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Molecular Orbital Studies of Organometallic Hydride Complexes. 1. Acidic vs. Hydridic Behavior of Some (η^5-C_5H_5)ML_nH Systems

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Abstract: Fenske–Hall molecular orbital calculations have been used to investigate the acidic vs. hydridic nature of several organometallic hydride complexes. The acidic behavior of $CpW(CO)_3H$ ($Cp \equiv \eta^5$-C_5H_5) vis-à-vis the hydridic behavior of $CpW(NO)_2H$ is explained by a comparison of the orbital energetics of the conjugate bases of the Cr analogues. For $CpCr(CO)_3^-$, the HOMO is Cr–CO bonding leading to a sizable HOMO/LUMO gap. In $CpCr(NO)_2^-$, the two-legged piano stool geometry leads to a nonbonding HOMO that is destabilized relative to the other occupied metal-based orbitals and that is energetically very close to the LUMO. It is proposed that this HOMO instability in the $CpM(NO)_2^-$ anion accounts for the preferential formation of the $CpM(NO)_2^+$ cation through H^- dissociation. The effects that destabilize the HOMO in the dinitrosyl system are much smaller for $CpFe(CO)_2^-$, consistent with its existence as a stable species. It is suggested that $CpFe(CO)_2H$ and related systems may be amphoteric.

Organometallic hydride complexes are ubiquitous species in transition-metal chemistry, and their roles in numerous catalytic cycles have certainly contributed to their chemical importance.[1] Most organometallic hydrides function as either proton or hydride donors in polar solvents:

$$L_nM\text{-}H \rightarrow L_nM^- + H^+ \qquad \text{acidic}$$

$$L_nM\text{-}H \rightarrow L_nM^+ + H^- \qquad \text{hydridic}$$

The acid–base chemistry of the more common organometallic hydrides has been described in many reports, but the effects that determine whether a given metal hydride is acidic or hydridic are not very well understood. Recently, Labinger and Komadina[2] noted that the tendency of a metal hydride complex to behave as a hydride donor appeared to depend mostly on the position of the metal in the periodic table. Thus, the hydrides of early transition-metal cyclopentadienyl complexes, particularly those of group 4A metals, exhibit hydridic behavior in their ability to deprotonate alcohols and reduce ketones:

$$Cp_2Zr(H)Cl + H\text{-}OR \rightarrow Cp_2Zr(OR)Cl + H_2$$

$$Cp_2MoH_2 + F_3CC(O)CH_3 \rightarrow F_3CCH(OH)CH_3$$

$$Cp \equiv \eta^5\text{-}C_5H_5$$

The reducing strength of these bis(cyclopentadienyl) hydride complexes decreases with increasing atomic number of the metal across the period.

In contrast to the early transition-metal systems, most mononuclear hydride complexes of the later transition metals act as proton donors, yielding H^+ and the corresponding 18-electron organometallic anion. Schunn[3] has tabulated the K_a values of various transition-metal carbonyl hydride complexes and reports that the strongest proton donor is the cobalt complex $HCo(CO)_4$, with considerable reductions in acidities observed in $H_2Fe(CO)_4$ and $HMn(CO)_5$.

$$HCo(CO)_4 + H_2O \rightleftharpoons H_3O^+ + Co(CO)_4^- \qquad K_a < 2$$

$$H_2Fe(CO)_4 + H_2O \rightleftharpoons H_3O^+ + HFe(CO)_4^-$$

$$K_{a_1} = 3.6 \times 10^{-5} \qquad K_{a_2} = 1.0 \times 10^{-14}$$

$$HMn(CO)_5 + H_2O \rightleftharpoons H_3O^+ + Mn(CO)_5^- \qquad K_a = 8 \times 10^{-8}$$

There does appear to be, then, considerable support for a correlation between the periodic table position of the central metal atom and the H reactivity. It might be argued, however, that ligands influence the behavior of the hydride complex by their varying abilities to stabilize the resulting anionic or cationic complex resulting from proton or hydride dissociation. For example, since CO is a stronger π-acceptor than Cp, it follows that loss of hydrogen as a proton and formation of the corresponding anion are more facile in the carbonyl hydride complexes than in the bis(cyclopentadienyl) derivatives. Thus, it would seem that in these systems the acid–base tendencies of metal hydrides, $H\text{-}ML_n$, are consistent with both the position of M and the type of ligand L.

