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The Electronic Structures of $[\mathrm{CpFe(NO)}]_2$, $[\mathrm{CpCo(CO)}]_2$, $[\mathrm{CpCo(NO)}]_2$, and $[\mathrm{CpNi(CO)}]_2$. A Comparison of the Molecular Orbital Results with the Valence Bond Formalisms for Metal–Metal Bonding

Kimberly A. Schugart and Richard F. Fenske*

Contribution from the Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706. *Received January 21, 1986*

Abstract: The electronic structures of $[\mathrm{CpFe(NO)}]_2$, $[\mathrm{CpCo(CO)}]_2$, $[\mathrm{CpCo(NO)}]_2$, and $[\mathrm{CpNi(CO)}]_2$ were examined with use of the Fenske–Hall molecular orbital method. The results were analyzed with a view to discerning the similarities and differences among these four complexes in terms of metal–metal and metal–bridge interactions. Additionally, a correlation between a simple valence bond description of the metal–metal interaction and a bond order derived from the electronic structure was established for these complexes.

Considerable interest and speculation have been directed at the nature of bonding in transition-metal dimer complexes of the general formula $[\mathrm{CpM(EO)}]_2$.[1-4] Here M is Fe, Co, or Ni, E is C or N, and Cp is η^5-$\mathrm{C_5H_5}$. A schematic description of these complexes is shown in Figure 1. An earlier discussion of this series of transition-metal dimers has been presented by Pinhas and Hoffmann,[1] who used the hypothetical complex $[\mathrm{CpCo(CO)}]_2^{2-}$ as the basis of their discussion. We undertook this investigation to see whether substantive differences occur upon alteration of metal and/or bridge ligands. In particular, we wish to probe more deeply into the nature of the metal–metal and metal–bridge interactions in these complexes. We are especially interested in the metal–metal interactions, for despite the differences in bond multiplicities that are indicated by the valence bond structures, the metal–metal separations are essentially the same within this series, as shown in Table I. We examined the series of neutral diamagnetic compounds $[\mathrm{CpFe(NO)}]_2$, $[\mathrm{CpCo(CO)}]_2$, $[\mathrm{CpCo(NO)}]_2$, and $[\mathrm{CpNi(CO)}]_2$ by means of molecular orbital theory to discern the nature of the metal–metal and metal–bridge interactions. In this paper, we investigate the molecular orbital structure of each complex and identify the electronic similarities and differences within this series. On the basis of this analysis, we attempt to correlate the molecular orbital analysis of the interactions between metals and with the simple valence bond pictures of the metal–metal interactions to determine the relationship of the bond orders in these complexes to the metal–metal separations in this series. Finally, we use the foundations generated in this study as a starting point in the following paper to understand the implications of the addition or subtraction of electrons from these complexes.

Calculation Details

Molecular orbital calculations were performed on a Harris/7 computer system with use of the Fenske–Hall molecular orbital method which has been described elsewhere[5] and its uses reviewed.[6,7] A nonempirical, nonparametrized molecular orbital method, the results of a calculation (eigenvectors and eigenvalues) are completely determined by the geometry of the molecule and the nature and size of the basis set.

Basis Functions. Clementi's free atom double-ζ Hartree–Fock functions[8] were used for C, N, and O. All except the valence shell p functions were curve-fit to single-ζ form with use of the criterion of maximum overlap.[9] A value of 1.16 was used for the hydrogen 1s atomic orbital because it minimizes the energy of methane.[10] The functions 1s through 3d for Fe, Co, and Ni were taken from tables of Richardson, Nieuwport, Powell, and Edgell.[11] The exponents for the single-ζ 4s and 4p orbitals were set to 2.0.

Table I. Metal–Metal Separations of $[\mathrm{CpM(EO)}]_2$ Complexes

molecule	M–M (Å)	ref
$[\mathrm{CpFe(CO)}]_2$	2.326	12
$[\mathrm{(Me_5Cp)Co(CO)}]_2$	2.338	3
$[\mathrm{CpCo(NO)}]_2$	2.372	2
$[\mathrm{CpNi(CO)}]_2$[a]	2.357	14

[a] Average of two molecules in asymmetric unit.

Structures. The molecular geometries for $[\mathrm{CpFe(NO)}]_2$ and $[\mathrm{CpCo(NO)}]_2$ were taken from X-ray crystal structure data for $[\mathrm{CpFe(NO)}]_2$[12] and $[\mathrm{CpCo(NO)}]_2$.[2] The geometry for $[\mathrm{CpCo(CO)}]_2$ was taken from the X-ray crystal structure data for $[\mathrm{C_5Me_5Co(CO)}]_2$,[2,13,14] since no structural data for $[\mathrm{CpCo(CO)}]_2$ exist in the literature. The geometry for bent-core $[\mathrm{CpNi(CO)}]_2$ was taken from the X-ray crystal structure for this compound,[14] and the geometry for the planar version was set to maintain the same metal–cyclopentadienyl ligand, metal–bridge ligand, and metal–metal separations that exist in the bent-core structure.

General Considerations

The arrangement of the atoms in the dimers and their placements with respect to each other and the master coordinate system are shown in Figure 2. The metal atoms, each flanked by a cyclopentadienyl ring, lie along the positive and negative y axis of the master coordinate system. The bridge ligands lie on the master coordinate positive and a negative z axis. The local coordinate axes of each metal and bridge ligand atom are also shown in Figure 2. The z axis of the local coordinate system on each atom points to the origin of the master coordinate system.

The symmetry and, consequently, labeling of the molecular orbitals of these molecules must be examined from the point of view of the orientation of the cyclopentadienyl ligands with respect to each other. If the cyclopentadienyl rings are staggered with respect to each other, the molecule conforms to the Schoenflies point group C_i. If the cyclopentadienyl rings are eclipsed with respect to each other, the molecule belongs to the point group C_{2h}. We chose the higher symmetry C_{2h} labels to describe the molecular orbitals in this discussion. The cyclopentadienyl ligand orbital

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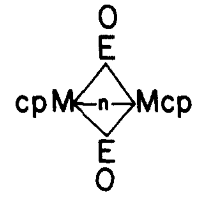

M	E	n(bond order)
Fe	N	2.0
Co	C	2.0
Co	N	1.0
Ni	C	1.0

Figure 1. Schematic description of complexes with the general formula [CpM(EO)]$_2$.

