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.

Acknowledgment. We gratefully acknowledge the National Science Foundation (CHE-8207434) for generous financial support.

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

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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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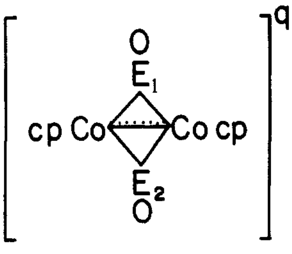

E_1	E_2	q
C	C	-1
C	N	0

Figure 1. Arrangement of atoms in $[CpCo(CO)]_2^-$ and $Cp_2Co_2(CO)(NO)$.

parent $[CpCo(CO)]_2$.[6] The synthetic versatility of the neutral diamagnetic dimer $[CpCo(CO)]_2$ has been demonstrated by several investigators.[3-5] However, this complex is unstable with respect to decomposition in solution.[3,6-8] This phenomenon stands in stark contrast to the behavior of the pentamethylcyclopentadienyl derivative[6] as well as the behavior of the paramagnetic complexes $[CpCo(CO)]_2^-$[9,10] and $Cp_2Co_2(CO)(NO)$.[9,11] While these latter two complexes exhibit synthetic versatilities indicative of the multiple bond between the metals,[12] they do not undergo the decomposition in solution that occurs with $[CpCo(CO)]_2$. Interestingly, the electrochemical oxidation of $Cp_2Co_2(CO)(NO)$ to $[Cp_2Co_2(CO)(NO)]^+$, which is isoelectronic to $[CpCo(CO)]_2$, is irreversible, indicating the decomposition of that complex as well. To discern the electronic factors that may be responsible for the relative chemical instability of $[CpCo(CO)]_2$ with respect to decomposition in solution in light of the stability of $[CpCo(CO)]_2^-$ and $Cp_2Co_2(CO)(NO)$ and the reasons for the irreversibility of the oxidation of $Cp_2Co_2(CO)(NO)$, we undertook Fenske–Hall molecular orbital calculations to elucidate the similarities and differences between the electronic structures of the paramagnetic $[CpCo(CO)]_2^-$ and $Cp_2Co_2(CO)(NO)$ and diamagnetic $[Cp_2Co_2(CO)(NO)]^+$. The information that can be derived from the molecular orbital analysis provides a fine correlation with the exhibited chemical and electrochemical behavior and serves as a focal point to which future investigations of the kinetic and thermodynamic factors may be directed.

Method of Calculation

The Fenske–Hall molecular orbital method, a nonparametrized, nonempirical molecular orbital method, has been described elsewhere[13] and its uses have been reviewed.[14,15] The results are dependent entirely on the basis set and atomic coordinates. The basis sets for all of the orbitals are the same as in our previous study.[2] The geometries for $Cp_2Co_2(CO)(NO)$ and $[CpCo(CO)]_2^-$ are taken from the crystal structure data. Calculations for the hypothetical $[CpCo(CO)(NO)]^+$ were undertaken with use of the structure of the neutral complex and the structure of $[CpCo(CO)]_2$. The results differ only slightly and point to the same lines of analysis.

General Considerations

The coordinate system about each atom in the metal–bridge plane is shown with respect to the master coordinate system in Figure 2. The bridge ligands lie on the master coordinate positive and negative z axis. The metal atoms, each flanked by a cyclopentadienyl ring, lie along the master coordinate system positive and negative y axis. The z axis of each local coordinate system points to the origin of the master coordinate system.

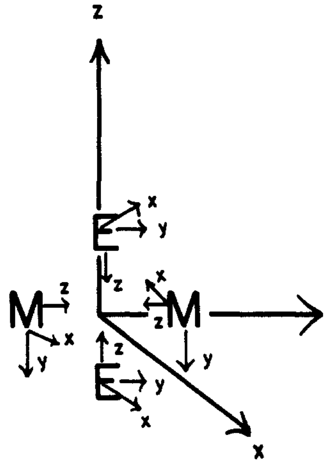

Figure 2. Local coordinate system on atoms with respect to the master coordinate system.

