loss of electrons ($\theta \approx 40$–45°).

The total electron density at a particular carbon (C_μ) is the sum of the densities in the a′ and a″ orbitals at that carbon, $\rho_T^\mu = \rho_\pi^\mu(a') + \rho_\pi^\mu(a'')$, and the π-charge is then $q_\pi^\mu = 1.0 - \rho_T^\mu$. The values in Table II show that in all cases, q_π for the central carbon (C_2) is more positive than q_π for the terminal carbon (C_1). Hence, charge control would always direct an incoming nucleophile to the central carbon contrary to what is experimentally observed.

The total charge (q_T) on the allyl fragment includes charges incurred in the C–H σ bonds and in interactions of the allyl σ framework with the metal fragment (although these latter interactions are not large, there are many of them). Consequently the total charge differs from q_π, but the general trend is the same; namely, C_2 is always more positive than C_1.

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Appendix

An idealized geometry was used in the EHMO calculations. For the $X_3(CO)_2Mo$ fragments, the ligands were placed on the *x*, *y*, and *z* axes at appropriate distances (Mo–Cl = 2.50 Å; Mo–N = 2.10 Å, Mo–C = 2.00 Å, C–O = 1.15 Å; C–N = 1.16 Å; C–H = 1.0 Å). The allyl group lay in a plane parallel to the *xy* plane and 2.0 Å above it. The Mo–$C_{1,3}$ distance was 2.33 Å; M–C_2 was 2.14 Å, and the C–C–C angle was 116°. For the Cp_2Mo complex, the Mo–Cp centroid distance was 2.0 Å, and the Cp–Mo–Cp angle was 140°. The plane of the allyl group was 2.0 Å from the Mo (Mo–$C_{1,3}$ = 2.33 Å; Mo–C_2 = 2.14 Å). In the CpLM(allyl) complexes, the Cp–M–L angle was 120° and the Cp–Rh and Cp–Co distances were 1.90 and 1.70 Å, respectively. The allyl group was in planes 1.90 and 1.70 Å from the metal (Rh and Co, respectively). The atomic parameters used in the EHMO calculations are collected in Table III.[9] No attempt was made to adjust these parameters for the different overall charges on the complexes since it has been shown by charge iteration calculations that overall molecular charge has little effect on the EHMO parameters.[22]

Registry No. **2** (M = Mo, X = L = HCN), 89676-73-3; **2** (M = Mo, X = L = Cl), 89676-74-4; **12**, 62742-80-7; **13**, 86022-48-2; $Cp_2Mo(\eta^3\text{-}C_3H_5)^+$, 53449-94-8; $Cl_2Pd(\eta^3\text{-}C_3H_5)^-$, 35428-96-7; $(CO)_4Fe(\eta^3\text{-}C_3H_5)^+$, 49865-93-2; $CpCo(PH_3)(\eta^3\text{-}C_3H_5)^+$, 89676-75-5; $CpCo(CO)(\eta^3\text{-}C_3H_5)^+$, 71744-59-7; $CpRh(PH_3)(\eta^3\text{-}C_3H_5)^+$, 89676-76-6; $CpRh(CO)(\eta^3\text{-}C_3H_5)^+$, 89676-77-7.

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Molecular Orbital Studies of Organometallic Hydride Complexes. 2. The Correlation of Hydrogen Atom Reactivity with Valence Orbital Energetics

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The relative acidic or hydridic strengths of several isostructural hydride complexes $L_nM\text{–}H$ have been correlated with the valence orbital energetics of the deprotonated hydrides L_nM^-. The acidities of the carbonyl-phosphine proton donor series $HCo(CO)_{4-n}L_n$ (n = 0–3; L = PPh_3 or $P(OPh)_3$), $HMn(CO)_{5-n}L_n$, and $HV(CO)_{6-n}L_n$ (n = 0, 1; L = PPh_3) can be ranked within each series by the magnitude of the HOMO/LUMO separations found for their conjugate bases. Larger HOMO/LUMO gaps are calculated for the anions of the stronger acids. The relative hydridic strengths of Cp_2ML_nH (Cp ≡ $\eta^5\text{-}C_5H_5$; M = Zr, Nb, Mo; L = H, CO) hydride donors can be determined by both the magnitude of the HOMO/LUMO separations and the separations between the HOMO and the second highest occupied molecular orbital in the deprotonated species.