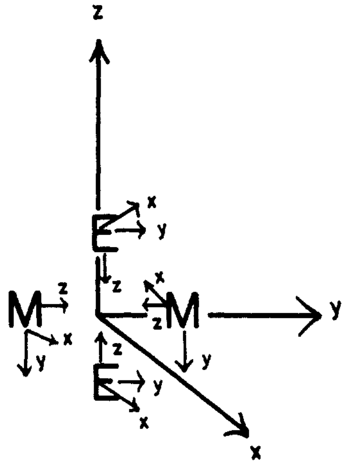

Figure 2. Master coordinate system and local coordinate axes on metal and bridge atoms.

levels have been omitted from the molecular orbital diagrams and the drawings that clarify the metal–metal and metal–ligand interactions. Their presence in a particular molecular orbital, however, will be included in the discussion of that orbital.

[CpFe(NO)]$_2$ and [CpCo(CO)]$_2$. The molecular orbital diagrams for these two complexes are shown in Figure 3. The molecular orbital scheme on the left-hand side of the diagram corresponds to the orbital interactions for [CpFe(NO)]$_2$ while the one on the right-hand side corresponds to the orbital interactions for [CpCo(CO)]$_2$. On the left-hand side of each molecular orbital scheme in Figure 3 are the values for the energies of the metal 3d orbitals. The less electronegative iron 3d level is expectedly higher in energy than the cobalt 3d level. The right-hand sides of the molecular orbital schemes consist of the energy levels for the bridge–ligand orbitals. For each carbonyl or nitrosyl ligand, these consist of a filled 5σ donor level, lower in energy than the metal 3d orbitals, and a doubly degenerate empty 2π acceptor level, higher in energy than the metal 3d orbitals. The values for the energies of the metal and bridge–ligand levels are listed in Table II.

Despite the isoelectronic nature of these two systems, only the HOMOs and LUMOs are directly comparable, consisting of the same type of metal–metal and metal–ligand interactions as well as their placements with respect to the rest of the molecular orbitals in these complexes. The LUMO, labeled 5_{ag} in these two complexes, is in both cases an antibonding arrangement of metal d_{xz} orbitals. These d_{xz} orbitals also interact with cyclopentadienyl ligand character. No bridge ligand character is present in this level since no linear combinations of bridge-ligand orbitals can form a symmetric complement to the metal–metal interaction.

The HOMO of each complex, labeled 4bu in both molecules, is the bonding combination of the metal orbitals that were antibonding in the LUMO. The d_{xz} orbitals on each metal in each dimer are arranged in phase with respect to each other. Also present with the metal–metal bond is a metal–ligand bond formed from the participation of bridge-ligand 2π character. The metal–ligand interaction is bonding, making this level simultaneously metal–metal and metal–ligand bonding. Cyclopentadienyl ring character is also present in this level.

Table II. Fock Matrix Diagonal Elements for Metals and Bridge Ligands

molecule	ϵ metal d (eV)	ϵ bridge (eV)		$\Delta\epsilon$ metal–bridge (eV)
[CpFe(NO)]$_2$	−11.32	−7.12	2π	4.20
		−17.83	5σ	6.51
[CpCo(CO)]$_2$	−11.90	−2.23	2π	9.67
		−14.87	5σ	2.97
[CpCo(NO)]$_2$	−11.80	−6.79	2π	5.10
		−18.91	5σ	7.11
[CpNi(CO)]$_2$	−13.47	−2.47	2π	11.0
(Planar)		−15.95	5σ	2.48

The gap between the HOMO and the LUMO is larger for the iron dimer, 3.65 eV, than for the cobalt complex, 1.95 eV. This is because the LUMO in the iron system is at higher energy than the LUMO of the cobalt system, and the HOMO of the iron complex is at lower energy than the HOMO of the cobalt dimer. Initially the lower energy HOMO of the iron dimer relative to the cobalt dimer seems somewhat surprising, since the more electronegative cobalt has its d orbitals at lower energy than iron does. This is shown in Table II. However, the HOMO in each case consists of a metal–bridge interaction, and the bridge orbital energy and interaction with the metals must be analyzed as well. The nitrosyl 2π acceptor orbitals have been documented as superior π acceptors compared to the carbonyl 2π levels[28] when the nitrosyl 2π levels are found lower in energy and, consequently, closer in energy to the metal d orbital energy levels. The difference between the iron d levels and the nitrosyl 2π levels is 4.20 eV, while the difference between the cobalt d levels and the carbonyl 2π levels is 9.67 eV. Table II lists the values for the iron and cobalt d orbital energies and the nitrosyl and carbonyl 5σ and 2π energies. Overall, the iron–nitrosyl interaction synergistically results in greater stabilization of this particular molecular orbital over the corresponding cobalt–carbonyl interaction.

The characters and compositions of the molecular orbitals differ considerably after this point in a comparison of levels which are the same number of levels below the HOMOs. As an example, the second highest occupied molecular orbital in the iron dimer, 3bu in character, is an antibonding combination of $d_{x^2-y^2}$ and d_{z^2} orbitals on the metals. Neither nitrosyl nor cyclopentadienyl ligand levels participate. Conversely, the second highest occupied molecular orbital in the cobalt complex, labeled 3bg, consists of metal d_{yz} orbitals combined with carbonyl 2π and cyclopentadienyl ligand character. The metal–metal interaction is antibonding, the metal–carbonyl one bonding. The nature of the metal–metal interactions in both cases is antibonding, but the metal d orbitals that participate in this orbital for the iron dimer are different than those that participate in the same level in the cobalt complex.