Table I. Metal and Bridge Ligand Orbital Energies

complex	ε metal (eV)	ε ligand (eV)
$[CpCo(CO)]_2$	−11.90	−14.87 (5σ) −2.23 (2π)
$[CpCo(CO)]_2^-$	−5.49	−9.37 (5σ) 3.10 (2π)
$Cp_2Co_2(CO)(NO)$	−11.88	−14.79 (CO 5σ) −2.17 (CO 2π)
		−18.89 (NO 5σ) −6.68 (NO 2π)
$[Cp_2Co_2(CO)(NO)]^+$	−18.15	−20.14 (CO 5σ) −7.38 (CO 2π)
		−24.36 (NO 5σ) −12.04 (NO 2π)

The symmetry labels for the molecular orbital diagrams are from the Schoenflies point group C_{2h}. Although $Cp_2Co_2(CO)(NO)$ does not conform to this point group, this choice of labeling scheme facilitates the comparison between this complex and $[CpCo(CO)]_2^-$ as well as the neutral parent $[CpCo(CO)]_2$. The cyclopentadienyl ligand levels have been omitted from both the molecular orbital diagrams and the drawings that clarify the metal–metal and metal–ligand interactions.

$[CpCo(CO)]_2^-$. The molecular orbital diagram for $[CpCo(CO)]_2^-$ is depicted in Figure 4 and that of its neutral parent in Figure 3. The molecualr orbital scheme shows some differences from the earlier work of Pinhas and Hoffmann[16] on the hypothetical dianion $[CpCo(CO)]_2^{2-}$. While the character and composition of the HOMO are in agreement in this study and their study, there are two levels below the HOMO that differ in metal atomic orbital composition in the Pinhas and Hoffmann study from the results of our calculations. However, the metal–metal antibonding character of the level just below the HOMO is reflected in our calculations, and the metal–metal bonding character of the level that lies two levels below the HOMO is realized in our calculations as well.

The paramagnetism of $[CpCo(CO)]_2$ has been demonstrated by several workers. The 15-line ESR spectrum of $[CpCo(CO)]_2^-$ taken in THF, glyme, acetone, and acetonitrile is a pattern characteristic of a hyperfine interaction of the unpaired electron with both ^{59}Co nuclei[17-19] ($I = {}^7/_2$, abundance 100%) in accord