Introduction

Two different ionic dissociative routes are available to organometallic hydride complexes in polar solvents.[1]

$$L_nM\text{–}H \rightarrow L_nM^- + H^+ \quad \text{proton donor}$$

$$L_nM\text{–}H \rightarrow L_nM^+ + H^- \quad \text{hydride donor}$$

Although several research groups have recently reported systematic studies of the thermodynamic and kinetic reactivities of organometallic hydride systems,[2-4] very little is presently known about the electronic influences responsible for the proton or hydride dissociation from metal hydride complexes. We have recently reported[5] that the reactivity of the hydride ligand in $L_nM\text{–}H$ hydride complexes is closely related to the orbital energies of the conjugate base L_nM^- as calculated by the Fenske–Hall molecular orbital method.[6] Indeed, we have found that the hydridic character of $CpM(NO)_2H$ (Cp ≡ $\eta^5\text{-}C_5H_5$; M = Mo, W) complexes vis-à-vis the acidic nature of the

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seemingly similar CpM(CO)$_3$H (M = Cr, Mo, W) complexes can be explained by a comparison of the orbital energetics of the deprotonated hydrides CpCr(NO)$_2^-$ and CpCr(CO)$_3^-$. An obvious difference noted between the molecular orbital energetics of CpCr(NO)$_2^-$ and CpCr(CO)$_3^-$ was the separation between the HOMO and LUMO (lowest unoccupied molecular orbital). A much smaller HOMO/LUMO energy difference of 1.6 eV was calculated for CpCr(NO)$_2^-$ as compared to the corresponding energy separation of 6.3 eV for CpCr(CO)$_3^-$. We feel that the magnitudes of these HOMO/LUMO gaps offer additional information regarding the enhanced stability of CpCr(CO)$_3^-$ over CpCr(NO)$_2^-$. Further, as it has been our experience that larger HOMO/LUMO separations are invariably found for stable closed-shell molecules and smaller separations for unstable systems, it would appear that the size of the HOMO/LUMO energy separation may be directly related to the complex stability.

Inasmuch as the acid strength of an acidic compound is believed to depend largely on the electronic stability of the resulting conjugate base,[7] it was our feeling that the protonic strength of an organometallic hydride complex, L$_n$M–H, could be directly related to the magnitude of the HOMO/LUMO energy separation calculated for its conjugate base L$_n$M$^-$. We define this energy separation for the anion as ΔE^{CB} for the parent hydride

$$\Delta E^{\mathrm{CB}} = \epsilon(\mathrm{LUMO}) - \epsilon(\mathrm{HOMO})$$

where the orbital energies are those of the deprotonated hydride. The relevance of an acid strength/ΔE^{CB} relationship might allow a qualitative assessment of K_a values for proton donors that do not lend themselves experimentally to acidic strength determinations because of high thermal instabilities or low aqueous solubilities. Here we report the results of Fenske–Hall molecular orbital calculations on several organometallic hydride systems which support the notion that the relative acidic or hydridic strength can be related to the calculated ΔE^{CB} values.

Calculational Details

Molecular orbital calculations were done on Amdahl 470/V8 computer system using the Fenske–Hall method.[6]

The calculations on the anionic cobalt systems were carried out by assuming a tetrahedral arrangement of ligands for each anion and using PH$_3$ and P(OH)$_3$ as model ligands for PPh$_3$ and P(OPh)$_3$. Other bond angles and all bond lengths used for the carbonyl, phosphorous, and dinitrogen ligands are listed in Table I.

An octahedral arrangement of ligands was chosen for the geometries of V(CO)$_6^-$ and V(CO)$_5$PH$_3^-$. For Mn(CO)$_5^-$, the X-ray crystallographic results[8] were idealized to give a D_{3h} trigonal-bipyramidal geometry. A corresponding C_{3v} geometry was assumed for the apical isomer of Mn(CO)$_4$PH$_3^-$. All other bond lengths used for the carbonyl and phosphine–carbonyl V and Mn systems are given in Table I.