A most significant and interesting discrepancy in the bonding in these complexes is born out in the levels labeled 3ag and 2bu. These levels consist of linear combinations of $d_{x^2-y^2}$ and d_{z^2} metal orbitals arranged in a bonding manner in one level and an antibonding manner in the other. Bridge-ligand 2π character participates in the antibonding arrangement of metal orbitals, and the metal–ligand interaction is bonding. In [CpCo(CO)]$_2$, the metal–metal bonding level 3ag lies lower in energy than the metal–metal antibonding, metal–ligand bonding level 2bu. This anticipated arrangement is reversed in the case of the iron–nitrosyl dimer. The metal–metal antibonding, metal–ligand bonding level 2bu lies lower in energy than its metal–metal bonding counterpart 3ag which contains no ligand character. The proximity of the energy of the nitrosyl 2π levels to the iron d levels relative to the energetic disparity of the carbonyl 2π levels to the cobalt d orbital accounts for this phenomenon. The counterintuitive ordering of

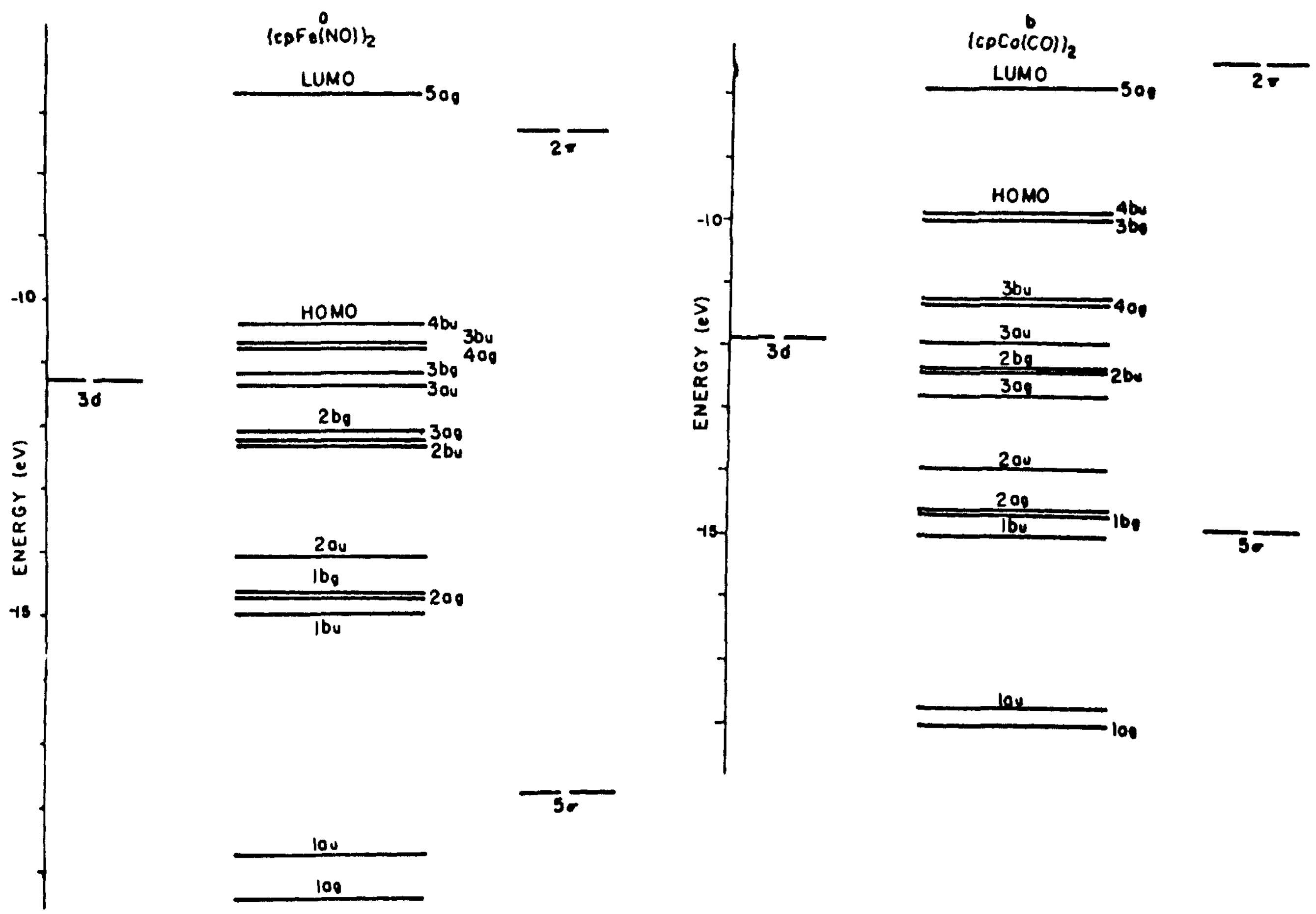

Figure 3. Molecular orbital diagram for [CpFeNO)]$_2$ (a) and [CpCo(CO)]$_2$ (b).

orbitals in the iron–nitrosyl dimer can be traced to the amount of nitrosyl participation relative to the amount of carbonyl participation. The metal–metal antibonding, metal–ligand bonding orbital in the nitrosyl case contains 63% total bridge–ligand character, while this level in the cobalt–carbonyl complex contains only 30% bridge–ligand character. The impact of the synergistic iron–nitrosyl interaction is both counterintuitive and significant. The strength of the metal–ligand interaction over the metal–metal interaction is most aptly demonstrated in this orbital reversal.