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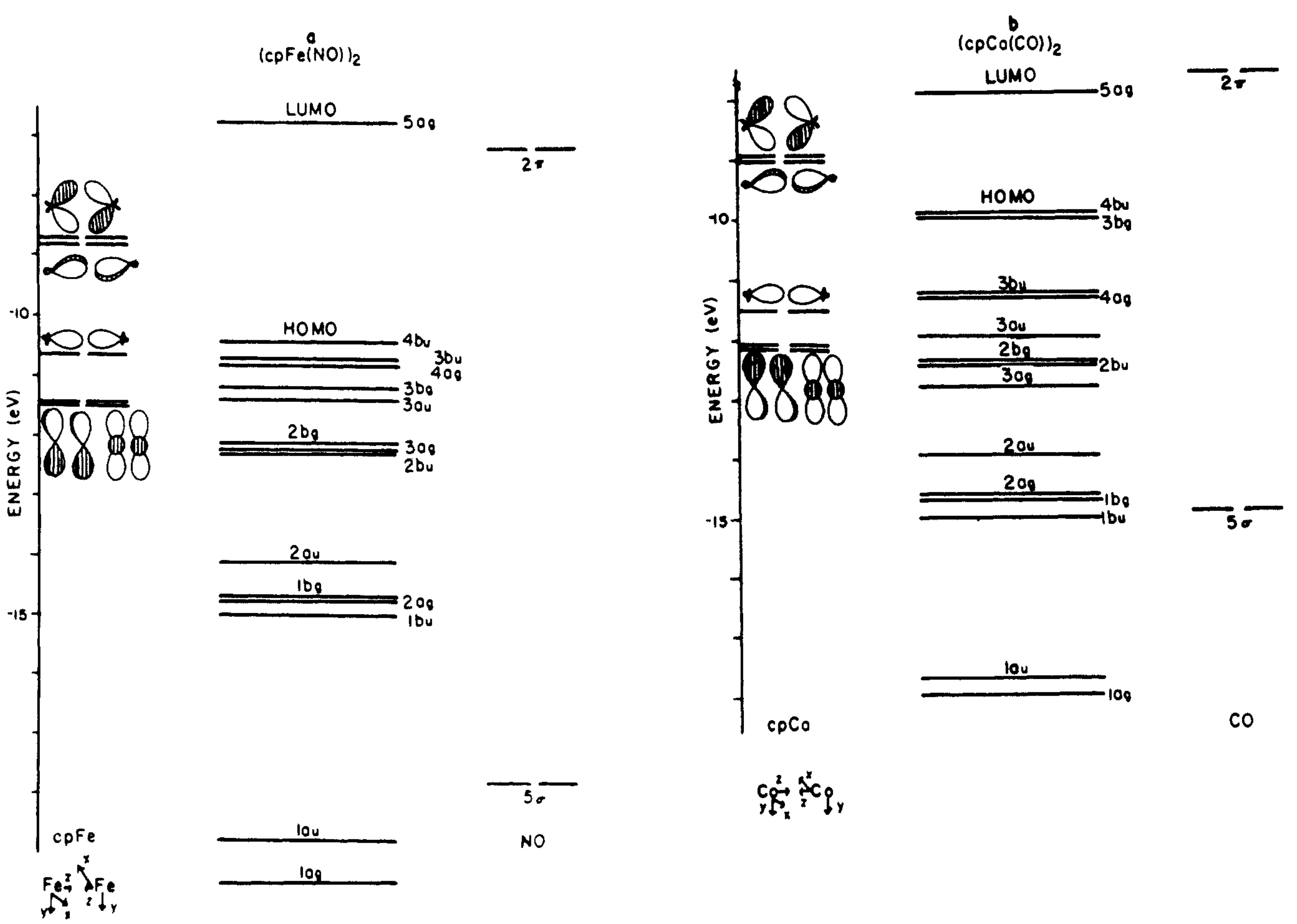

Figure 3. Molecular orbital diagram for $[CpCo(CO)]_2$ and $[CpFe(NO)]_2$.

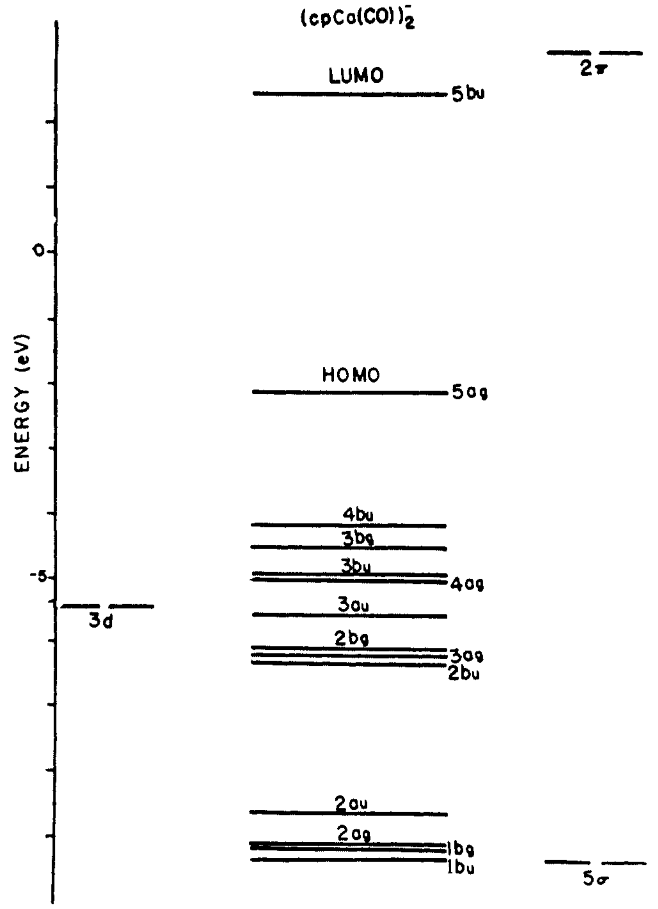

Figure 4. Molecular orbital diagram for $[CpCo(CO)]_2^-$.

with the molecular orbital data depicting the presence of the metal d orbitals in the HOMO. The metal atom d orbitals that participate are the d_{xz} orbitals on each cobalt arranged in an antibonding manner with respect to each other. The cyclopentadienyl rings contribute as well and are present in an arrangement antibonding to the metal atoms.

