$^+$ where it can be easily demonstrated that a degenerate ^{3}E′ state is accessible in the C_{3v} geometry but this time from the (e)^3(a$_1$)^1 d^4 configuration. In [benzene-Nb(CO)$_3$]$^+$ ^{3}A″ is a minimum and ^{3}A′ is a transitions state, and the two have nearly identical energies. In [CpMo(CO)$_2$Cl] both triplet states are minima, and ^{3}A′ is calculated to be 19 kcal/mol higher in energy than ^{3}A″.

At the B3LYP level, ^{3}A″ in [CpMo(CO)$_2$Cl] is 1.3 kcal/mol higher in energy than ^{1}A′-b, and the latter is thus predicted to be the ground state. A similar prediction is made by other DFT and ab initio methods as summarized in Table 1. In comparison to other methods, the employed CASSCF

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(24) The point *Z* in the figure is defined by the intersection point between the normal from the metal to the plane of the Cp ring. The Cp plane was defined using the coordinates of the symmetry unique carbon atom and the coordinates of the two carbons opposite to it.

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Table 1. Relative Energy of the Low Energy States of $[CpMo(CO)_2Cl]$ Calculated by Different Theoretical Methods[a]

	^{1}A′-a	^{1}A′-b	^{3}A″	^{3}A′
B3LYP[b]	19.2	0.0	1.3	22.5
BPW91[c]	20.0	0.0	4.1	25.1
CCSD(T)[b]	21.3	0.0	3.4	24.4
CASSCF[b,d]	25.4	0.0	7.6	26.3

[a] Energies given in kcal/mol relative to ^{1}A′-b. [b] Geometry minimized at the B3LYP level. [c] Geometry minimized at the BPW91 level. [d] Energy calculated using an (8,7) active space composed of the 3 valence metal d-orbitals and their 4 electrons, the 2 filled Cl πorbitals and electrons, and two empty π^* CO MOs having a′ and a″ symmetries.

Table 2. Relative Energy of the Four Low Energy States in $[CpMo(CO)_2X]$ Calculated at the B3LYP Level (in kcal/mol)[a]

X	^{1}A′-a $(1a')^2(1a'')^2$	^{1}A′-b $(1a')^2(2a')^2$	^{3}A″ $(1a')^2(1a'')^1(2a')^1$	^{3}A′ $(1a'')^2(1a')^1(2a')^1$
F	17.2	0.0	0.9	26.4
Cl	19.2	0.0	1.3	22.5
Br	18.6	0.0	1.1	21.0
I	17.8	0.0	1.0	19.2
CN	6.6 0.0 (^{1}A)[b]	(TS)[c]	0.0	12.1
H	0.0	12.1 (TS)[d]	3.1	13.6
CH_3	6.3	3.7 (TS)[e] −4.3 (agostic)	0.0	16.2
CO[f]	0.0	5.7 (TS)	1.8	2.1 (TS)

[a] For each substituent, the lowest energy species minimized in C_s is given a value of zero. Values do not include ZPE and thermal terms. "TS" indicates that the geometry of the specified state is a transition structure. The details of such species are discussed in the text. [b] ^{1}A is the electronic state of the asymmetric isomer of ^{1}A$_1$-b (Figure 4). [c] TS is described in Figure 4. [d] TS is described in Figure 5. [e] TS and the geometry with the agostic M−CH bond are described in Figure 6. [f] Results for $CpNb(CO)_3$ are from ref 12. The TSs are related to the one given in Figure 2.

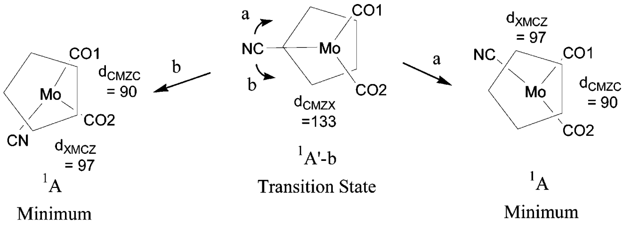


Figure 4. Geometry of ^{1}A, the asymmetric isomer of ^{1}A′-a. Arrows on ^{1}A′-b are for the normal coordinate of the imaginary frequency leading to two equivalent ^{1}A.