There are several instances in which these empirical trends are not followed, however. For example, Shore and co-workers[4] have characterized the $HRu_3(CO)_{11}^-$ anionic cluster as a hydride donor based on its reaction with CO to give $Ru_3(CO)_{12}$ and H^-. Related neutral clusters, such as $H_4Ru_4(CO)_{12}$, however, act as weak acids: Ford et al.[5] have determined the pK_a values of several $H_xM_y(CO)_z$ cluster complexes to lie in the range of ~11–15 in methanol. It might be argued that the anionic cluster can alleviate its excess charge by donating a hydride ion rather than a proton. The situation is even less clear for some mixed-ligand, mononuclear hydrides, $L'_mL_nM\text{-}H$, however. These can pose a more difficult problem as the reactivity of the metal-coordinated hydrogen atom can vary with both the number and type of ligands attached to the metal atom. As an example, consider the seemingly similar 18-electron hydrides $CpW(CO)_3H$ and $CpW(NO)_2H$. The tricarbonyl complex, characterized by Fischer[6] nearly 30 years ago, acts as a moderately strong acid; by contrast, the dinitrosyl complex, recently synthesized by Legzdins and Martin,[7] exhibits only hydridic behavior:

$$CpW(CO)_3H + H_2O \xrightleftharpoons{pK_a \sim 6} CpW(CO)_3^- + H_3O^+ \qquad \text{proton donor}$$

$$\left.\begin{aligned} &CpW(NO)_2H + NEt_3 \not\rightarrow [HNEt_3]^+[CpW(NO)_2]^- \\ &CpW(NO)_2H + HX \rightarrow CpW(NO)_2X + H_2 \end{aligned}\right\} \text{hydride donor}$$

In each case, the tungsten atom is flanked by good π-acid ligands although the number and type of each differ. The terminal, linear nitrosyl ligand, usually formulated as NO^+, is generally considered

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Table I. Structural Parameters Used in $CpM(XO)_n^-$ Calculations[a]

compd	M-C(Cp)[b]	M-X	X-O	∠X-M-X, deg
$CpCr(CO)_3^-$	1.83	1.79	1.17	89
$CpCr(NO)_2^-$	1.85	1.72	1.14	90
$CpMn(NO)(CO)^-$	1.79	1.72[c]	1.16[c]	90
$CpFe(CO)_2^-$	1.72	1.76	1.13	90

[a] All bond lengths are in Å. [b] C(Cp) is the centroid of the η^5-C_5H_5 ligand. [c] Same bond length used for the NO and CO ligands.

a better π-acceptor than the isoelectronic CO ligand.[8,9] If the nitrosyl is considered to be NO^+, the d count on the W center increases by two from the tricarbonyl to the dinitrosyl. It was therefore our belief that changing the nature of the π-acceptor ligand could lead to significantly different electronic structures for these two systems.

In this paper we report nonempirical Fenske–Hall molecular orbital calculations[10] related to the reactivity of the coordinated H atom in $CpW(CO)_3H$ and $CpW(NO)_2H$. It is proposed that the reactivity of the hydrogen is closely related to the orbital energetics of the conjugate acid or base of the metal hydride and that these simple molecular orbital arguments may provide an explanation for the reactivity in these and related systems.

Computational Section

Molecular orbital calculations were done on an Amdahl 470/V8 computer system using the Fenske–Hall method.[10]

In all calculations the cylopentadienyl ring has local D_{5h} symmetry with C–C and C–H bond lengths of 1.38 and 1.08 Å. Other bond lengths and angles used for each structure in the calculations are listed in Table I. The molecular geometry of $CpCr(CO)_3^-$ was taken from its crystal structure[11] and was idealized to C_s symmetry. The bond lengths used in the $CpML_2^-$ calculations are summarized in Table I. As the structures of these anions are not known, the calculations were performed with a variety of dihedral and bond angles, as will be detailed below.

All atomic wave functions were generated by using the method of Bursten, Jensen, and Fenske.[12] Contracted double-ζ representations were used for the metal nd AO's and for the C, N, and O 2p AO's. An exponent of 1.16 was used for the hydrogen 1s AO's.[13] Basis functions for the metal atoms were derived for +1 oxidation states with all 4s exponents fixed at 2.0. The 4p exponents for Cr, Mn, and Fe were set at 1.6, 1.8, and 2.0, respectively. The calculations were performed by using a fragment analysis in which the transformed molecular orbitals of $C_5H_5^-$, NO^+, and CO were allowed to interact with the metal atomic orbitals. In all calculations, the carbonyl and nitrosyl 3σ and 6σ orbitals, the first three occupied C_5H_5 orbitals, and all virtual orbitals above the e_2'' level were deleted from the basis transformation set.[14]

Results and Discussion

Previous molecular orbital treatments on organic systems have successfully correlated relative acidities to the atomic charge density computed for the active hydrogen atom.[15,16] Such correlations between hydrogen charge and reactivity do not exist for organometallic hydrides, however. Indeed, from simple electronegativity considerations, all transition-metal hydride bonds should be somewhat polar with a greater electron density on H. For this reason, the effective charge on the hydride ligand calculated from a Mulliken population analysis is slightly negative for all hydride complexes.[17]

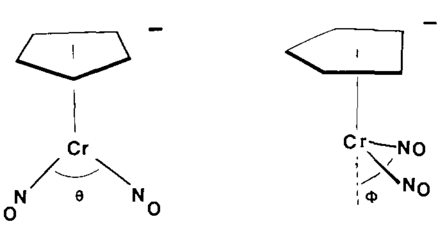

Figure 1. Definition of the angles θ and ϕ used in describing the structure of $CpCr(NO)_2^-$.