The ordering of the molecular orbitals in $[CpCo(CO)]_2^-$ is quite similar to the ordering found in the neutral $[CpCo(CO)]_2$. The difference between the electronic structures of the neutral parent $[CpCo(CO)]_2$ and its monoanion can be traced to the change in energy of the d orbitals in going from the neutral complex to the monoanion. Placing the unpaired electron into an orbital primarily metal in character and containing no bridge-ligand character confines the negative charge primarily on the d orbitals and raises them with respect to the bridge-ligand 2π levels. The differences in energy between the metal and bridge-ligand levels in the neutral complex and in the monoanion are shown in Table I. Overall, the metal levels are placed closer to the bridge-ligand 2π levels by 1 eV in moving from the neutral complex to the monoanion. The infrared stretching frequencies testify to the increase in metal-to-ligand back-bonding ability that occurs upon reduction of the neutral complex. The neutral dimer bridging carbonyl stretching frequency occurs at 1798 cm^{-1} [3,4] while the monoanion exhibits the bridge carbonyl band at 1690 cm^{-1}.[20] While the decrease in stretching frequency is not unexpected in the change from a neutral compound to an anion, it is important to realize that this change is effected indirectly; the orbital in which the

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unpaired electron resides contains no bridging carbonyl character. Consequently, the change in backbonding ability comes about as the metal levels alone are raised in energy.

The improvement in the energy match between the d orbitals on the metal and the bridge-ligand 2π acceptor levels is reminiscent of the energetic proximity of the iron d orbitals to the nitrosyl 2π levels in the iron–nitrosyl dimer [CpFe(CO)]$_2$. While the electronic structure of the monoanion [CpCo(CO)]$_2^-$ is similar to that of the neutral parent complex [CpCo(CO)]$_2$, the differences in the ordering of the molecular orbitals in the monoanion correlate to an important difference in the electronic structure of the iron–nitrosyl dimer with respect to the cobalt–carbonyl case. The orbitals labeled 2bu and 3ag in the molecular orbital diagrams consist of linear combinations of d_{z^2} and $d_{x^2-y^2}$ arranged in a bonding manner in one level and an antibonding fashion in the next. The level containing the antibonding combination of metal d orbitals contains bridge-ligand character in a metal–bridge bonding manner. The ordering of 2bu and 3ag in the molecular orbital scheme for [CpCo(CO)]$_2^-$ is the same as it is for [CpFe(CO)]$_2$.[2] These levels reflect a reversal of the usual arrangement of a bonding molecular orbital below an antibonding one. The reason for this level reversal in the iron–nitrosyl dimer and cobalt–carbonyl monoanion but not in the neutral cobalt–carbonyl [CpCo(CO)]$_2$ is the impact of the bridge-ligand 2π level on an energetically proximate metal orbital. The energetic proximity of the bridge ligand in both the iron–nitrosyl dimer and cobalt–carbonyl monoanion is greater than in the neutral parent cobalt–carbonyl dimer. Since the bridge ligand only participates in the metal–metal antibonding molecular orbital and can participate to a greater extent in that orbital when the level of the metal d orbitals is raised, this interaction can ultimately control the ordering of particular molecular orbitals.