Similarly, the next ten orbitals in each complex differ in composition and character. Lowest in energy, in both the iron and cobalt system molecular orbital schemes are two levels which are the same in both complexes. These levels are the lowest energy metal–metal interactions and include metal–bridge character. In one of these levels, the bridge 5σ orbitals interact with the metal d_{yz} along with some metal 4p_z character to produce the 1au level. The second level consists of a linear combination of metal d_{z^2} and 4s interacting with bridge–ligand 5σ to produce a 1ag level. Some cyclopentadienyl ring character is present in both the 1ag and 1au orbitals. The amounts of metal and bridge-ligand participation in these molecular orbitals differ between the iron and cobalt complexes. In the iron dimer, very little metal orbital contribution is observed relative to the cobalt complex. The reason for this discrepancy between these two isoelectronic and isostructural analogues is again found in an analysis of the relative energies of the metal and ligand orbitals. The 5σ orbitals of the carbonyl ligand are closer in energy to the cobalt d orbitals than the 5σ orbitals of the nitrosyl ligand are to the iron d orbitals. The difference in energy between the iron d orbitals and the nitrosyl 5σ level is 6.51 eV, while the difference in energy between the cobalt d orbitals and the carbonyl 5σ is 2.97 eV. These values and the energies of the metal d orbitals and the ligand 5σ levels are listed in Table II. The energetic proximity of the carbonyl 5σ levels to the cobalt d orbitals results in a better admixture of these two components in this molecular orbital while the difference in value between the iron 3d and the nitrosyl 5σ levels results in a molecular orbital dominated by the 5σ contribution.

A second slightly different view of the electronic makeup of these complexes reveals the reasons for the striking differences in orbital character and composition in the levels below the HOMO between these two molecules. Figure 4 depicts the molecular orbital diagrams of these two complexes in a manner that better describes the impact of the cyclopentadienyl rings on the different metal d orbitals. Both metals within each dimer exhibit the same d orbital interactions and splittings. The left-hand side of each molecular orbital diagram shows the metal d orbital hybrids formed upon complexation of the metal with the cyclopentadienyl ligand alone. The right-hand side contains the energy levels of the bridge-ligand orbitals. The local coordinate axes that define the orbital representations are also depicted in Figure 4.

The metal d orbitals of each compound fall roughly into the expected three-below-two splitting arrangement. Highest in energy among these levels is the degenerate set of d_{xz} and d_{yz} orbitals in antibonding arrangements with the cyclopentadienyl rings. Below this set lies an orbital primarily d_{z^2} in character. In both the set of d_{xz} and d_{yz} type orbitals and the d_{z^2} type orbitals, the shape and direction of the orbital is toward the other metal center of the molecule and away from the cyclopentadienyl ligand. Lowest in energy is a second twofold degenerate level. This level consists of the remaining d orbitals, $d_{x^2-y^2}$ and d_{xy}. The composition of this level is almost entirely d orbital in nature. This is not unexpected since these orbitals lie parallel to the plane of the cyclopentadienyl ring and, consequently, are least perturbed in metal–ring interactions.

There are some differences between these complexes in the splittings and energetics of the d orbitals. While the d_{z^2} and degenerate d_{xy} and $d_{x^2-y^2}$ orbitals of the cobalt complex are at lower energy than these same d orbitals in the iron complex, the d_{xz} and d_{yz} orbitals of iron and cobalt are quite close in energy in these two compounds. The similarity in the energy values of these two

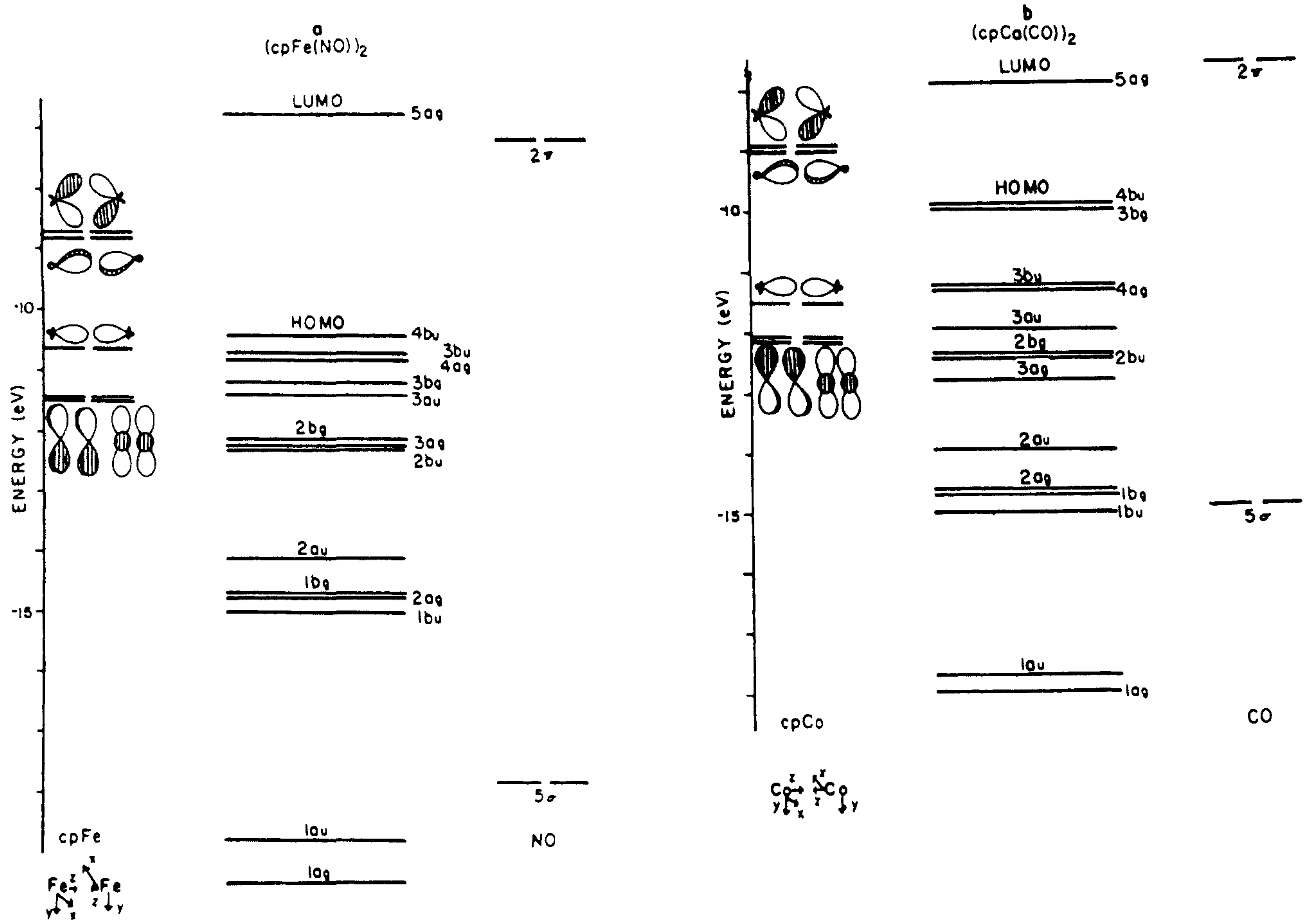

Figure 4. Molecular orbital diagram for $[CpFe(NO)]_2$ (a) and $[CpCo(CO)]_2$ (b). Local coordinate axes shown refer to both complexes.