Our calculations on the acidic $HMn(CO)_5$, $H_2Fe(CO)_4$, $HFe(CO)_4^-$, and $HCo(CO)_4$ systems are not supportive of any relationship between H charge and relative reactivity, i.e., the most acidic hydrides do not have the least negatively charged hydrogen atoms. This lack of charge/reactivity correlation has also been observed experimentally. Jolly and co-workers,[18] using photoelectron spectroscopic shifts, have assigned the charge on the H atoms of $HCo(CO)_4$, $H_2Fe(CO)_4$, and $HMn(CO)_5$ as −0.75, −0.3, and −0.80 e^-, respectively, an ordering that is qualitatively consistent with our calculated Mulliken charges but not with the relative acid strengths, namely $HCo(CO)_4 \gg H_2Fe(CO)_4 > HMn(CO)_5$. More recently, Sweany and Owens have used matrix isolation infrared data to compare the charge distributions in metal carbonyl hydrides $HM(CO)_n$ and the corresponding radicals $\cdot M(CO)_n$.[19] Their findings are consistent with those of Jolly's in that the hydrogen atoms were found to be negatively charged in all complexes. ^1H NMR has also been uninformative in correlating spectral data with hydrogen reactivity in transition-metal hydride complexes.[3,7,20]

As was the case for the aforementioned spectroscopic studies, we found no correlation between the orbital energetics or charge distributions of the hydride complexes and their reactivities; all of the calculations on hydride complexes yielded straightforward bonding pictures with the large HOMO/LUMO separations characteristic of stable closed-shell molecules. We therefore approached the problem by assuming that the acidity of the hydride complex L_nMH is related to the orbital energetics of the L_nM^- anion which would be formed upon proton dissociation.

$CpCr(CO)_3^-$ vs. $CpCr(NO)_2^-$. We first addressed the difference in H reactivity in the acidic $CpM(CO)_3H$ (M = Cr, Mo, W) and the hydridic $CpM(NO)_2H$ (M = Mo, W) complexes. We felt that the differences in the acid–base chemistry of these two hydrides presented a particularly challenging problem since our approach of determining H reactivity based on relative ion stabilities could suggest greater acidic character in $CpM(NO)_2H$ since $CpM(NO)_2^-$ might be expected to be more stable than $CpM(CO)_3^-$ due to the better π-back-bonding ability of NO^+ as compared to CO.

Although the chemistry of the $CpML_nH$ systems is best characterized for the tungsten compounds, we performed calculations on the Cr anions since Fenske–Hall atomic wave functions do not account for relativistic effects inherent in the heavier elements. Parallel results are obtained in the calculations of the third-row complexes, albeit without relativistic corrections.

It is appropriate to discuss briefly the geometries that have been assumed for these anions, especially for $CpCr(NO)_2^-$ since it is unknown. Structural studies[11] of $[NMe_4][CpCr(CO)_3]$ indicate that the anion is a three-legged piano stool with OC–Cr–CO angles of ~ 90°. Thus it is structually analogous to the neutral isoelectronic species $CpMn(CO)_3$.[21] This is yet another example of an 18-electron anion structurally mimicking the corresponding 18-electron neutral molecule, as has been found for $Mn(CO)_5^-$,[22] $HFe(CO)_4^-$,[23] $Fe(CO)_4^{2-}$,[24] and $Co(CO)_4^-$.[25] In fact, we know

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Table II. Mulliken Population Analysis of the Charge Distributions in $CpM(XO)_n^-$ Systems

compd	metal AO populations			Cp ligand populations		XO ligands	
	3d	4s	4p	e_1''	e_2''	total 5σ donation	total 2π acceptance
$CpCr(CO)_3^-$	4.76	0.16	0.94	3.41	0.13	1.78	2.51
$CpCr(NO)_2^-$	4.82	0.28	1.02	3.48	0.10	0.88	3.32
$CpMn(NO)(CO)^-$	5.75	0.28	0.80	3.54	0.11	NO: 0.44	1.72
						CO: 0.56	0.88
$CpFe(CO)_2^-$	6.82	0.29	0.54	3.64	0.13	1.04	1.65

