to be the case, and, in fact, arguments have been advanced[7] for the superiority of the latter model. The united-atom model is also clearly more successful in calculating the force constants (Figure 2). The general trend of force constant within each horizontal row is reproduced quite well. The errors in the calculated values for this observable are relatively much larger than for the internuclear distance. The reasons for this are perhaps most evident when the problem is viewed in terms of the Hellmann-Feynman theorem. The expectation value for internuclear distance is dependent on the equilibrium wave function, for which the Hartree-Fock atomic wave function for the neutral atom of $Z + 1$ nuclear charge is apparently a good approximation. The stretching-force constant, however, involves an expression of the form[8]

$$k = \frac{2Z}{r^3} + \int \Psi^*\Psi \frac{\partial^2 V_{\mathrm{ne}}}{\partial r^2}\,\mathrm{d}\tau + \int \frac{\partial(\Psi^*\Psi)}{\partial r}\frac{\partial V_{\mathrm{ne}}}{\partial r}\,\mathrm{d}\tau \tag{9}$$

where V_{ne} is the nuclear-electronic attraction operator, $V_{\mathrm{ne}} = \Sigma_\alpha - 1/r_{\alpha\mathrm{H}}$, where the sum is over all electrons. The last term in this equation is a measure of relaxation in the electron distribution accompanying nuclear motion. In the Platt model this term is assumed to be zero. Only a fortunate cancellation with another large term of opposite sign can yield a satisfactory value for k. Such a cancellation does apparently exist, but k is nevertheless not as accurately predicted as r_{e}.

Acknowledgment. Calculations were performed at the University of Illinois Digital Computer Laboratory.

Application of Platt's Model for Diatomic Hydrides to Metal Carbonyl Hydrides[1]

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Abstract: Platt's united-atom model for diatomic hydrides is extended to metal carbonyl hydrides. The equations are the same as for the diatomic case, except that a classical approximation is employed to take account of net charge which may be present on the CO groups. The model provides a simple picture for metal-hydrogen bonding and accounts nicely for the similarity in M-H stretching frequency with the corresponding diatomic metal hydride. The following values are estimated for equilibrium M-H distances: $Mn(CO)_5H$, 1.60 A; $Co(CO)_4H$, 1.40 A; $Fe(CO)_4H^-$, 1.40 A; $Cr(CO)_5H^-$, 1.50 A.

The transition metal carbonyl hydrides are an interesting and varied group of compounds.[2,3] The purpose of the present contribution is to consider the metal-hydrogen bond in terms of an extension of Platt's model for diatomic hydrides.[4,5]

The metal carbonyl hydrides can be considered to derive in principle from a parent metal carbonyl molecule or ion by abstraction of a proton from the nucleus of the central metal atom.[6] The abstracted proton is allowed to move out through an electronic environment which is forced to remain unchanged, except for relatively minor C-M-C bond angle changes. When the nuclear-electronic attractive forces on the proton equal the proton-nuclear repulsive forces, the proton comes to rest. Some examples of the process envisaged are

$$Fe(CO)_5 \longrightarrow Mn(CO)_5H$$

$$Mn(CO)_5^- \longrightarrow Cr(CO)_5H^-$$

$$Ni(CO)_4 \longrightarrow Co(CO)_4H$$

$$Co(CO)_4^- \longrightarrow Fe(CO)_4H^-$$

If it is assumed that the proton exerts a slight net repulsive effect on the CO groups, it may then be expected to occupy somewhat less space than the surrounding CO groups. Thus in $Mn(CO)_5H$ the axial-radial C-Mn-C angle is 97°;[7] the average CO-CO distance is only slightly less than in the parent $Fe(CO)_5$.