The increase in stability we attribute to [CpCo(CO)]$_2^-$ relative to [CpCo(CO)]$_2$ with respect to decomposition is traced to the ability of the metal d orbitals to better back donate in the monoanion than in the neutral parent. The enhanced stability attributable to this effect has been documented in a parallel manner: in terms of the stability of the neutral pentamethylcyclopentadienyl complex [(Me$_5$C$_5$)Co(CO)]$_2$ with respect to [CpCo(CO)]$_2$. The pentamethylcyclopentadienyl complex does not decompose in solution as its unsubstituted analogue does. [(Me$_5$C$_5$)Co(CO)]$_2$ undergoes the same type of chemical reactivity as [CpCo(CO)]$_2$, indicating the steric constraints imposed by the pentamethylcyclopentadienyl rings are not responsible for this behavior. Evidence for the increase in backbonding ability of the cobalt atoms in the pentamethyl complex relative to the unsubstituted pentamethyl analogue comes from inspection of the infrared spectra of these two complexes. While [CpCo(CO)]$_2$ exhibits a solution stretching frequency at 1798 cm^{-1},[3,4] [(Me$_5$C$_5$)Co(CO)]$_2$ reveals the corresponding frequency at 1750 cm^{-1},[6-8] testifying to the increase in energetic proximity of the d orbitals to the 2π levels in [(Me$_5$C$_5$)Co(CO)]$_2$ relative to [CpCo(CO)]$_2$. The same trend is observed in the solid-state spectra.[3,6] The inductive effects of methyl groups relative to hydrogens have been documented and analyzed elsewhere.[21-26] Altogether the pentamethylcyclopentadienyl complex stability with respect to decomposition relative to the unsubstituted cobalt–carbonyl dimer can be seen from the molecular orbital standpoint as attributable to the increase in back-bonding ability from the metal d orbitals into the bridge-ligand 2π levels. The simplicity of this analysis lends it to extrapolation to the case of the monoanion stability in solution in the face of the neutral parent complex decomposition. Most interesting, though, is that the stability in the monoanion is accrued by means of the occupation of an orbital primarily antibonding in character. Hence, stability for [CpCo(CO)]$_2^-$ relative to [CpCo(CO)]$_2$ with respect to decomposition is effected indirectly and in an unusual and unexpected manner.

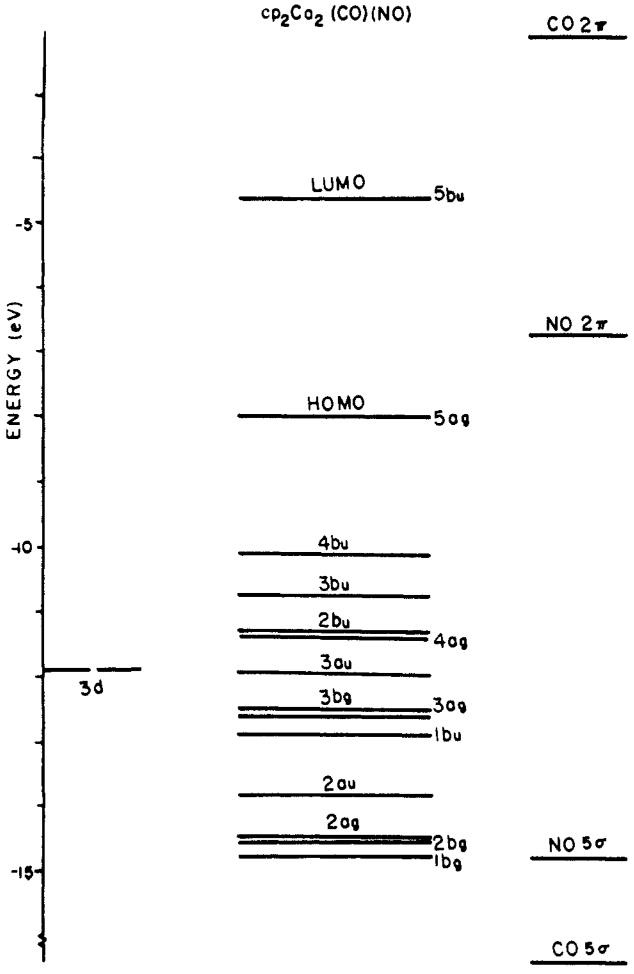

Figure 5. Molecular orbital diagram for Cp$_2$Co$_2$(CO)(NO).