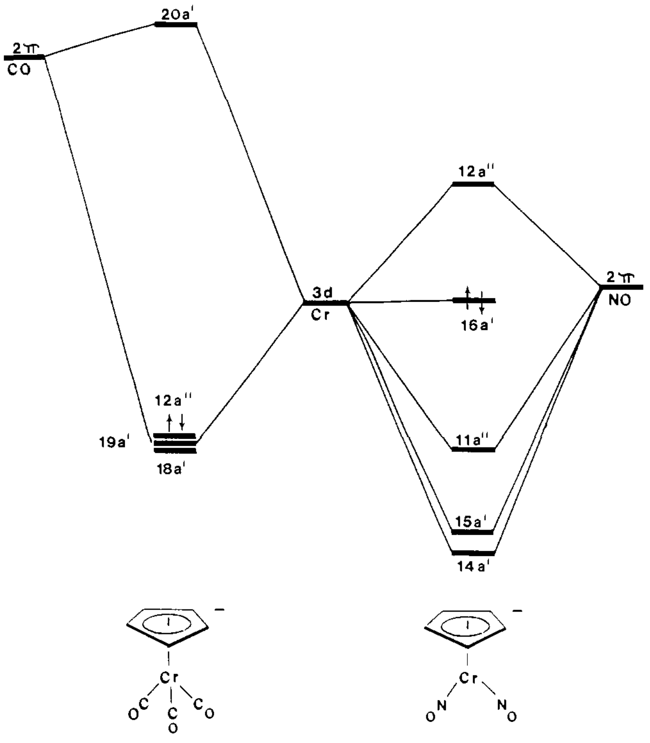

Figure 2. Comparative molecular orbital diagrams of $CpCr(CO)_3^-$ and $CpCr(NO)_2^-$.

of no instances in which an 18-electron anion is not structually analogous to an isoelectronic neutral molecule. Since $CpCr(NO)_2^-$ is isoelectronic with $CpCo(CO)_2$, it is our belief that the best geometry to assume for the anion is a two-legged piano stool in which the $Cr(NO)_2$ plane is orthogonal to the plane of the Cp ring; this structure, with a OC–Co–CO angle of 93.7 (2)°, has been determined for $(Me_5C_5)Co(CO)_2$.[26] Preliminary structural results on $[N(n\text{-}Bu)_4][CpFe(CO)_2]$ indicate that the OC–Fe–CO angle is ~ 90° as well,[27] and we would thus expect the ON–Cr–NO angle in $CpCr(NO)_2^-$ to be near 90° also. However, since this anion is not known, we have considered other possible structures. Figure 1 defines two structural angles, θ and ϕ, which have been varied. Molecular orbital calculations have been performed on the geometries corresponding to all combinations of θ = 90, 100, 110, and 120°, and ϕ = 0, 10, 20, 30, 40, 50, and 60°. In addition, for the case θ = 90° and ϕ = 0°, the Cr–N–O angle has been allowed to decrease from 180 (linear nitrosyl) to 120° (bent nitrosyl), where both the in-plane and out-of-plane bends have been considered. The molecular orbital results for all these cases are qualitatively similar with the most stable orbital energetics, as determined by the criteria to be discussed shortly, found for the linear nitrosyl case with θ = 90° and ϕ = 0°, i.e., very similar to the geometry found for $(Me_5C_5)Co(CO)_2$.[26]

Table III. Orbital Energies and Mulliken Percent Characters of the Higher Occupied and Lower Unoccupied Orbitals of $CpM(XO)_n^-$ Systems

$CpCr(CO)_3^-$

	MO	ϵ, eV	Cr 3d	Cr 4s	Cr 4p	Cp e_1''	CO 2π
	21a'	5.88	44	7	8	2	38
	13a''	5.31	43	0	10	13	33
LUMO	20a'	5.27	43	0	10	13	33
HOMO	12a''	−1.10	59	0	2	3	35
	19a'	−1.10	59	0	1	3	36
	18a'	−1.19	53	2	1	0	40

$CpCr(NO)_2^-$

	MO	ϵ, eV	Cr 3d	Cr 4s	Cr 4p	Cp e_1''	CO 2π
	18a'	7.33	58	5	5	2	30
	13a''	7.19	40	0	0	3	57
	17a'	6.99	68	0	0	9	18
LUMO	12a''	4.65	12	0	5	7	76
HOMO	16a'	2.97	89	7	0	3	0
	11a''	0.56	55	0	0	2	43
	15a'	−0.85	25	0	13	0	61
	14a'	−1.04	37	1	1	0	58

$CpMn(NO)(CO)^-$

	MO	ϵ, eV	Mn 3d	Mn 4s	Mn 4p	Cp e_1''	NO 2π	CO 2π
	30a	7.09	46	3	9	6	5	29
	29a	5.71	56	0	2	6	35	0
LUMO	28a	5.09	37	0	4	6	47	5
HOMO	27a	1.86	91	6	1	2	0	0
	26a	0.60	72	0	2	2	0	22
	25a	−0.52	37	0	7	0	49	5
	24a	−0.86	48	1	1	1	33	15