In all the bis(cyclopentadienyl) anion calculations, the cyclopentadienyl rings have local D_{5h} symmetry with C–C and C–H bond lengths of 1.38 and 1.08 Å. Structures for Cp$_2$TiH$^-$, Cp$_2$VH$_2^-$, Cp$_2$V(CO)$^-$, and Cp$_2$CrH$^-$ were adapted from various X-ray studies of similar compounds.[9,10] A trigonal geometry was assumed for Cp$_2$ML$^-$ and a distorted tetrahedral ligand arrangement for Cp$_2$VH$_2^-$: each has C_s point symmetry. All M–H bond distances are 1.60 Å. Other bond distances and angles are given in Table I.

Table I. Assumed Structural Parameters for Co(CO)$_{4-n}$L$_n^-$, Mn(CO)$_{5-n}$L$_n^-$, V(CO)$_{6-n}$L$_n^-$ and Cp$_2$ML$_n^-$ Systems

bond lengths, Å		bond angles, deg	
Co-C	1.75		
C-O	1.15	H-P-H	102
Co-P	2.25	O-P-O	100
P-H	1.42	P-O-H	98.2
P-O	1.61		
O-H	0.96		
Co-N	1.81[a]		
N-N	1.11[a]		
Mn-C$_{eq}$	1.80		
Mn-C$_{ax}$	1.82		
Mn-P	2.25		
V-C	2.00		
V-P	2.50		
Ti-CP[b]	2.05	CP-Ti-CP	120
V-CP	2.05	CP-V-CP	112
Cr-CP	1.85	CP-Cr-CP	130
		H-V-H	90

[a] Bond length taken from HCo(N$_2$)(PPh$_3$)$_3$ crystal structure.[23] [b] CP denotes C$_5$H$_5$ ring centroid.

All atomic wave functions were generated by using the method of Bursten, Jensen, and Fenske.[11] Contracted double-ζ representations were used for the metal 3d AO's, C and O 2p AO's, and the P 3p AO's. An exponent of 1.16 was used for the H 1s atomic orbital.[12] Metal basis functions were derived for the neutral atoms with the 4s exponent fixed at 2.0 for Ti, V, Cr, and Mn and 2.2 for Co. The 4p exponents were set at 1.2, 1.4, 1.6, 1.8, and 2.0 for Ti, V, Cr, Mn, and Co, respectively. In all calculations, the CO 3σ and 6σ orbitals, PH$_3$ 1a$_1$ and 3a$_1$, P(OH)$_3$ 1a$_1$, 1e, 6e, and 6a$_1$, and the first three occupied Cp orbitals and all virtual orbitals above the e$_2''$ level were deleted from the basis transformation set.[13]

Results and Discussion

Relative Acid Strength in Mixed Phosphine–Carbonyl Hydride Complexes. Most organometallic proton donors behave as moderately weak acids in aqueous solution, with K_a values between 10^{-2} and 10^{-8}.[1] The extent of proton dissociation depends directly on the effectiveness with which the coordinated ligands withdraw electron density from the metal atom in the conjugate base anion. For example, Hieber[14,15] and others[16-19] have observed that for the hydridocobalt complexes HCo(CO)$_{4-n}$L$_n$ (n = 0–4, L = P(OPh)$_3$ or PPh$_3$), the acid strength decreases monotonically upon sequential substitution of CO by L. Hieber attributed the decrease in acidity in the series HCo(CO)$_4$ > HCo(CO)$_3$P(OPh)$_3$ > HCo(CO)$_3$PPh$_3$ to the relative abilities of the ligands to deplete charge from the Co–H region. It was argued that this would quite naturally follow the relative π-accepting abilities of the ligands, namely, CO > P(OPh)$_3$ > PPh$_3$. From the hydride ligand reactivity