Cp$_2$Co$_2$(CO)(NO). The molecular orbital diagram for Cp$_2$Co$_2$(CO)(NO) is depicted in Figure 5. The HOMO contains one unpaired electron in an orbital metal–metal antibonding in character. The paramagnetism of this compound was first demonstrated by Müller and Schmitt.[11] Several investigators have undertaken the ESR spectroscopy of this complex, and discerning the 15-line pattern with relative intensity ratios 1/2/3...7/8/7...3/2/1 suggested that the unpaired electron is equally delocalized over the two ^{59}Co nuclei[9,18,27] (I = $^7/_2$; abundance ca. 100%). Additionally, these authors observed no extra splitting of the signal due to the nitrogen nucleus of the nitrosyl bridge, indicating the unpaired electron is in an orbital that contains no bridge-ligand character, in accord with the molecular orbital analysis.

The electronic structure of [CpCo(NO)]$_2$ more closely parallels the electronic structure of [CpFe(NO)]$_2$ than that of [CpCo(CO)]$_2$. The five highest occupied molecular orbitals of [CpCo(NO)]$_2$ are identical in composition and character with the LUMO and four highest occupied molecular orbitals of [CpFe(NO)]$_2$.[2] In Cp$_2$Co$_2$(CO)(NO), however, the presence of a bridge nitrosyl does not seem to have the same impact in the ordering of the molecular orbitals as it did in [CpCO(NO)]$_2$.

The influence of the nitrosyl bridge, however, is not entirely absent. The transposition of the 2bu and 3ag orbitals in Cp$_2$Co$_2$(CO)(NO) relative to their ordering in [CpCo(CO)]$_2^-$ testifies to the bridging nitrosyl impact. The orbital labeled 3ag

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is a linear combination of $d_{x^2-y^2}$ and d_{z^2} orbitals on each cobalt. These orbitals are arranged in phase with respect to each other, and no bridge-ligand character is present in this level. The level labeled 2bu consists of the linear combination of these same orbitals; however, in this case they are combined in an antibonding manner. Bridge-ligand character is present in this level. From the molecular orbital diagram of Figure 5, the orbital containing the metal–metal antibonding combination of orbitals lies lower in energy than the one containing the bonding combination. The counterintuitive reversal of these two levels occurs via the participation of the bridge ligands, but in particular the nitrosyl bridge. The nitrosyl 2π character accounts for almost 25% of the orbital character in this molecular orbital. The carbonyl 2π level contributes slightly more than 5%. Overall, both bridge ligands are present in this orbital, but the nitrosyl bridge character is present in a much larger amount and contributes a strong stabilizing influence to this level, stabilizing the orbital containing the metal–metal antibond relative to the level containing the metal–metal bond. The flip-flop of the expected ordering of molecular orbitals in $Cp_2Co_2(CO)(NO)$ compared to $[CpCo(CO)]_2$ is reflected in $[CpFe(NO)]_2$ shown in Figure 3. The energetic proximity of the nitrosyl 2π level to the cobalt orbitals, relative to that of the carbonyl 2π, clearly accounts for the reversal in levels found in $Cp_2Co_2(CO)(NO)$ relative to $[CpCo(CO)]_2$.

The electrochemistry of $Cp_2Co_2(CO)(NO)$ described by Bernal and co-workers[9] indicates that this complex is easily and reversibly reduced to $[Cp_2CO_2(CO)(NO)]^-$, a compound isoelectronic to $[CpCo(NO)]_2$. The oxidation of $Cp_2Co_2(CO)(NO)$ is not reversible. Formation of the cation $[CpCo(CO)(NO)]^+$ would yield a complex isoelectronic to $[CpCo(CO)]_2$ which is itself unstable with respect to decomposition in solution. The values shown in Table I reflect the energy of the metal and ligand orbitals and the changes in those levels that occur upon oxidation of $Cp_2Co_2(CO)(NO)$ to the hypothetical cation $[Cp_2Co_2(CO)(NO)]^+$. Since the electron is removed from an orbital primarily metal in character, but more importantly containing no bridge-ligand character, there is a substantial change in the relationship between the metal and ligand levels, resulting overall in a much poorer match between these two types of orbitals. Most noticeable from the data presented in Table I is the loss of strong metal–2π interactions. The change in metal orbital levels relative to ligand 2π levels is most striking. In the hypothetical cation the difference in energy between these levels is 6.21 eV for the metal–nitrosyl interaction and 10.77 eV for the metal–carbonyl one. These values are both greater than the difference between the metal and bridge-ligand orbitals in the neutral $Cp_2Co_2(CO)(NO)$. The acceptor capacity of the 2π levels is not diminished upon oxidation, but the ability of the metal to transfer electron density into these levels has been substantially reduced.