levels in these two compounds emphasizes the difference between the metal and bridge-ligand energy levels in these complexes and ultimately the difference in metal–bridge interaction. The degenerate d_{xz} and d_{yz} type orbitals of the cobalt complex are separated from the carbonyl bridge-ligand 2π level by 6.64 eV, while the difference between the iron and nitrosyl levels in the iron dimer is only 1.55 eV. Likewise, the separation between the remaining d orbitals in each complex and the bridge-ligand energy level of that complex is much greater in the case of the cobalt–carbonyl complex than in the case of the iron–nitrosyl dimer. Altogether, the composition and character of molecular orbitals below the HOMO can be seen to differ both in terms of the metal–bridge interactions as well as metal–bridge influenced metal–metal interactions.

Comparison of Molecular Orbital and Valence Bond Analyses of Metal–Metal Interactions

Despite the overall differences in compositions and ordering of the various orbitals, the valence bond description of the metal–metal interactions is identical for these dimers. A bond order of 2 is assigned to this interaction. The manifestation of this double bond is apparent as both complexes are seen to exhibit similar chemical reactivities. These iron and cobalt dimers undergo a variety of additions across the metal–metal interaction, yielding products that still retain some type of metal–metal linkage.[15-24] Similarly, both the iron dimer and the cobalt dimer undergo one-electron reductions while retaining some sort of a net metal–metal interaction.[15] One possible explanation from the molecular orbital viewpoint for the similarity in the chemical reactivities of these complexes is found in examining the availability of the orbitals that are most likely to participate in a chemical reaction, i.e., those at or near the HOMO or the LUMO. The molecular orbital schemes of both complexes show metal d_{xz} character in both the HOMO and the LUMO. Since the d_{xz} orbitals lie perpendicular to the plane containing the metals and bridges, a potential incoming adduct would not be sterically hindered in an attack on these dimers. The orbital availability alone, however, does not necessarily account for the retention of metal–metal linkage in the product of the hypothetically formed dimer–adduct complex, nor does it explain the retention of metal–metal interaction upon reduction of these dimers.

Although a molecular orbital analysis can describe the probable orbitals involved in a chemical reaction, it does not provide a description of the potential chemical and electrochemical reactivity of these complexes. However, in an attempt to discern the relationship between the molecular orbital and valence bond descriptions of the metal–metal interactions of these complexes, we examined all of the filled orbitals in these complexes that exhibited metal–metal interactions. Within this category fall those orbitals which additionally contain metal–ligand interactions. All the metal–metal interactions can be grouped into two classifications: those exhibiting metal–metal antibonding character and those

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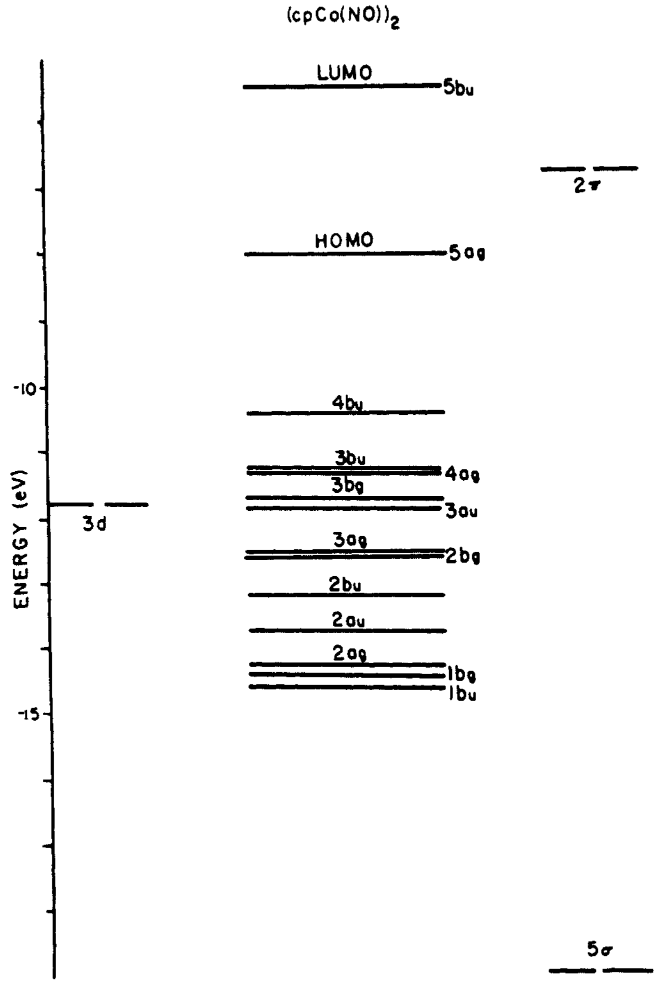

Figure 5. Molecular orbital diagram for $[CpCo(NO)]_2$.

exhibiting metal–metal bonding character. A summation and comparison of each of these classifications results in a net bond or antibond molecular orbital description of the metal–metal interactions in the complex to which the valence bond description can be compared. In the case of these dimers, the total number of molecular orbitals exhibiting metal–metal (and metal–ligand) bonding interactions exceeds by two the total number of molecular orbitals exhibiting metal–metal antibonding interactions. This value is in agreement with the bond order derived from the valence bond description. However, it is important to recognize that no set of single or particular interactions can be assigned to the bonds shown in the valence bond structure. The plethora of interactions that occur between the metals and between the metal and bridge ligands which are seen in the molecular orbital diagram can be neither qualitatively discerned from nor effectively translated into the simple valence bond description.