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Table II. The $HCo(CO)_{4-n}L_n$ (n = 0–3) Series in Order of Decreasing Acidity and the ΔE^{CB} Values

hydride	acidity	ref	model anion	ΔE^{CB}, eV
$HCo(CO)_4$	$K_a \approx 1.0$	14	$Co(CO)_4^-$	8.54
$HCo(CO)_3P(OPh)_3$	$K_a = 1.13 \times 10^{-5}$	14	$Co(CO)_3P(OH)_3^-$	7.38
$HCo(CO)_3PPh_3$	$K_a = 1.09 \times 10^{-7}$	14	$Co(CO)_3PH_3^-$	6.82
$HCo(CO)_2[P(OPh)_3]_2$	very weak	15	$Co(CO)_2[P(OH)_3]_2^-$	5.96
$HCo(CO)_2(PPh_3)_2$	very weak	15	$Co(CO)_2(PH_3)_2^-$	5.35
$HCo(CO)[P(OPh)_3]_3$	unknown but presumed weak	16	$Co(CO)[P(OH)_3]_3^-$	4.53
$HCo(CO)(PPh_3)_3$	weaker than $HCo(CO)_2(PPh_3)_2$	17	$Co(CO)(PH_3)_3^-$	4.09

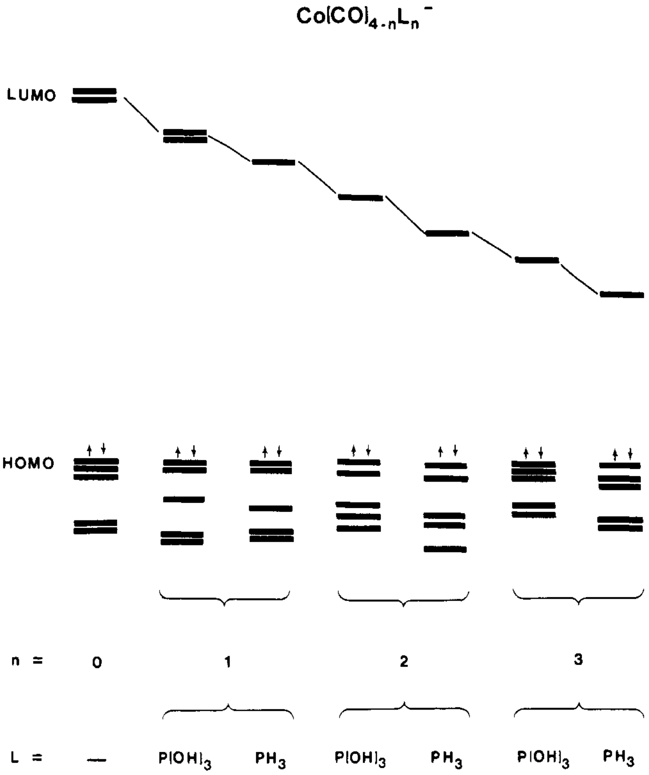

Figure 1. Comparative molecular orbital diagrams for $Co(CO)_{4-n}L_n^-$ (n = 0–3).

reported for the remaining members of the series, it can be inferred that their relative acid strengths are similarly determined by the combined ligand π-acidity, giving rise to the acidity ordering listed in Table II. The protonic characterization of each 18-electron member in this series, ranging from the strongly acidic $HCo(CO)_4$ to the nonacidic $HCo(dppe)_2$ (dppe = 1,2-(diphenylphosphino)ethane), provides the unique opportunity to examine ligand–acidity relationships in isostructural hydride complexes of the same metal center. We have performed Fenske–Hall molecular orbital calculations on the d^{10} anions $Co(CO)_{4-n}L_n^-$ to test the validity of a correlation of acidic strength of the cobalt hydrides with their conjugate base orbital energetics, particularly the HOMO/LUMO separations.

