Identification of Jahn–Teller Effects in both Singlet and Triplet Low-Energy States of $[(\eta^6\text{-benzene})Nb(CO)_3]^+$**

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Unsaturated 16e⁻ $[CpML_n]$ intermediates play important role in the thermal and photolytic chemistry of 18e⁻ $[CpML_{n+1}]$ complexes. A few isolated compounds and many theoretical studies have established that these intermediates have ground states with small singlet–triplet gaps, and geometries that lack the near C_{nv} symmetry characteristic of the 18e⁻ analogues (Cp treated as a point).[1] Surprisingly, discussions of these novel electronic and structural properties have been based largely on qualitative MO concepts.[2] Studies of CH activation by d⁸ [CpML] for example,[3] often refer to an extended Hückel theory (EHT) analysis[4] for an explanation of why the singlet and triplet states in this fragment are bent. An ab initio investigation of d⁶ [CpRuLX][5] was superseded by an EHT study from the same group[6a] to rationalize why [CpRuLX] is planar when other d⁶ $[CpML_2]$ complexes, such as $[CpMn(CO)_2]$,[7] are pyramidal. The same problem in $[CpFeL_2]^+$ was addressed by using DFT and EHT calculations.[6b] More recently, Poli and co-workers invoked EHT arguments to account for large geometric distortions in the singlet state of d⁴ $[CpMoL_2X]$ calculated by using DFT,[8] but did not address deformations calculated in the triplet state of these complexes that would actually be inconsistent with the EHT arguments. Similarly, Harris and co-workers have calculated a triplet state of d⁴ $[CpV(CO)_3]$ that deviated from pseudo-C_{3v},[9] but no comments were made on its origin.

In an attempt to better understand these systems, we use DFT in the present study[10] to examine the structural and electronic properties of d⁴ $[(\eta^6\text{-benzene})Nb(CO)_3]^+$. The applicability of the C_{3v} point group to this molecule allows us to demonstrate without ambiguity that both its singlet and triplet low-energy states are governed by Jahn–Teller effects[11] that have not been considered in previous studies. These effects are shown to be retained in the more chemically relevant $[\eta^5\text{-CpNb(CO)}_3]$ molecule, and to have implications for other unsaturated systems.

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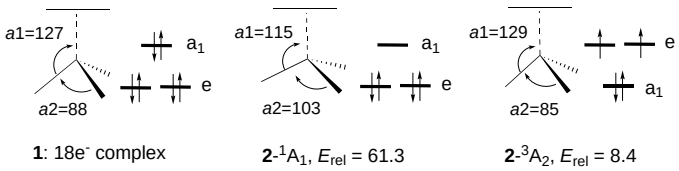
It is convenient to approach the given problem starting from the 18e⁻ $[(\eta^6\text{-benzene})Nb(CO)_3]^-$ complex (**1**; Figure 1). As found in previous studies,[12] the formally nonbonding d⁶ electrons of **1** in C_{3v} occupy an a_1 MO of d_{z^2}

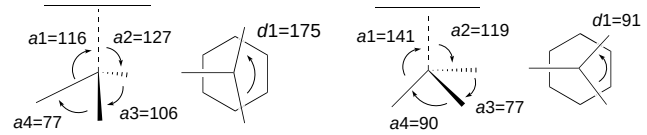


1: 18e⁻ complex **2**-$^1A_1$, E_{rel} = 61.3 **2**-$^3A_2$, E_{rel} = 8.4

Figure 1. Angular parameters minimized in C_{3v} (in degrees), and partial MO diagrams for **1**, **2**-$^1A_1$ and **2**-$^3A_2$. E_{rel} (in kJ mol⁻¹) is defined relative to the energy of the ground state of **2** (**2**-$^3A'$, Figure 3).

character, and a doubly degenerate e MO that is primarily a linear combination of d_{xy} and $d_{x^2-y^2}$, with additional mixing from d_{xz} and d_{yz}. Since a_1 is higher than e in **1**, the most trivial way to obtain the 16e⁻ $[(\eta^6\text{-benzene})Nb(CO)_3]^+$ complex (**2**) would be to remove the electron pair from the HOMO of **1**. Minimization of the resulting $^1A_1$ state affords **2**-$^1A_1$ (Figure 1), characterized as a second-order saddle point for ring slippage in either of two directions. This is a high-energy species of no interest to the present study.