The carbonyl hydride formation described above is an isoelectronic process and may be considered in terms of the Hellmann-Feynman theorem. Employing the integral form of this theorem,[8] we label the parent carbonyl compounds as the X state and the carbonyl hydride in its equilibrium configuration as the Y state. Then the difference in energy, ΔW, exclusive of the change in nuclear energy, is given by

$$\begin{aligned} W &= \Delta V_{\mathrm{nn}} + \frac{N}{S}\int \Psi_{\mathrm{X}} H'(1) \Psi_{\mathrm{Y}}\,\mathrm{d}\tau \\ W &= \Delta V_{\mathrm{nn}} + \frac{N}{S}\int \rho_{\mathrm{XY}}(1) H'(1)\,\mathrm{d}\tau(1) \end{aligned} \tag{1}$$

The first term on the right represents the difference in the classical nuclear-nuclear potential, $\Sigma_{jk}Z_jZ_k/r_{jk}$, where Z_j and Z_k are the charges on nuclei j and k, and r_{jk} is the internuclear distance. The normalized transi-

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[1] The research is supported by a grant from the National Science Foundation, NSF GP 6369X.

[2] R. B. King, *Advan. Organometal. Chem.*, **2**, 157 (1964).

[3] J. A. Ibers, *Ann. Rev. Phys. Chem.*, **16**, 389 (1965).

[4] J. R. Platt, *J. Chem. Phys.*, **18**, 932 (1950).

[5] W. G. McDugle, Jr., and T. L. Brown, *J. Am. Chem. Soc.*, **89**, 3111 (1967).

[6] A related idea was expressed 25 years ago by W. Hieber, *Die Chemie*, **55**, 24 (1942).

[7] S. J. LaPlaca, W. C. Hamilton, and J. A. Ibers, *Inorg. Chem.*, **3**, 1491 (1964).

[8] H. J. Kim and R. G. Parr, *J. Chem. Phys.*, **41**, 2892 (1964).

tion density $\rho_{XY}(1)$ is given by

$$\rho_{XY}(1) = \frac{N}{S}\int\Psi_X(1)\Psi_Y(1)\,d\tau(2)d\tau(3)\ldots d\tau(N)$$

$$S = \int\Psi_X(1, 2, \ldots, N)\Psi_Y(1, 2, \ldots, N)\,d\tau(1)\ldots d\tau(N)$$

The perturbation Hamiltonian H' is given by

$$H'(1) = V_{ne}{}^{Y}(1) - V_{ne}{}^{X}(1)$$

The elucidation of these expressions is greatly simplified if it is assumed that all interactions of the CO groups with one another and with the central metal are unchanged in the process X → Y. This means that only the term $\Sigma Z_j{}_H/r_{jH}$ remains in ΔV_{nn}, and that $H'(1) = \Sigma_\alpha(-1/r_{H\alpha})$, where α runs over all electrons. Although this assumption may seem a bit drastic, it is quite reasonable in terms of what data are available. The CO stretching frequencies in the infrared-active modes, for example, are not changed drastically, as the comparisons in Table I show. The CO frequencies in the hydride are very little different from those in the parent carbonyl, whereas they are much lower in the anion corresponding to complete removal of the proton.

Table I. Comparative CO Stretching Frequencies of Metal Carbonyl Derivatives

Compound	Infrared CO frequencies, cm^{-1}	Ref
$Ni(CO)_4$	2057	*a*
$Co(CO)_4H$	2062, 2043	*a*
$Co(CO)_4^-$	1886	*a*
$Fe(CO)_5$	2034, 2014	*a*
$Mn(CO)_5H$	2007, 2014, 2117	*b*
$Mn(CO)_5^-$	1898, 1863	*a*
$Co(CO)_{54}^-$	1886	*a*
$Fe(CO)_4H^-$	1897, 1937	*a*
$Fe(CO)_4^{-2}$	1786	*a*

[a] W. F. Edgell, J. Huff, J. Thomas, H. Lehman, C. Angell, and G. Asato, *J. Am. Chem. Soc.*, **82**, 1254 (1960). [b] P. S. Braterman, R. W. Harrill, and H. D. Kaesz, submitted for publication.