The calculated orbital energetics for the first seven members of this series are compared in Figure 1.[20] The orbital splittings follow the expected patterns for d^{10} systems under T_d, C_{3v}, and C_{2v} symmetries. The HOMO's of all these anions are essentially localized on the cobalt atom, and they are energetically close to the second highest occupied molecular orbitals. This is expected for stable species. The most apparent feature of Figure 1 is the steadily decreasing energy separation between HOMO and LUMO as the total π-accepting ability of the ligands decreases. Thus it appears that a correlation does exist between protonic strength and ΔE^{CB} magnitude for this series as shown in Table II; the largest ΔE^{CB} value of 8.54 eV belongs to the strongest acid $HCo(CO)_4$ and the smallest ΔE^{CB} value of 4.09 eV to the weakest acid $HCo(CO)(PPh_3)_3$, and intermediate ΔE^{CB} values are found for the other members. It is also seen in Table II that the ΔE^{CB} values decrease regularly by 0.8–1.0 eV with each successive replacement of carbonyl by the phosphorous ligands, reminiscent of some of the energetic trends evident in substitution derivatives of octahedral d^6 systems.[21] Further, Figure 1 implies that the acidity of the phosphito-substituted cobalt hydride is greater than that of the phosphine derivative for each $HCo(CO)_{4-n}(P(OPh)_3)_n$/$HCo(CO)_{4-n}(PPh_3)_n$ pair (n = 1–3). This behavior, already observed experimentally for the mono- and tetrasubstituted derivatives, further supports the notion that the acid strength of the hydridocobalt complexes is directly related to the π-accepting abilities of the ancillary ligands. Such a direct correlation between ligand π-acidity and hydride complex acidity would, for example, lead to the prediction that $HCo(N_2)(PPh_3)_3$[22] would be even a weaker acid than the isoelectronic $HCo(CO)(PPh_3)_3$ because the extent of back-bonding from Co to N_2[23] is less than that to CO. The relatively smaller ΔE^{CB} value of 3.77 eV we found for this dinitrogen-containing hydrido complex would certainly rank its acidity below that of $HCo(CO)(PPh_3)_3$. In fact, as no proton dissociation has been observed for either of these compounds, it may well be the case that hydride complexes of the types $HCoL_4$ with a $\Delta E^{CB} \leq 4.0$ eV are nonacidic or even hydridic.

Table III. Acid Dissociation Constants and ΔE^{CB} Values of $HM(CO)_n$ and $HM(CO)_{n-1}PPh_3$ Hydrides

hydride	K_a	ref	model anion	ΔE^{CB}, eV
			octahedral anions	
$HV(CO)_6$	~1.0	24	$V(CO)_6^-$	7.24
$HV(CO)_5PPh_3$	1.5×10^{-7}	24	$V(CO)_5PH_3^-$	5.44
			trigonal-bipyramidal anions	
$HMn(CO)_5$	8.0×10^{-8}	25	$Mn(CO)_5^-$	8.33
$HMn(CO)_4PPh_3$	10^{-13}	26	$Mn(CO)_4PH_3^-$	7.77
			tetrahedral anions	
$HCo(CO)_4$	~1.0	14	$Co(CO)_4^-$	8.54
$HCo(CO)_3PPh_3$	1.09×10^{-7}	14	$Co(CO)_3PH_3^-$	7.38

The successful qualitative correlation of conjugate base HOMO/LUMO separations with acidic strength for derivatives of $HCo(CO)_4$ is also applicable to other phosphine-substituted carbonyl hydride complexes. Table III

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[20] The homoleptic PH_3 and $P(OH)_3$ anions $Co(PH_3)_4^-$ and $Co(P(OH)_3)_4^-$ would converge only if P 3d AO's were included in the basis set. We are not yet certain whether this is an artifact of the Fenske–Hall method or whether it is indicative of increasing π-accepting ability by phosphines upon successive substitution. For this reason, the two homoleptic anions have not been included in this study.

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Table IV. Co 3d Mulliken Populations, Co 3d and CO 2π Diagonal Fock Matrix Elements, and HOMO and LUMO Energies for the Series $Co(CO)_n(PH_3)_{4-n}^-$

anion	Co 3d pop.	diagonal Fock elements, eV		ϵ(HOMO), eV	ϵ(LUMO), eV
		Co 3d	CO 2π		
$Co(CO)_4^-$	7.45	-0.70	6.03	-0.53	8.02
$Co(CO)_3PH_3^-$	7.64	1.97	7.35	2.37	9.12
$Co(CO)_2(PH_3)_2^-$	7.87	5.22	9.05	5.62	10.79
$Co(CO)(PH_3)_3^-$	8.23	9.80	11.83	10.05	13.91

Table V. Hydridic Character and ΔE^{CB} and ΔE^{HS} Values for Cp_2ML_nH Complexes

hydride	acetone reductn reactn time[a]	model anion	ΔE^{CB}, eV	ΔE^{HS}, eV
Cp_2ZrH_2	instantaneous	Cp_2TiH^-	0.13	6.99
Cp_2NbH_3	12 h	$Cp_2VH_2^-$	2.91	6.59
$Cp_2Nb(CO)H$	2 days	$Cp_2V(CO)^-$	1.07	1.54
Cp_2MoH_2	no reaction[b]	Cp_2CrH^-	2.12	0.05