$CpFe(CO)_2^-$

	MO	ϵ, eV	Fe 3d	Fe 4s	Fe 4p	Cp e_1''	CO 2π
	12a''	7.16	50	0	12	11	22
LUMO	17a'	7.15	37	0	6	6	50
HOMO	16a'	2.06	92	5	0	2	0
	15a'	1.35	55	0	7	2	35
	11a''	1.17	84	0	0	3	12
	14a'	0.50	67	0	0	1	30

Mulliken population analyses of $CpCr(CO)_3^-$ and $CpCr(NO)_2^-$ are given in Table II. Examination of the orbital populations for the ligands in both anions reveals that while the electron donation and acceptance of the Cp ligand is essentially the same in both, the nitrosyl ligand is, in fact, a better π-acceptor and a poorer σ-donor in $CpCr(NO)_2^-$ than the carbonyl groups are in $CpCr(CO)_3^-$. In fact, the two NO ligands relieve more electron density from Cr through backbonding than the three carbonyls combined. Thus, taken by itself, the ligand population analysis would predict $CpCr(NO)_2H$ to be at least as acidic as $CpCr(CO)_3H$ on the basis of the relative stabilizations of the conjugate base anions. That this is not the case requires a more detailed investigation of the orbital energetics of the anions.

A comparative molecular orbital diagram of the two anions is shown in Figure 2. The orbital energies and compositions are

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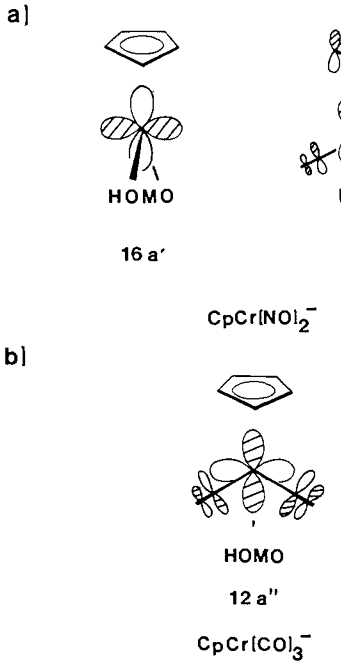

Figure 3. Pictorial representations of some of the orbitals of CpCr(XO)$_n^-$ systems: (a) HOMO and LUMO of CpCr(NO)$_2^-$; (b) HOMO of CpCr(CO)$_3^-$.

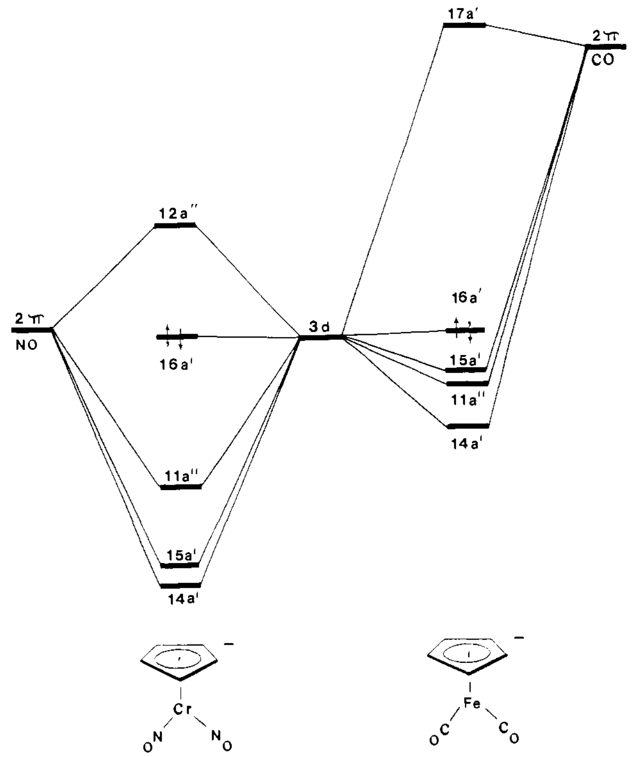

Figure 4. Comparative molecular orbital diagrams of CpCr(NO)$_2^-$ and CpFe(CO)$_2^-$. The MOs of CpFe(CO)$_2^-$ have been adjusted upward by 0.9 eV to match the HOMO energy with that of CpCr(NO)$_2^-$.