$[CpCo(NO)]_2$. The molecular orbital diagram for $[CpCo(NO)]_2$, which contains two more electrons and two more protons than the iron dimer or cobalt carbonyl complex, is shown in Figure 5. Only sketches of the orbitals important in comparisons of this complex to the other dimers are depicted. By examining the relative orbital energies of the metal 3d and bridge-ligand 2π and 5σ levels, it is clear that the metal d orbitals in this complex reside closer energetically to the nitrosyl 2π levels than they do to the nitrosyl 5σ levels. The difference between the metal 3d and the bridge-ligand 2π is 5.10 eV, while the difference between the metal 3d and nitrosyl 5σ is 7.11 eV. These values and the values of the energies of the 3d, 5σ, and 2π levels are listed in Table II. This situation, in which the metal orbitals are energetically closer to the bridge-ligand 2π levels than to the 5σ levels, is also seen in the case of the iron–nitrosyl dimer. Since the metal–ligand interactions are stronger than the metal–metal ones, we expect the electronic structure of the cobalt–nitrosyl dimer to be more similar to the iron–nitrosyl dimer than to the cobalt–carbonyl complex. This is indeed the case. The molecular orbital interactions for the first five filled orbitals are almost identical with the interactions found in the LUMO and first four filled molecular orbitals of the iron dimer. The HOMO of $[CpCo(NO)]_2$ is identical in character to the LUMO of $[CpFe(NO)]_2$. This level consists in both cases of the antibonding arrangement of metal d_{xz} orbitals together with some cyclopentadienyl ligand character. The cyclopentadienyl ligands are in an antibonding arrangement with the metal orbitals. The next four levels below this level in the cobalt–nitrosyl dimer mimic the molecular orbital scheme of the iron dimer and are different than the interactions found in the cobalt carbonyl complex. Most of the electronic interactions of the $[CpCo(NO)]_2$ complex found in levels below the five highest occupied molecular orbitals are unique to the cobalt–nitrosyl complex as the composition and character of all but two of the molecular orbitals below the five highest occupied levels do not parallel the composition and character of the levels in either the cobalt–carbonyl or iron–nitrosyl dimer. These last two are the same for all three complexes. The 1ag and 1au levels are the lowest levels depicted in the molecular orbital diagram and correspond to the lowest energy metal–metal and metal–ligand interactions. These levels reflect the expected trends of metal–ligand participation set by the iron–nitrosyl and cobalt–carbonyl compounds. The cobalt d orbitals, lower in energy than the iron d orbitals, participate to a greater extent in the interaction with the nitrosyl 5σ level than the iron levels do but do not reflect the same extent of participation of cobalt 3d character seen in the cobalt–carbonyl complex. The middle-level amount of participation of the cobalt d orbitals in the cobalt–nitrosyl complex relative to the iron–nitrosyl and cobalt–carbonyl dimers reflects the impact a single change of either metal or ligand can make in the bonding within a given framework.

A tally of the metal–metal bonding and metal–metal antibonding molecular orbital interactions indicates a net molecular orbital bond order of one. This is in agreement with the valence bond picture of this complex. The character and composition of the LUMO, an antibonding arrangement of metal d_{z^2} orbitals which are in phase with respect to the metal–bridge interactions and contain some cyclopentadienyl character as well, indicate that the single bond ought to be cleaved homolytically in a reduction of this complex. In fact, Bergman and co-workers have capitalized on production of the monomer $[CpCo(NO)]^-$ in this manner for use of a precursor in synthetic reactions.[25,26]

The valence bond description clearly points to a single bond between the two metal atoms. The pattern of cleavage of this dimer is clarified in examining the molecular orbital analysis of the character and composition of the LUMO. While the net molecular orbital bond analysis agrees with the valence bond description, the relationships of the metal and ligand orbitals to each other are perhaps more clearly delineated through examination of the molecular orbital diagram.

$[CpNi(CO)]_2$ Planar and Bent. The complex $[CpNi(CO)]_2$ is known to exist with the $Ni_2(CO)_2$ in both bent and planar forms. The bent form of $[CpNi(CO)]_2$ has been observed crystallographically,[14] and the planar form, along with the bent structure, is evidenced in the solution and solid-state infrared spectroscopic data.[14] Dahl and co-workers suggest a very low energy barrier exists between the two forms which are interconverted into each other through a butterfly-like motion that occurs in solution.[14] Since the planar structure is a member of the isostructural series of complexes we were investigating, we attempt to determine its relationship with respect to the other dimers in this series. We also consider briefly the nature of the interactions in the bent core structure.

The molecular orbital diagrams for the bent and planar core $[CpNi(CO)]_2$ complex are shown in Figure 6. The left-hand side of the figure reveals the molecular orbital scheme for the planar core nickel dimer on which we focus first. The right-hand side depicts the molecular orbital interactions for the bent core nickel complex which we examine later.

From an examination of the relative energies of the nickel 3d levels and carbonyl 2π and 5σ levels in the planar core complex,