[a] Data taken from ref 2. [b] Cp_2MoH_2 reduces the more electrophilic CF_3COCH_3 in 1 day.

compares the K_a and ΔE^{CB} values for $HV(CO)_6$, $HMn(CO)_5$, and $HCo(CO)_4$ with the corresponding values for $HV(CO)_5PPh_3$, $HMn(CO)_4PPh_3$, and $HCo(CO)_3PPh_3$. In each case, the notably weaker acid of each $HM(CO)_n/HM(CO)_{n-1}PPh_3$ pair, the phosphine-substituted one, has the smaller ΔE^{CB} value. Table III also illustrates that the relative acid strength/ΔE^{CB} dependence is limited to isostructural series since the relative acidities of hydrides that yield nonisostructural anions cannot be reliably determined by comparing their ΔE^{CB} values although this did not seem to be the case for the nonisostructural $CpCr(NO)_2^-$ and $CpCr(CO)_3^-$ systems.[27]

An analysis of the orbital characters of the HOMO and LUMO of the anions leads to an explanation of the changes in ΔE^{CB} with ligand substitution. The $Co(CO)_n(PH_3)_{4-n}^-$ series will be used to illustrate the trends, but the conclusions can be generalized to all of the acids discussed above. The HOMO in $Co(CO)_4^-$ is the t_2 orbital that is predominantly Co 3d in character. Throughout the series, the HOMO remains primarily Co 3d with smaller contributions from the CO 2π, CO 5σ, and PH_3 lone-pair orbitals. A consequence of the interaction of the t_2 set of d orbitals with both ligand acceptor and donor orbitals is that the orbital energy of the HOMO is nearly equal to the diagonal element of the Fock matrix for the Co 3d orbitals (Table IV). The LUMO throughout the series is predominantly CO 2π in character with a smaller, antibonding contribution from the Co 3d orbitals; even in $Co(CO)(PH_3)_3^-$ the LUMO is 63% CO 2π and 32% Co 3d with virtually no contribution from the PH_3 ligands.

The effect on ΔE^{CB} of replacing a CO by a phosphine is directly related to the increased donor ability of the latter, an influence which has been used to explain the increased reactivity toward Lewis acids of $HMn(CO)_4PPh_3$ relative to $HMn(CO)_5$.[4] As demonstrated in Table IV, the replacement of CO by PH_3 increases the Co 3d population, leading in turn to a more positive 3d diagonal Fock matrix element and thus a more positive ϵ_{HOMO}. The LUMO also rises in energy, but by a smaller amount owing to the lesser sensitivity of the CO 2π diagonal Fock matrix element to PH_3 substitution. Thus, the HOMO/LUMO separation decreases upon PH_3 substitution, an effect which is seen in the Mn and V series as well.

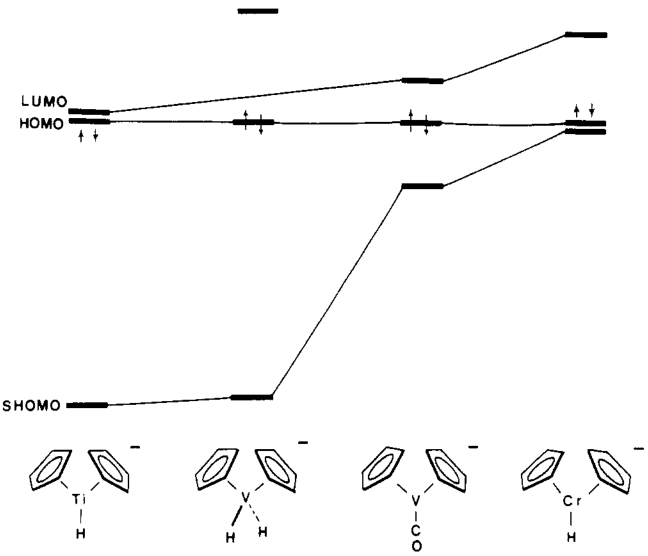

Figure 2. Comparative molecular orbital diagrams for $Cp_2ML_n^-$ systems illustrating the HOMO, LUMO, and SHOMO of each.