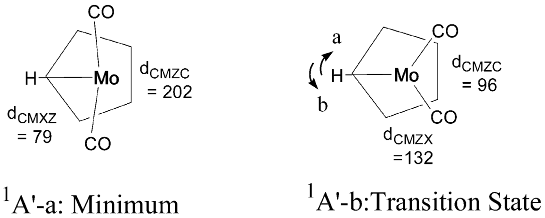


Figure 5. Geometry of ^{1}A′-a and ^{1}A′-b of $[CpMo(CO)_2H]$. The arrows on ^{1}A′-b are for the motion of the normal mode of vibration having an imaginary frequency.

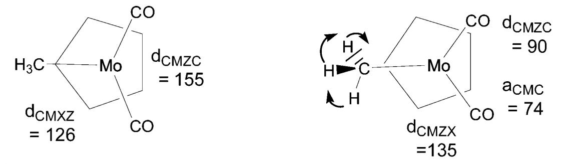
level, which was carried out on the B3LYP geometries and did not include dynamic electron correlation effects, appears to exaggerate the stability of ^{1}A′-b relative to ^{3}A″. There are currently no experimental data on the direction or magnitude of this gap. We note that, with all the methods tested, the unrestricted triplet states showed essentially no spin contamination, and the ab initio methods gave wave functions dominated by one single configuration. In the remaining part of the given study the dependence of the energy order of these four states is calculated at the B3LYP level.

Substituent Effects. The energy of the four electronic states of $[CpMo(CO)_2X]$ discussed above has been calculated for a series of systematically varied substituents. The results are collected in Table 2 in terms of E_{rel}, defined such that the lowest energy electronic state for each substituent is always assigned a value of zero. For the group of halogen complexes, the results reveal a remarkable *independence* of the energy order of ^{3}A″ and the two singlet states from the identity of the halogen, with ^{1}A′-a ca. 19 kcal/mol above ^{1}A′-b, and a constant singlet−triplet gap of 1.0 kcal/mol throughout the group. E_{rel} of ^{3}A′ on the other hand is lower in the heavier halogens. For example, E_{rel} = 26.4 kcal/mol for X = F, compared to 19.2 kcal/mol for X = I.

The order of the given four electronic states is largely modified when the halogen is replaced by CN. Perhaps most important is that the energy of the two singlet states becomes comparable in $[CpMo(CO)_2CN]$, with ^{1}A′-a only 3.6 kcal/mol above ^{1}A′-b. In addition, the 12 kcal/mol separation between the two triplet states in the cyano complex is substantially smaller than in the halogens. Moreover, ^{1}A′-b in the cyano complex is not a minimum, but is a transition state characterized by one imaginary frequency (ν_i = 105i cm^{-1}) for movement of CN toward one of the two carbonyls as illustrated by the arrows in Figure 4. Minimization in C_1 yields ^{1}A with a geometry similar to that of ^{1}A′-a, but with a carbonyl at a position trans to CN. Thus, ^{1}A′-a and ^{1}A are two geometrical isomers of the same state, and ^{1}A′-b is a transition state connecting two ^{1}A geometries in a process having an activation energy of 3.0 kcal/mol. At the B3LYP level, ^{1}A and ^{3}A″ are calculated to have the same energy. We note that the geometry of ^{3}A″ continues to be closely related to that of ^{3}A″ given in Figure 3 for X = Cl.

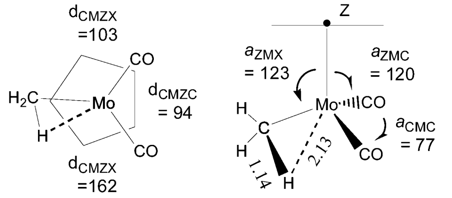
For the complex with X = H, ^{1}A′-a is calculated to be the ground state, and has a geometry that exhibits an extreme degree of distortion from the symmetrical $CpML_3$ motif (d_{CMZC} = 202°; Figure 5). A related structure has been reported for $[CpMo(PH_3)_2H]$.[14] In $[CpMo(CO)_2H]$ ^{1}A′-b is 12 kcal/mol above ^{1}A′-a and has one imaginary frequency (ν_i = 501i cm^{-1}) for motion of the hydride in either one of the two directions leading to the asymmetric trans H−Mo−CO isomer of ^{1}A′-a (Figure 5). Attempts to locate this isomer in C_1 always converged to the symmetric ^{1}A′-a geometry. For this substituent, both ^{3}A′ and ^{3}A″ are minima, and ^{3}A′ is 10.5 kcal/mol above ^{3}A″. The singlet−triplet gap between ^{1}A′-a and ^{3}A″ is 3.1 kcal/mol in favor of a singlet ground state.