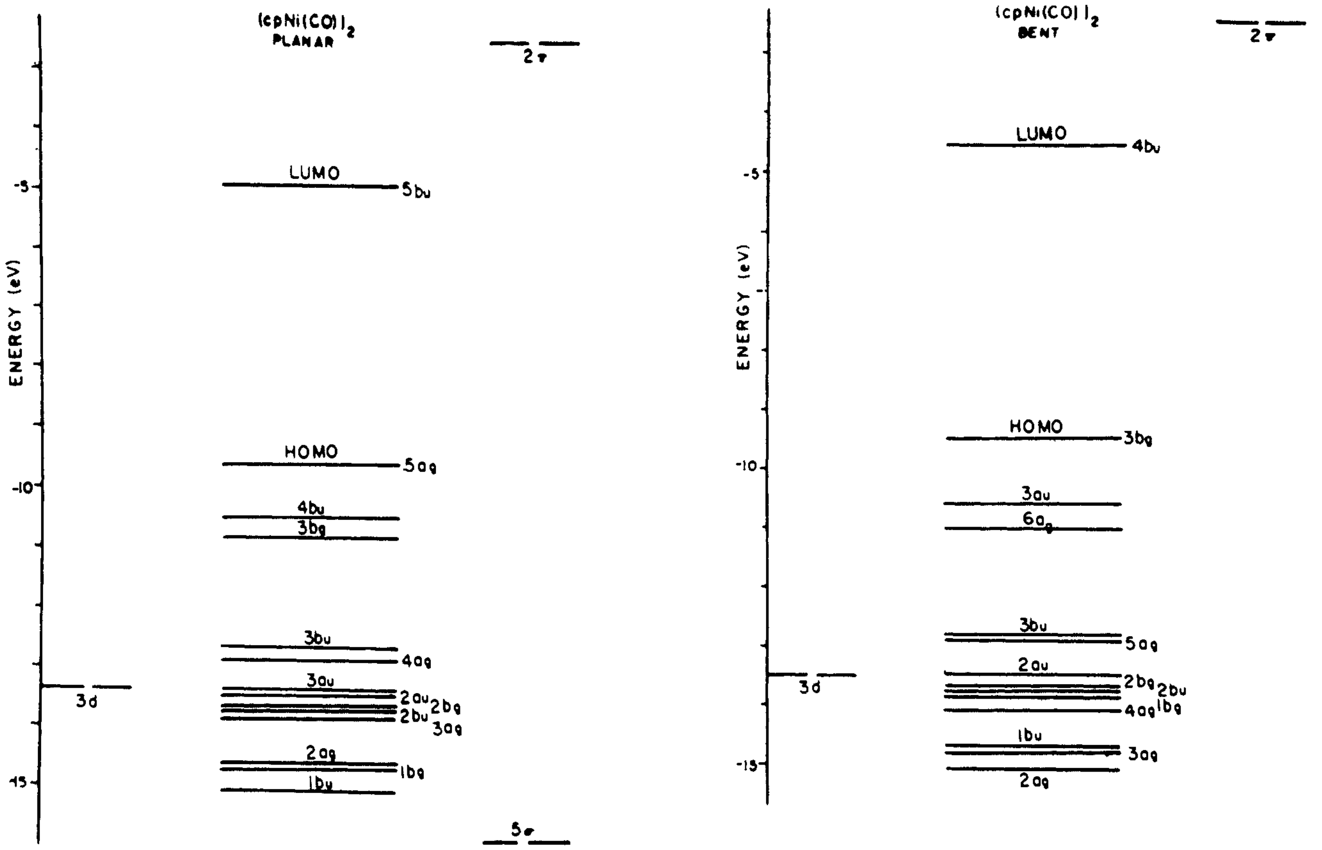

Figure 6. Molecular orbital diagram for [CpNi(CO)]$_2$. Planar core is on the left (a) and bent core is on the right (b). Labeling scheme for (b) is same as in (a) for ease of comparison.

it is clear that the nickel d orbitals reside closer energetically to the carbonyl 5σ levels than they do to the carbonyl 2π levels. The difference between the metal 3d and bridging carbonyl 5σ levels is 2.48 eV, while the differences between the metal 3d and bridge-ligand 2π is 11.0 eV. The values of the nickel d orbital and carbonyl 5σ and 2π levels are listed in Table II. This situation, in which the metal orbitals are energetically closer to the bridge-ligand 5σ levels than to the bridge 2π levels, is analogous to the situation found in the cobalt–carbonyl dimer. Consequently, we expect the electronic structure of the nickel–carbonyl complex to be more like the electronic structure of the cobalt–carbonyl dimer than the electronic structure of the iron–nitrosyl or cobalt–nitrosyl molecules. This is exactly what we encounter. The six highest occupied molecular orbitals of the nickel–carbonyl complex are almost identical in character and composition to the LUMO and five highest occupied molecular orbitals of the cobalt carbonyl complex. The LUMO of [CpNi(CO)]$_2$ in the planar core framework is the same in nature as the LUMO of [CpCo(NO)]$_2$. Both consist of an antibonding combination of d_{z^2} orbitals which interact in a bonding manner with the complementary bridge-ligand character. The HOMO of [CpNi(CO)]$_2$ in planar form is of the same composition as the LUMO of [CpCo(CO)]$_2$. This level consists in both cases of the antibonding arrangement of metal d_{xz} orbitals together with some cyclopentadienyl character, arranged in a bonding manner with the metal orbitals of the complex. The participation of bridge-ligand character in this level is not allowed on symmetry grounds. The next five levels below this one parallel the bonding interactions found in [CpCo(CO)]$_2$ but, except for the two lowest energy levels, are different than the interactions found in any of the other dimers. These two lowest energy levels are the same 1ag and 1au levels found in other complexes. These two levels follow the trend of metal–bridge ligand participation already delineated in the analysis of the other dimers. In this nickel complex, the interaction of nickel d orbitals with carbonyl 5σ is greater than it is in the case of the cobalt–carbonyl complex, which to this point exhibited the most equal admixture of metal d and bridge 5σ character.

The valence bond structure of this complex reveals a metal–metal interaction identical with the metal–metal one in [CpCo(NO)]$_2$. Again, the molecular orbital net orbital interaction analysis agrees but, as in all other cases, does not give an indication of the nature of the metal–metal interactions. Since the character of the LUMO is the same in both the planar [CpNi(CO)]$_2$ and [CpCo(NO)]$_2$, we expect the nickel complex to behave in a manner similar to the cobalt compound upon reduction. Populating the LUMO should result in a homolysis of the nickel dimer.

The bent core [CpNi(CO)]$_2$, like its planar core analogue, exhibits d orbital energies much closer to the bridge-ligand 5σ levels than to the 2π levels. The character and composition of the LUMO in this complex are also the same as they are in the planar core [CpNi(CO)]$_2$ complex and the cobalt–nitrosyl dimer. Other than the two similarities this complex shows in relative metal–ligand energetics and LUMO character and composition, the bent core [CpNi(CO)]$_2$ exhibits markedly different interactions compared to the other planar core complexes as shown in the right-hand side of Figure 6. This is hardly surprising, though, in light of the deformations incurred upon moving both bridge ligands and cyclopentadienyl rings into a new arrangement. The difference in energy between the bent and planar core forms is slight. Summation of the 13 highest occupied molecular orbitals (those orbitals which contain metal–metal and metal–bridge 2π character) shows relatively little difference, testifying to the facile interconversion of the two forms.