Another configuration of the d⁴ electrons in **2** would be $(a_1)^2(e)^2$, which would give rise to $^3A_2$, $^1A_1$, and ^1E states.[13] The triplet state leads to the true minimum **2**-$^3A_2$ (Figure 1). Unfortunately, calculation of $^1A_1$ has not been feasible with the single determinant methods employed in this study. This state is expected to be significantly higher in energy than **2**-$^3A_2$ and has not been pursued further. The ^1E state from the given configuration would be subject to a Jahn–Teller effect of the general E ⊗ e type,[11] meaning that the ^1E electronic state would couple with a degenerate e vibration, and the molecule would distort in two directions, one leading to a minimum and one to a transition state. In **2**, Jahn—Teller distortion lowers the point group from C_{3v} to C_s, and the symmetry of the three nonbonding d orbitals becomes a′, a′, and a″. Two $^1A'$ states can then be obtained from the $(a')^2(a'')^2$ and $(a')^2(a')^2$ configurations of the d⁴ electrons. The minimized geometry of these states (**2**-$^1A'a$ and **2**-$^1A'b$ in Figure 2) can be



2-$^1A'a$: $(a'')^2(a')^2$ **2**-$^1A'b$: $(a')^2(a')^2$

Minimum; E_{rel} = 9.1 Transition State; E_{rel} = 28.1

Figure 2. Angular parameters (in degrees) and occupancy of the d⁴ electrons of **2**-$^1A'a$ and **2**-$^1A'b$. E_{rel} (in kJ mol⁻¹) is defined relative to the energy of the ground state of **2** (**2**-$^3A'$, Figure 3).

readily related to a parent C_{3v} structure that has undergone distortion in opposite directions. Most apparent is the dihedral between the two equivalent carbonyl ligands, *d*1,[14] which is near 180° in **2**-$^1A'a$ but is 91° in **2**-$^1A'b$. Bending of the carbonyl ligands from the benzene ring is also relevant. In **2**-$^1A'a$, for example, *a*1 is substantially smaller than *a*2 (116° versus 127°), whereas in **2**-$^1A'a$ the reverse is the case (141°

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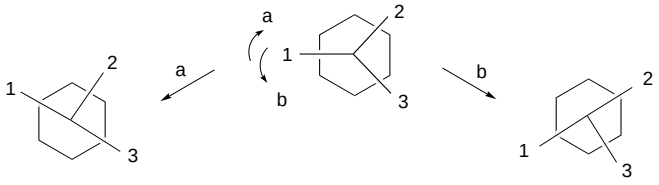
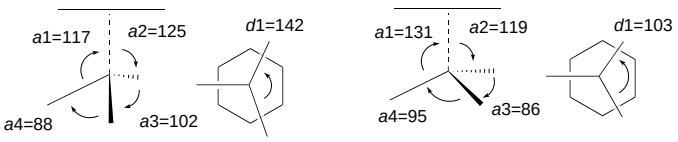
versus 119°). Not independently, the relative magnitude of the angles between the carbonyls (*a*3 and *a*4) is also reversed. The metal–carbonyl bond lengths, on the other hand, are comparable in the two geometries. From this, it may be inferred that the Jahn–Teller active vibration in this system is a linear combination of mostly two e normal modes, related to bending and inversion of the metal–carbonyl moiety.

Normal mode analysis reveals that **2**-^{1}A′a is a true minimum. **2**-^{1}A′b on the other hand is a transition state characterized by a vibration having an imaginary frequency ($\nu_i = 153$i cm^{-1}) with vector coordinates for a motion connecting two equivalent **2**-^{1}A′a minima as shown in Scheme 1. The activation energy for this transformation (ΔE_{act}) is 19.0 kJ mol^{-1}. **2**-^{1}A$_1$ located in C_{3v} (Figure 1) is 52.1 kJ mol^{-1} above **2**-^{1}A′a.



Scheme 1. Motion of the normal mode in **2**-^{1}A′b connecting two equivalent minima of **2**-^{1}A′a.