Relative Hydridic Strength in $Cp_2M(L)_nH$ Complexes. It occurred to us that if ΔE^{CB} values are directly related to acidic strength in proton donors, they may by inversely related to the hydridic strength in hydride donors. Labinger and Komadina[2] recently reported that the relative hydridic strength, as determined by reaction rates for the reduction of ketones to alcohols, decreases across a series of early transition metal bis(cyclopentadienyl) hydrides as $Cp_2ZrH_2 > Cp_2NbH_3 > Cp_2Nb(CO)H > Cp_2MoH_2$ (Table V). These systems do act as proton donors because the weakly π-accepting Cp ligands cannot adequately stabilize the resulting organometallic anion. In order to determine whether a relationship exists between the reactivities and orbital energetics for these systems, Fenske–Hall calculations were performed on the deprotonated hydrides for the first-row analogues Cp_2TiH^-, $Cp_2VH_2^-$, $Cp_2V(CO)^-$, and Cp_2CrH^-. The resulting molecular orbitals are in good accord with previous calculations on some neutral Cp_2ML_n analogues.[28,29] A comparison of the molecular orbital diagrams of these four

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(27) We have also observed that HOMO/LUMO separations are extremely sensitive to basis set choice. This poses no real problem for a series of isostructural anions of the same metal atom since the relative magnitudes of HOMO/LUMO gaps remain constant upon varying basis sets. However, a comparison of isostructural anions of different metals requires that the metal atomic basis sets used are for the same metal oxidation state and that there is consistency in the selection of exponents for the low-lying vacant s and p functions.

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anions is given in Figure 2 and Table V. For the isostructural anions, Cp_2TiH^-, $Cp_2V(CO)^-$, and Cp_2CrH^-, a gradual increase in the size of the HOMO/LUMO gaps is observed across the series. In this series, the ΔE^{CB} values suggest Cp_2ZrH_2 is the weakest proton donor and so by extension, the strongest hydride donor; Cp_2MoH_2 is the strongest acid or weakest hydride donor, and that intermediate hydridic character is expected for $Cp_2Nb(CO)H$. Hence, the relative hydridic activities predicted by the energetics of these anions agree with experiment. Figure 2 shows that the magnitude of the HOMO/LUMO separation for the $Cp_2VH_2^-$ anion disrupts the trend of the smooth increase in HUMO/LUMO gaps across the series; this is not unexpected since this anion is not isostructural with Cp_2TiH^-, $Cp_2V(CO)^-$, and Cp_2CrH^-. That the ΔE^{CB}'s correctly determine the relative hydridic strength of Cp_2ZrH_2, $Cp_2Nb(CO)H$, and Cp_2MoH_2 species suggests that a ΔE^{CB}/relative H reactivity correlation may exist for isostructural hydridic as well as protonic hydride complexes.

The electronic structures for the d^2 Cp_2TiH^- and $Cp_2VH_2^-$ systems also reveal relatively large energy separations between the HOMO and the second highest occupied molecular orbital (SHOMO). We define the quantity ΔE^{HS} as

$$\Delta E^{HS} = \epsilon(\text{HOMO}) - \epsilon(\text{SHOMO})$$

We believe that a large ΔE^{HS} is suggestive of preferential cation formation and hence hydridic character for the parent hydride. Both the small HOMO/LUMO gaps and the large ΔE^{HS} values imply destabilization in these two anions. The magnitude of the ΔE^{HS} values decreases across the series (Table V), and in contrast to the d^2 Cp_2TiH^- and $Cp_2VH_2^-$ cases, the HOMO is much more stabilized in the d^4 $Cp_2V(CO)^-$ and Cp_2CrH^- systems. Hence it appears that the anion ΔE^{HS} values can be used to correctly determine the relative hydridic strength for all members of this series whereas the HOMO/LUMO gaps cannot. A steady decrease in ΔE^{HS} was also observed[5] across the series $CpCr(NO)_2^-$, $CpMn(NO)(CO)^-$, and $CpFe(CO)_2^-$, consistent with the decreasing hydridic strength in their parent hydrides.