The last substituent we consider is the methyl group. In this case, ^{1}A′-b is lower than ^{1}A′-a, but by only 2.6 kcal/mol. ^{1}A′-b has an imaginary frequency (ν_i = 287i cm^{-1}) for CH_3 rotation whose value would be unusually large for a transition state of a mere M−CH_3 conformational change. Indeed, lifting the C_s constraint leads to an agostic bond between a methyl hydrogen and the metal center (Figure 6) and lowers the energy by 8.3 kcal/mol. In the final geometry with the agostic bond, the angle between the two carbonyls



^{1}A'-a: Minimum

^{1}A'-b: TS for Me rotation



^{1}A: Minimum related to ^{1}A'-b with agostic bond

Figure 6. Stationary points for the singlet states of [CpMo(CO)$_2$Me]. The arrows on ^{1}A′-b are for the motion of the normal mode with an imaginary frequency.

is 77° (a_{CMC}, Figure 6). Such a small a_{CMC} angle is a characteristic structural feature of ^{1}A′-b (Figures 1 and 2), and suggests that the electronic state of ^{1}A′-b does not change when the agostic bond is added. For the given methyl complex, the triplet ^{3}A″ state is 5.7 kcal/mol higher than the singlet with the agostic bond, and ^{3}A′ is 16 kcal/mol above ^{3}A″. No stationary point with agostic bond could be located on the triplet energy surface. This is in accord with the study of CpMo(PH$_3$)$_2$(CH$_3$)[14] where an agostic bond had been reported only for the singlet state.

Given the collective data in Table 2, it becomes desirable to be able rationalize some of the calculated trends based on general qualifiers commonly associated with the variable ligand. One important question for example is what determines whether ^{1}A′-a would be lower or higher than ^{1}A′-b, and a simple answer may be based on the π-properties of X. H and CN, as well as CO in the case of [CpNb(CO)$_3$], lack a π-electron donor capacity, and their complexes have an ^{1}A′-a singlet ground state. The halogens on the other hand are classified as π-electron donor ligands and yield an ^{1}A′-b ground state. The methyl group would also have some π-donor capacity, albeit a weak one because the π-orbitals have some σ-CH bonding character. Consistently, when X = CH$_3$, ^{1}A′-b is lower than ^{1}A′-a. The π-properties of X seem also to have a large influence on the magnitude of the gap between the two triplet states of [CpMo(CO)$_2$X]. The halogens for example yield large triplet−triplet gaps (18−25 kcal/mol), whereas H and CN afford much smaller gaps (less than 12 kcal/mol). An intermediate gap (16 kcal/mol) is calculated for the complex with the weak π-donor CH$_3$ group. In CpNb(CO)$_3$ the difference between the two triplet states is less than 1 kcal/mol.

The importance of the π-properties of ligands is known in transition metal chemistry[26,27] and has been used in some studies to interpret unusual trends. Goldman and Krogh-Jespersen, for example, invoked a role for π-effects to explain counterintuitive trends in the carbonyl stretching frequency and redox potentials in [Ir(PR$_3$)$_2$(CO)X].[28] Similarly, Caulton used π-arguments to rationalize unusual nucleophilicity trends.[29] Eisenstein and co-workers demonstrated that when X is a π-donor the ground singlet state in [d^6-Ir(PH$_3$)$_2$XH$_2$] is different from than when X = H.[30] In line with explanations given in these studies, qualitative arguments based on orbital interactions involving the metal nonbonding d-orbitals may be used to account for, at least in part, how π-effects may influence the energy order of the electronic states in [CpMo(CO)$_2$X]. For this purpose we utilize the energy level diagram of the singlet states of [CpMo(CO)$_2$Cl] given in Figure 7.[31]