One last configuration of the d^4 electrons of **2** in C_{3v} would be $(a_1)^1(e)^3$, which would yield a Jahn—Teller active triplet state (^{3}E). In C_s, ^{3}A′ and ^{3}A″ states are then obtained from $(a'')^2(a')^1(a')^1$ and $(a')^2(a')^1(a'')^1$, respectively. The geometries of the states (**2**-^{3}A′ and **2**-^{3}A″, Figure 3) have exactly the same



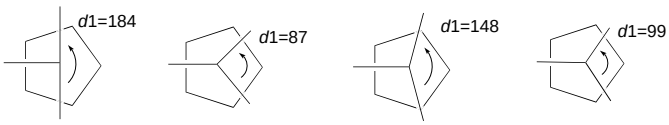
2-^{3}A′: $(a'')^2(a')^1(a')^1$ Minimum; E_{rel} = 0.0

2-^{3}A″: $(a')^2(a')^1(a'')^1$ Transition State; E_{rel} = 0.3

Figure 3. Angular parameters (in degrees) and occupancy of the d^4 electrons of **2**-^{3}A′ and **2**-^{3}A″. **2**-^{3}A′ is the ground state of **2**, and is used to define E_{rel} (in kJ mol^{-1}).

distortion patterns as the singlet states, but to a substantially smaller degree. While **2**-^{3}A′ is a minimum, **2**-^{3}A″ has one imaginary frequency with coordinates similar to the loose vibration in **2**-^{1}A′b. The value of ν_i in **2**-^{3}A″ is fairly small, 24i cm^{-1} (or 70i cm^{-1} at the HF level) reflecting a rather facile intramolecular carbonyl conversion on the triplet energy surface. Consistently, **2**-^{3}A″ is only 0.3 kJ mol^{-1} above **2**-^{3}A′. The symmetric **2**-^{3}A$_2$ (Figure 1) is 8.4 kJ mol^{-1} above **2**-^{3}A′.[15] In turn, **2**-^{3}A′ is 9.1 kJ mol^{-1} below **2**-^{1}A′a, and is predicted to be the ground state of **2**.

In the Cp analogue of **2**, [CpNb(CO)$_3$] (**3**), two singlet and two triplet states can still be defined in C_s (Figure 4). The geometries of these states exhibit the same distortion patterns found in **2**, and can therefore be attributed to the same Jahn—Teller effects. In **3**, ^{1}A′a is calculated to be the ground state,



3-^{1}A′a $(a'')^2(a')^2$ Minimum E_{rel} = 0.0

3-^{1}A′b $(a')^2(a')^2$ Transition State E_{rel} = 24.0

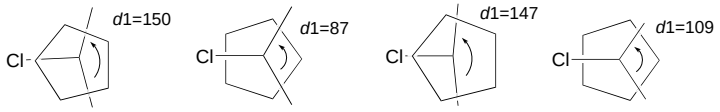
3-^{3}A′ $(a'')^2(a')^1(a')^1$ Minimum E_{rel} = 7.5

3-^{3}A″ $(a')^2(a'')^1(a')^1$ Transition state E_{rel} = 8.8

Figure 4. Angular parameters (in degrees), occupancy of the d^4 electrons, and relative energy (in kJ mol^{-1}) of the low-lying singlet and triplet states of [CpNb(CO)$_3$].

and the triplet **3**-^{3}A′ is 7.9 kJ mol^{-1} higher in energy, a value unchanged at the CCSD(T) level. In turn, **3**-^{1}A′b is a transition state connecting two **3**-^{1}A′a, with $\nu_i = 180$i cm^{-1}, and $\Delta E_{act} =$ 24.0 kJ mol^{-1}. Similarly, **3**-^{3}A″ is a transition state with $\nu_i =$ 39i cm^{-1} and $\Delta E_{act} = 1.4$ kJ mol^{-1}, and carries a residual frequency of 10i cm^{-1} for Cp rotation. At the CCSD(T) level, the given ΔE_{act} values become 19.4 and 3.7 kJ mol^{-1}, respectively.

To illustrate potential significance of the given Jahn—Teller effects beyond explaining the geometries of **2** and **3**, we consider d^4 [CpMo(CO)$_2$Cl] (**4**), proposed as an intermediate in reactions of [CpMo(CO)$_3$Cl].[16] As in **3**, two singlet and two triplet states can be specified for **4** in C_s (Figure 5). The geometries of theses states are close to those of **3**,[14] but they are all minima, a behavior analogous to the Jahn–Teller active d^8 ML$_3$[17a] and d^6 ML$_5$[17b] systems when substituted.