While it appears that a correlation does exist between hydride reactivity and the orbital energetics of the deprotonated hydrides, it must be pointed out that the experimental data on such systems consists entirely of kinetic, rather than thermodynamic, measurements. It is our implicit assumption that the magnitudes of the equilibrium constants for the process

$$L_nMH \rightleftarrows L_nM^+ + H^-$$

follow the same trend as the kinetic data reported by Labinger and Komdaina.[2] The validity of this assumption awaits further experimental measurements on these systems. Nevertheless, we are encouraged that an apparent correlation does exist.

Conclusions

We have demonstrated that the Fenske–Hall molecular orbital method can determine both the mode of hydrogen reactivity and the relative protonic or hydridic strength in a series of isostructural transition-metal complexes. We again emphasize that the acid–base nature of organometallic hydrides can be predicted by examining the orbital energetics of the deprotonated hydrides rather than the actual hydride complexes. It thus appears the electronic stability found for the anion (as judged by the position of the HOMO relative to both the LUMO and the SHOMO) is directly related to acidic strength and inversely related to hydridic strength. This concept of conjugate base stability has long been utilized in ranking acidities within classes of organic acids and inorganic oxyacids where the compounds with the more electronegative groups or atoms are the stronger acids.

It is apparent that, in attempting to correlate the acidity of organometallic hydrides with the electronic structures of the corresponding conjugate bases, we have neglected two important aspects of the solution acid–base process, namely, the nature of the base used to deprotonate the hydride and the effects of solvation. The first of these is difficult to address since there have been no studies of the dependence of K_a for these systems upon the base used. With regard to the effects of solvation, the major thermodynamic solvent effect would be the difference in $\Delta H_{solvatn}$ of L_nMH and L_nM^- (assuming the same base is used throughout). It is our expectation that for the systems under investigation, this difference will be essentially constant; the pertinent point is that consideration of solvation involves a comparison of a hydride to its conjugate base, *not* a comparison of the relative solvation enthalpies of two different anions. Further support is obtained from a recent theoretical investigation by McKinney and Pensak.[30] In their study of the calculation of reaction enthalpies from molecular orbital theory, they considered the reactions

$$H_mM(CO)_n + H_2O \rightarrow H_{m-1}M(CO)_n^- + H_3O^+$$

where $H_mM(CO)_n = HCo(CO)_4$, $H_2Fe(CO)_4$, $HMn(CO)_5$, or $HFe(CO)_4^-$. They found a good correlation between ΔH and pK_a for the three neutral hydrides but not for $HFe(CO)_4^-$. It is apparent that the difference in solvation enthalpy between a monoanionic hydride and its dianionic conjugate base should be different from that of a neutral hydride and its monoanionic conjugate base, and it seems a certainty that solvation effects will be important in comparing hydride complexes with different charges.

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Registry No. $HCo(CO)_4$, 16842-03-8; $HCo(CO)_3P(OPh)_3$, 57574-46-6; $HCo(CO)_3PPh_3$, 19537-79-2; $HCo(CO)_2[P(OPh)_3]_2$, 57574-48-8; $HCo(CO)_2(PPh_3)_2$, 21517-65-7; $HCo(CO)[P(OPh)_3]_3$, 29189-83-1; $HCo(CO)(PPh_3)_3$, 21329-67-9; $Co(CO)_4^-$, 14971-27-8; $Co(CO)_3P(OH)_3^-$, 89746-19-0; $Co(CO)_3PH_3^-$, 89746-20-3; $Co(CO)_2[P(OH)_3]_2^-$, 89746-21-4; $Co(CO)_2(PH_3)_2^-$, 89746-22-5; $Co(CO)[P(OH)_3]_3^-$, 89746-23-6; $Co(CO)(PH_3)_3^-$, 89746-24-7; $HV(CO)_6$, 89746-25-8; $HV(CO)_5PPh_3$, 89746-26-9; $HMn(CO)_5$, 16972-33-1; $HMn(CO)_4PPh_3$, 16925-29-4; $V(CO)_6^-$, 20644-87-5; $V(CO)_5PH_3^-$, 62363-95-5; $Mn(CO)_5^-$, 14971-26-7; $Mn(CO)_4PH_3^-$, 71518-87-1.

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