tabulated in Table III. Figure 2 indicates why CpCr(NO)$_2^-$ is expected to be far less stable than CpCr(CO)$_3^-$. The highest occupied molecular orbital (HOMO), which is primarily metal based in each, is found to be nonbonding in CpCr(NO)$_2^-$ but bonding in CpCr(CO)$_3^-$, resulting in an energetically higher HOMO in the former. The other d-based orbitals in CpCr(NO)$_2^-$ are strongly stabilized by the NO 2π orbitals. Hence the gap between the HOMO and the second highest occupied orbital is much greater in CpCr(NO)$_2^-$ than in CpCr(CO)$_3^-$. The difference in molecular geometries in the anions is largely responsible for the nature of the HOMO in each anion. The pseudo-C_{2v} symmetry of CpCr(NO)$_2^-$ allows no ligand orbital interaction with the HOMO $d_{z^2-x^2}$ whereas interaction of the CO 2π orbital with a similar metal orbital ($d_{z^2-y^2}$) can and does occur in the local C_{3v} symmetry of CpCr(CO)$_3^-$. A schematic representation of these important orbitals is illustrated in Figure 3. Another major difference in the electronic structures of CpCr(NO)$_2^-$ and CpCr(CO)$_3^-$ lies in the energy separation between the lowest unoccupied molecular orbital (LUMO) and the HOMO. A much smaller HOMO/LUMO energy separation is realized for CpCr(NO)$_2^-$ (1.67 eV) than for CpCr(CO)$_3^-$ (6.37 eV). Thus, in comparing the orbital energetics of the d^6 three-legged piano stool CpCr(CO)$_3^-$ to those of the d^8 two-legged piano stool CpCr(NO)$_2^-$ it is seen that the latter has a nonbonding HOMO destabilized relative to the other d-based orbitals, a large gap between the HOMO and the second-highest occupied orbital, and a small HOMO/LUMO gap.[28] The electronic structure of CpCr(NO)$_2^-$ thus implies that stabilization could occur by loss of the two electrons from the HOMO, resulting in formation of the CpCr(NO)$_2^+$ cation. Our calculated electronic structure for this 16-electron cation is similar to but not identical with that proposed for the isoelectronic neutral fragment CpMn(CO)$_2$ by Hofmann.[29]

It is our belief that the difference in the electronic structures of CpCr(CO)$_3^-$ and CpCr(NO)$_2^-$ explains the difference in the acid-base behavior of CpW(CO)$_3$H and CpW(NO)$_2$H. Dissociation of H$^+$ from CpW(CO)$_3$H leads to formation of the electronically stabilized anion CpW(CO)$_3^-$. Dissociation of H$^+$ from CpW(NO)$_2$H would generate the unstable conjugate base CpW(NO)$_2^-$, however. By comparison, loss of H$^-$ from CpW(NO)$_2$H followed by solvation would lead to the more stable 18-electron cation CpW(NO)$_2$S$^+$, a d^6 three-legged piano stool that is electronically equivalent to CpW(CO)$_3^-$.

CpCr(NO)$_2^-$ vs. CpFe(CO)$_2^-$. The orbital energetics of the two-legged piano stool, CpML$_2$, found to be the destabilizing effect in CpCr(NO)$_2^-$, naturally challenges the existence of the isoelectronic and presumably isostructural d^8 anion CpFe(CO)$_2^-$. Molecular orbital calculations for this well-known system were next undertaken to ascertain the electronic factors inherent to its stability. A direct comparison between CpCr(NO)$_2^-$ and CpFe(CO)$_2^-$ was made by using the same approach taken with CpCr(NO)$_2^-$ and CpCr(CO)$_3^-$.

As before, Mulliken population analysis (Table II) of the ligands shows CO to be a slightly better σ-donor and a much poorer π-acceptor than NO$^+$ in the different anions and by themselves do not account for the chemical differences of CpCr(NO)$_2^-$ and CpFe(CO)$_2^-$. The molecular orbital energetics again must be considered.

If both CpCr(NO)$_2^-$ and CpFe(CO)$_2^-$ are considered to be d^8 ions, the principal differences between them would be an overall stabilization of the 3d orbitals and destabilization of the ligand 2π orbitals in the iron anion; formalistically, one is changing the metal from Cr(−2) to Fe(0) and the ligands from NO$^+$ to CO. Both of these effects will tend to weaken the dπ–L 2π interactions in CpFe(CO)$_2^-$ as these orbitals become more energetically separated. A comparison of the frontier molecular orbitals of CpCr(NO)$_2^-$ and CpFe(CO)$_2^-$, given in Figure 4 and Table III, shows this to be the case. The HOMO of CpFe(CO)$_2^-$, like that