4-^{1}A′a $(a')^2(a'')^2$ E_{rel} = 80.2

4-^{1}A′b $(a')^2(a')^2$ E_{rel} = 0.0

4-^{3}A′ $(a'')^2(a')^1(a')^1$ E_{rel} = 94.0

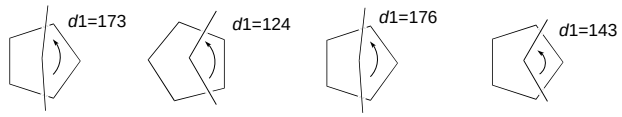
4-^{3}A″ $(a')^2(a')^1(a'')^1$ E_{rel} = 5.4

Figure 5. Angular parameters (in degrees), occupancy of the d^4 electrons, and relative energy (in kJ mol^{-1}) of the low-lying singlet and triplet states of [CpMo(CO)$_2$Cl].

Remarkably, Figure 4 and 5 reveal that the relative order of the two low singlet states is reversed in **3** and **4**. The same is true for the triplet states. For related systems there may be no reason to anticipate the correct order of these species, and it becomes essential to account explicitly for all of them. Moreover, although **4**-^{1}A′a has a much higher energy than **4**-^{1}A′b (Figure 5), **4**-^{1}A′a is actually the adiabatic product of CO dissociation from the ground state of [CpMo(CO)$_3$Cl].[18] Thus, two singlet adiabatic energy surfaces would be needed to capture the main features of the reaction. Calculated reaction coordinates for CO and N$_2$ addition to the related d^4 [CpMo(PH$_3$)$_2$Cl] complex have been recently used to interpret observed differences in the rates of these reactions,[19] but only one singlet energy surface was considered.[20]

Finally, if one ligand in the 16e$^-$ d^4 [CpML$_3$] system is substituted by an electron pair, the product would be a d^6 [CpML$_2$] complex. This suggests that the alternative planar or

pyramidal geometries known for the singlet state of d^6 [$CpML_2$] and [CpMLX] systems may actually belong to two distinct electronic states, rather than being the result of pseudo Jahn–Teller distortions in the same electronic state as previously proposed.[6, 21] Indeed, by altering the occupancy of the d^6 electrons in [$CpMn(CO)_2$] (**5**) we located a nearly planar bound stationary state (**5**-^{1}A′b, Figure 6),[22] 167 kJ mol^{-1} above the pyramidal structure (**5**-^{1}A′a). More



5-^{1}A'a	**5**-^{1}A'b	**5**-^{3}A'	**5**-^{3}A"
$(a')^2(a')^2(a')^2$	$(a')^2(a')^2(a'')^2$	$(a')^2(a'')^2(a')^1(a')^1$	$(a')^2(a')^2(a')^1(a'')^1$
E_{rel} = 198	E_{rel} = 31.4	E_{rel} = 0.0	E_{rel} = 14.5

Figure 6. Angular parameters (in degrees), occupancy of the d^6 electrons, and relative energy (in kJ mol^{-1}) of the low-lying singlet and triplet states of [$CpMn(CO)_2$].

importantly, extension of the given argument to the triplet state of **5** affords two minima (**5**-^{3}A′ and **5**-^{3}A″, Figure 6), both of which are *lower* in energy than **5**-^{1}A′a. Calculated frequencies of **5** have been invoked in the past to aid the characterization of transient intermediates observed in the photolysis of [$CpMn(CO)_3$],[7b] but only one triplet species was accounted for.

In conclusion, results from the present study reveal that both the singlet and triplet low-energy states of the unsaturated [$CpML_3$] system are subject Jahn–Teller effects. This finding can provide a basis for interpreting the geometries in other unsaturated [$CpML_n$] compounds, and suggests a need to consider more than one state in electronic structure studies of related systems.

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Remarkable Boosting of the Binding of Ion-Paired Organic Salts by Binary Host Systems**

Grazia Cafeo, Giuseppe Gattuso, Franz H. Kohnke, Anna Notti, Salvatore Occhipinti, Sebastiano Pappalardo, and Melchiorre F. Parisi*

The formation of host–guest complexes is normally achieved by the combined action of a number of weak noncovalent forces between the binding sites of the receptor and the target substrate.[1] However, for host–guest complex-

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