Conclusions

From the molecular orbital descriptions of this series of dimers two general conclusions can be drawn. First, there are three ways in which the bridge–metal bonds may be formed. The metal–bridge bond may consist almost exclusively of metal orbitals interacting with bridge 2π orbitals, as in the case of the iron–nitrosyl dimer. Alternatively, the metal orbitals may interact primarily with bridge-ligand 5σ orbitals, as in the nickel–carbonyl dimer. These two metal–ligand interactions represent the extreme forms of metal–ligand admixtures, and a third intermediate type consists of metal orbitals interacting with both bridge-ligand 2π and 5σ orbitals. The cobalt–carbonyl and cobalt–nitrosyl dimers are representative of this last type of metal–bridge interaction. Finally, it is to be noted that there are no orbitals that are purely bridge-ligand in character as some authors have speculated.[1,2]

The second general conclusion which can be drawn from the molecular orbital analysis concerns the influence of the bridge ligands on the metals. From a comparison of the different molecular orbital diagrams, it is clear that the nature of the bridge ligands more strongly influences the ordering, and hence electronic structure, of the dimers than does the choice of the metal atoms. This conclusion is born out in the comparative analysis of these systems. The iron–nitrosyl and cobalt–carbonyl dimers are quite different electronically, yet the cobalt–nitrosyl dimer is much more similar in the arrangement of its molecular orbitals to the iron–nitrosyl dimer than it is to the cobalt–carbonyl complex. Although there is no other nickel complex to which we can compare the planar core nickel–carbonyl, it is important to note the strong similarities between the electronic structure and ordering of orbitals of this complex and the cobalt–carbonyl system. The planar core nickel–carbonyl complex electronic structure does not parallel that of the iron–nitrosyl dimer.

Since the ordering of molecular orbitals is dependent upon the metal–bridge interactions and not the metal–metal ones, it appears that the metal–bridge interactions will more strongly influence the metal–metal separation in these complexes than the metal–metal interactions. This finding is in agreement with that of Pinhas and Hoffmann. Ultimately, then, in light of the differences we have delineated in the bondings and electronic structures that occur upon alteration of either a bridge ligand or a metal atom in these dimers, predictions of the metal–metal separations based upon comparisons of the simple valence bond structures in this series of dimers do not seem entirely feasible. While the valence bond analysis may point to differences in bond multiplicities among the members of this series, these differences are best perceived as indications of metal–metal separations.

Finally, the agreement found between the net molecular orbital bond analysis and the valence bond descriptions shows that a relationship between these two models exists for this series of dimers. Furthermore, this relationship is synergistic, as the molecular orbital analysis can provide insight to the product of a chemical reaction (as in the reduction of $[CpCo(NO)]_2$), while the valence bond description provides an immediate picture of the expected chemical reactivity. However, a previous investigation on a different set of complexes indicates that the agreement between the new molecular orbital bond order and valence bond order analysis may not always hold true.[27] Consequently, the results here should not be extrapolated to other systems without careful investigation.

Altogether, the valence bond analysis is reflected in the molecular orbital descriptions of these complexes. However, the bond orders derived from the valence bond description are seen best as benchmarks to the expected chemical or electrochemical reactivity of these complexes and not as guides to the metal–metal separations among this series of complexes. The impact that a single change in metal or bridge-ligand atom makes in this series of compounds in quite apparent from the molecular orbital analysis but clearly cannot be interpreted qualitatively from the simple valence bond descriptions.

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Stabilization of Transition-Metal Dimers through the Occupation of a Metal–Metal Antibonding Molecular Orbital

Kimberly A. Schugart and Richard F. Fenske*

Contribution from the Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706.

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Abstract: The occupation of antibonding molecular orbitals is generally perceived as a detriment to molecular stability. However, in this paper we discuss from a molecular orbital standpoint how this phenomenon enhances the stability of $Cp_2Co_2(CO)(NO)$ and $[CpCo(CO)]_2^-$ relative to $[CpCo(CO)]_2$ which decomposes easily in solution. In $[CpCo(CO)]_2^-$, the added electron occupies a molecular orbital metal–metal antibonding in character. By placing an extra electron on the metals and forming the monoanion, the metal donor levels are raised with respect to the ligand acceptor levels and consequently form a stronger metal–ligand bond than in the neutral complex. In the complex $Cp_2Co_2(CO)(NO)$ a similar situation arises. The oxidation of $Cp_2Co_2(CO)(NO)$ results in decomposition. Molecular orbital calculations indicate that the electron is removed from an orbital primarily metal–metal antibonding in character. In removing the electron, the metal donor levels are lowered substantially with respect to the ligand acceptor levels, detracting from the strength of the metal–ligand bond.

The occupation of a molecular orbital primarily antibonding in character has generally been construed as a detriment to overall molecular stability.[1] We report that populating a molecular orbital of an organometallic transition-metal compound that is primarily antibonding in character can stabilize the complex by indirectly enhancing the interactions in other bonding molecular orbitals. There are two complexes that fall into this category, $[CpCo(CO)]_2^-$ and $Cp_2Co_2(CO)(NO)$. The arrangement of the atoms of these dimers is depicted in Figure 1. These planar paramagnetic transition-metal dimers each contain one more electron than $[CpCo(CO)]_2$, a neutral diamagnetic complex whose bonding was discussed in the previous paper in this issue.[2] Some workers have suggested the unpaired electron in $[CpCo(CO)]_2^-$ and $Cp_2Co_2(CO)(NO)$ residues in an orbital primarily metal–metal antibonding in character, reducing the bond order between the metal atoms to 1.5 from the 2.0 of the neutral diamagnetic

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