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(28) The molecular orbital calculations on the alternate structures of CpCr(NO)$_2^-$ all show a nonbonding HOMO, characteristic of an ML$_2$ fragment, which is energetically close to the LUMO and 2.4–3.0 eV higher in energy than the second-highest occupied molecular orbital (SHOMO). The smallest HOMO/SHOMO and largest HOMO/LUMO separations were found for the structural analogue of C$_5$Me$_5$Co(CO)$_2$, i.e., $\theta = 90°$ and $\phi = 0°$, and it is the results of this calculation that we used above. As θ is increased from 90 to 120°, the HOMO/SHOMO separation decreased from 1.6 to 0.4 eV. For each value of ϕ, the HOMO/SHOMO gap increased and the HOMO/LUMO gap decreased as ϕ was increased from 0 to 60°. For $\theta = 90°$, $\phi = 0°$, the in-plane bending of the Cr–N–O angles slightly decreased the HOMO/SHOMO gap to 2.2 eV but greatly decreased the HOMO/LUMO gap to 0.05 eV. Both separations decreased by about 0.2 eV upon bending the Cr–N–O angles out-of-plane.

(29) Hofmann, P. *Angew. Chem., Ed. Engl.* 1977, *16*, 536–537.

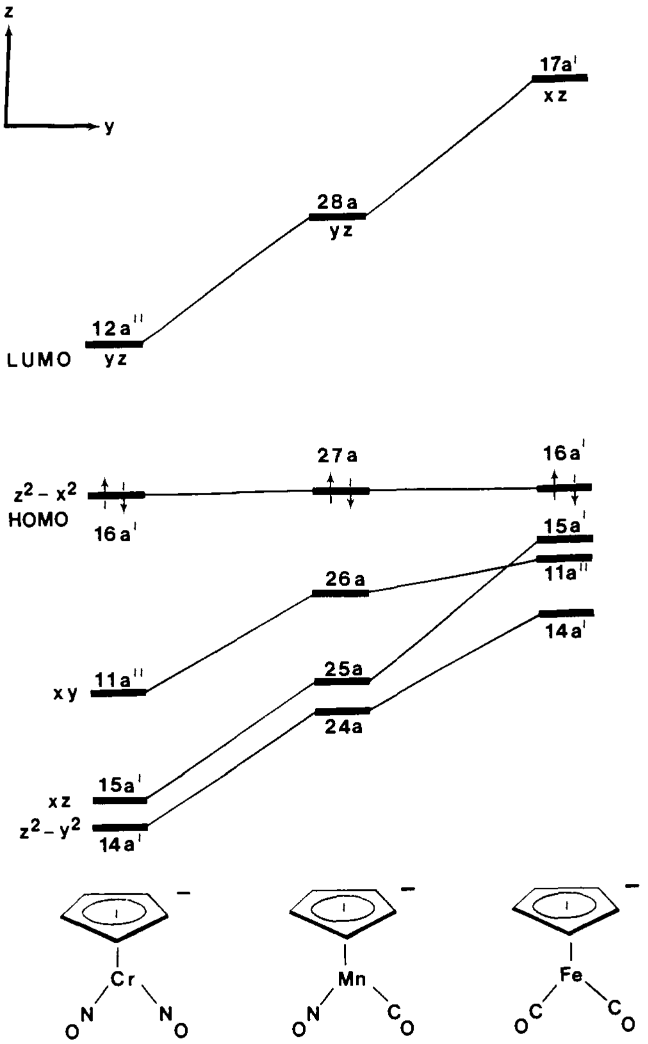

Figure 5. Comparative molecular orbital diagrams of $CpCr(NO)_2^-$, $CpMn(NO)(CO)^-$, and $CpFe(CO)_2^-$.

of $CpCr(NO)_2^-$, is nonbonding, but it is ~0.9 eV lower in energy. More importantly, there is no longer a large gap between the HOMO and the other d-based orbitals since the latter are not stabilized nearly as much in $CpFe(CO)_2^-$ as they are in $CpCr(NO)_2^-$. The energetic rise of the carbonyl 2π orbitals relative to those of nitrosyl also results in a much larger (5.09 eV) HOMO/LUMO gap in $CpFe(CO)_2^-$ than was found in $CpCr(NO)_2^-$. Thus, the metal 3d and ligand 2π orbital energy differences account for the unstable HOMO in $CpCr(NO)_2^-$ and the absence of this in $CpFe(CO)_2^-$ even though both two-legged piano stool structures give rise to the same nonbonding (~99% metal) HOMO. The enhanced stability of $CpFe(CO)_2^-$ over $CpCr(NO)_2^-$ allows $CpFe(CO)_2H$ to function as a proton donor whereas the group 6 dinitrosyl hydrides apparently do not. At the same time, the electronic structure of the iron anion also suggests that two electrons might be easily lost from the energetically high, nonbonding HOMO, giving rise to the cationic species $CpFe(CO)_2^+$. This possibility of amphoterism in $CpFe(CO)_2H$ will be discussed later.