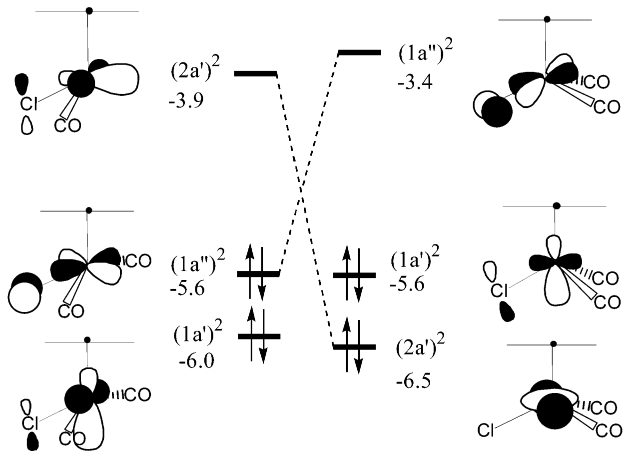


Figure 7. Correlation diagram and schematic sketches of the valence MOs in ^{1}A′-a and ^{1}A′-b states of [CpMo(CO)$_2$Cl]. Orbital energies are given in electronvolts.

In absence of π-effects, the σ-MoX interactions in [CpMo(CO)$_2$X] would formally impart antibonding character to 1a′ and 2a′. This is expected to disfavor ^{1}A′-b with the $(1a')^2(2a')^2$ configuration. For a strong σ-donor such as H, the preference for ^{1}A′-a would be large, and this is consistent with the 12 kcal/mol gap between ^{1}A′-a and ^{1}A′-b in [CpMo(CO)$_2$H]. When X is a halogen, on the other hand, it would have two filled π-orbitals of a′ and a″ symmetry. In ^{1}A′-a with the $(1a')^2(1a'')^2$ d^4 configuration, there would be two π-MoX repulsion terms. Altering the d^4-electron occupancy into $(1a')^2(2a')^2$ replaces one of these by a favored bonding interaction. The large decrease in energy calculated when ^{1}A′-a is changed to ^{1}A′-b in the halogen complexes (ca. 20 kcal/mol) suggests therefore that the extent of net π-stabilization introduced when the orbital occupancy is altered overweighs the accompanying σ-destabilization. However, the π-donor strength of the halogen is believed to decrease

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down the group,[28,29] and based on the given π-argument alone one would expect greater preference for the $^1A'$-b state in the lighter halogens. An expected increase in the halogen σ-donor strength down the group should also increase the preference of $^1A'$-b over $^1A'$-a in the lighter halogens. Accordingly, one should expect a decrease in the gap between $^1A'$-a and $^1A'$-b down the halogen group of complexes, but Table 2 shows that this is not the case. Clearly, more subtle factors determine the quantitative details of separation of the two singlet states. Similarly, given the large variations in the electronic properties of the substituents in Table 2, it would be difficult to come up with a simple explanation that would account for the finding that the triplet $^3A''$ is always similar in energy to the lowest singlet state, which can be either $^1A'$-a or $^1A'$-b.

Conclusions

Unlike the case of coordinatively saturated 18-electron transition metal complexes, the geometry and electronic structure of unsaturated 16-electron compounds may not be always straightforward to predict.[32] [d^4-$CpML_3$] complexes are prototypes of unsaturated complexes that have been reported to exhibit a variety of geometries and electronic ground states depending on the details of the substituents. By carrying out systematic calculations on a series of related [$CpMo(CO)_2X$] complexes, the present study brings two new contributions to understanding the unsaturated [$CpMoL_3$] system. First, it illustrates that two distinct closed shell singlet and two triplet states of the given system can have comparable energies. The importance of this finding is appreciated when it is realized that the energy order of the given states is dependent on X, leading to different ground states for different substituents. Because of spin and symmetry considerations, fragments with different electronic ground states are likely to have different reactivities. The second contribution pertains to the structure of these four states, which is interpreted in terms of Jahn−Teller distortions in the idealized pseudo C_{3v} 3-leg piano stool skeletal frame of $CpML_3$.

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Supporting Information Available: Four pages including Cartesian coordinates for the B3LYP minimized geometry of the four electronic states of $CpMo(CO)_2Cl$ and their CCSD(T) and CASSCF energies (Table 1), and a table for the absolute B3LYP energies of the four electronic states of all the substituents considered (Table 2). This material is available free of charge via the Internet at http://pubs.acs.org.

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