Lowering the metal levels with respect to the bridge-ligand 2π levels in an oxidation increases the ability of the metal levels to interact with the 5σ levels of the bridge ligand. Table I reveals the energy differences between the metal d orbitals and the carbonyl and nitrosyl 5σ levels. Clearly the cobalt 5σ interaction becomes enhanced. From Table I, it is clear that the difference between the metal d levels and carbonyl 5σ levels in the neutral complex $Cp_2Co_2(CO)(NO)$ and the hypothetical cation becomes smaller upon oxidation. The effect of oxidation on the metal–nitrosyl 5σ interaction is the same, i.e., the metal levels are in closer proximity to the nitrosyl 5σ levels. However, the difference between metal and 5σ levels in both the neutral and cationic species is still much greater than the metal–carbonyl difference. In the neutral compound, $Cp_2Co_2(CO)(NO)$, the cobalt d orbitals are separated from the nitrosyl 5σ levels by 7.00 eV. In the hypothetical cationic species, this value is 6.21 eV, and indicative overall of virtually no increase in the amount of cobalt d orbital interaction with the nitrosyl 5σ levels. Overall, the amount of metal d level–carbonyl 2π interaction decreases substantially upon oxidation of $Cp_2Co_2(CO)(NO)$, and the metal d–carbonyl 5σ interactions increase. However, the increase in proximity of the metal d and nitrosyl 5σ orbitals does not result in any significant change in the bonding since these levels still remain quite far apart energetically. Consequently, the loss in cobalt–2π interaction coupled with the lack of a significant and compensatory cobalt–nitrosyl 5σ interaction upon oxidation can be construed as the trigger to the decomposition of $Cp_2Co_2(CO)(NO)$.

Conclusion

The instability of $[CpCo(CO)]_2$ with respect to decomposition in solution can be best understood in light of the perturbations on this system that are manifested in $[CpCo(CO)]_2^-$ and $Cp_2CO_2(CO)(NO)$. The neutral paramagnetic $Cp_2Co_2(CO)(NO)$ undergoes decomposition in solution when it is oxidized to $[Cp_2Co_2(CO)(NO)]^+$, isoelectronic to neutral $[CpCo(CO)]_2$. Similarly, the paramagnetic monoanion $[CpCo(CO)]_2^-$ remains stable in solution as well. Placing an electron into a molecular orbital containing no bridge-ligand character brings the metal d orbitals into closer proximity with the ligand 2π levels than they were in the neutral complex. The overall stability of $[CpCo(CO)]_2^-$ relative to its neutral parent appears to be mediated through the occupation of a molecular orbital primarily metal–metal antibonding in character.

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Unimolecular Dissociation of Primary Alkanediazonium Ions. Ab Initio and Semiempirical Molecular Orbital Calculations

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Abstract: Molecular orbital calculations for the loss of nitrogen from the methane, ethane, and propanediazonium ions are reported with use of semiempirical (MNDO, AM1) and ab initio procedures. At the MP3/6-31G**//HF/6-31G* level, corrected to 298 K, the enthalpies of dissociation to the classical ions are predicted to be 38, 11, and 10 kcal mol^{-1}, respectively. The semiempirical methods led to similar, although slightly higher dissociation enthalpies. MNDO calculations are reported for the dissociation of related diazonium ions.

Although the existence of alkane diazonium ions is well established, their precise role in reactions involving them is still not fully resolved.[1] Neither is there as yet any experimental structural information for any simple alkanediazonium ion.[2] One uncer-