It is also of interest to note that the high-energy, nonbonding HOMO in $CpM(CO)_2^-$ (M = Fe, Ru) has recently been exploited in the formation of heterobimetallic complexes between the early and late transition metals.[30] Thus it is apparent that while these anions are not so unstable as to preclude their formation, the high energy of the HOMO leads to the enhanced reactivity of the $CpM(CO)_2^-$ systems relative to the $CpM(CO)_3^-$ (M = Mo, W) systems.

A calculation on the third member of the still unknown isoelectronic and isostructural anion, $CpMn(NO)(CO)^-$, provides a bridge between the $CpCr(NO)_2^-$ and $CpFe(CO)_2^-$ calculation. The important structural features of the HOMO/frontier orbital separation and the HOMO/LUMO gap in the two extremes are intermediate in $CpMn(NO)(CO)^-$ (Figure 5). Table II shows that the the Mulliken populations for $CpMn(NO)(CO)^-$ are consistent with a smooth trend across the series.

We had hoped that the orbital energetics of the cationic systems would provide extra information on the hydridic nature of the hydride donors as the calculations on the anions support proton dissociation for the acidic complexes. Hence calculations have been done on $CpML_n(NCH)^+$, where HCN, which we found to be energetically very similar to CH_3CN, mimics the effect of a coordinating solvent. The results, however, give a stable bonding description with small HOMO/second-highest orbital gaps and large HOMO/LUMO gaps for the cations of all the $CpML_nH$ systems. This result is not entirely surprising as all the solvated cations of the hydrides studied here have indeed been isolated as stable BF_4^- or PF_6^- salts. We therefore do not believe that the cation calculations are informative in relating hydridic behavior to orbital energetics. However, it appears we can use the anion calculations to determine whether some hydride complexes are hydride donors; calculations on the anionic systems yield fairly unstable orbital energetics for those complexes that tend to be hydridic. This was seen here for $CpW(NO)_2H$, and similar results have been obtained for the hydridic Cp_2ZrH_2, Cp_2NbH_3, $Cp_2Nb(CO)H$, and Cp_2MoH_2 systems.[31]

Our calculations also suggest that $CpM(CO)_2H$ (M = Fe, Ru, Os) may be amphoteric. $CpOs(CO)_2H$, in contrast to $CpFe(CO)_2H$, is generally considered to be hydridic, but the studies of its hydridic character have been limited to reactions with powerful hydride abstractors such as the trityl and tropylium ions.[32] We feel that hydride abstraction under such forcing conditions does not necessarily preclude acidic behavior as well; $CpW(CO)_3H$ reacts readily with trityl,[33] and our own studies[31] reveal that $CpW(CO)_3H$ completely reacts with $[C_7H_7][BF_4]$ faster than does $CpOs(CO)_2H$. Little is known about the acid-base chemistry of $CpOs(CO)_2H$ and even less about that of $CpFe(CO)_2H$, but our calculations provide support for the formation of either the d^8 two-legged piano stool $CpM(CO)_2^-$ (known for M = Fe) or the d^6 three-legged piano stool $CpM(CO)_2S^+$ (known for M = Fe, Os).

Conclusions

Relating the hydridic vs. acidic character of organometallic hydrides to the electronic structures of their corresponding anions appears to be very promising. Our calculations on other known hydridic systems, such as early transition metal bis(cyclopentadienyl) hydrides, indicate that a large HOMO/second-highest orbital separation in the singly deprotonated anion seems diagnostic of hydridic behavior. It also appears that relative acid strength in a series of related complexes,[31] e.g., $HCo(CO)_{4-n}(PR_3)_n$, is directly related to the magnitudes of both the HOMO/second-highest orbital gap and the HOMO/LUMO gap. These studies will be detailed in a later publication.

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Registry No. $CpCr(CO)_3^-$, 48121-47-7; $CpCr(NO)_2^-$, 89302-97-6; $CpMn(NO)(CO)^-$, 89302-98-7; $CpFe(CO)_2^-$, 12107-09-4; $CpCr(CO)_3H$, 36495-37-1; $CpCr(NO)_2H$, 89302-99-8; $CpMn(NO)(CO)H$, 89303-00-4; $CpFe(CO)_2H$, 35913-82-7; $HMn(CO)_5$, 16972-33-1; $H_2Fe(CO)_4$, 12002-28-7; $HFe(CO)_4^-$, 18716-80-8; $HCo(CO)_4$, 16842-03-8; $CpW(CO)_3H$, 12128-26-6; $CpW(NO)_2H$, 69532-01-0; $CpW(CO)_3^-$, 12126-17-9; $CpW(NO)_2^-$, 89303-01-5; $CpOs(CO)_2H$, 42442-16-0; $[C_7H_7][BF_4]$, 27081-10-3.

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