From this point it is possible to make still further simplifying assumptions. The common view of the neutral metal carbonyls is that the central metal atom carries essentially zero charge. Although it is difficult to gather definitive evidence on this point, the isomer shift in the Mössbauer spectrum[9] of $Fe(CO)_5$ and related compounds is consistent with near-zero charge on the metal. The appearance potentials of neutral as well as positively charged metal carbonyl fragments parallel the ionization potentials of the metal atoms or ions of corresponding charge remarkably well,[10] a further indication that the over-all charge of the metal carbonyl moiety is a measure of the metal atom charge. It is possible then to consider that the nuclear–nuclear and nuclear–electronic components of ΔW which involve the C and O nuclei and electron density localized in the CO regions cancel for the proton. There remains just the interaction with the central nucleus and transition density centered thereon

$$\Delta W = \frac{Z}{r_{MH}} - \frac{N}{S}\int\rho_{XY}{}^{M}(1)\frac{1}{r}\,d\tau(1) \tag{2}$$

If that part of Ψ centered on M is assumed to be invariant to the X → Y process, then ρ_{XY} becomes simply the one-electron charge density on M, $\rho_M(1)$

$$\Delta W = \frac{Z}{r_{MH}} - \int\rho_M(1)\frac{1}{r}\,d\tau(1) \tag{3}$$

We desire $\partial\Delta W/\partial r_{MH} = 0$ at the equilibrium CO distance, which gives

$$\frac{Z}{r_e{}^2} = \int_0^{r_e}\frac{\rho_M{}^{(1)}}{r^2}\,d\tau(1) \tag{4}$$

If ρ_M is spherically symmetric, this is just Platt's model for a diatomic hydride. The force constant follows in the usual way. Although the net charge in the metal carbonyl may be zero as assumed, it is of interest to explore the consequences of the assumption that it is not. We assume again that the CO–CO and CO–M interactions are the same in the X and Y states. Further, the proton–electron and proton–nuclear interactions with the CO groups are assumed to yield a net potential energy, $\Sigma_i S_i/r_{iH}$, where S_i is the net charge on the ith CO group, and r_{iH} is the distance from the proton to the center of the ith CO bond. Thus, if the metal is assumed to have a net charge of -1 in $Mn(CO)_5H$, $+0.20$ unit of charge may be assigned to each CO group. Alternatively, it might be assumed that the axial CO group has a different net charge than the radial, etc. The components of ΔW relating to the central atom and electron density centered there remain unchanged. Then

$$\Delta W = \frac{Z}{r_{MHH}} - \int\rho_M\frac{1}{r}\,d\tau + \sum_i\frac{S_i}{r_{iH}} \tag{5}$$

$$\frac{\partial\Delta W}{\partial r_{MH}} = 0 = \frac{-Z}{r_e{}^2} + \int\frac{\rho_M}{r^2}\,d\tau - \sum_i\frac{S_i\cos\theta_{iH}}{r_{iH}{}^2} \tag{6}$$

The charge density ρ_M in eq 6 is that appropriate to the metal atom in a zero or nonzero charge state, depending on ΣS_i and the total net charge on the parent carbonyl. Aside from assignment of charge state, there is the problem of choosing the appropriate configuration, which may be different from that in the free metal of the same charge. An attempt has been made to evaluate the sensitivity of the results to this variable. It should be pointed out that the scaling procedure applied to diatomic M-H systems[6,11] has been employed in the same manner as before.

A few qualitative conclusions can be drawn immediately from the proposed model. If the charge on the metal in the parent carbonyl is near zero, then it follows that the metal–hydrogen bond should possess about the same stretching force constant and equilibrium nuclear distance as in the corresponding diatomic hydride. The evidence regarding distances is somewhat tenuous at present (*vide infra*), but the force constant results are qualitatively as expected, as evidenced by the comparisons of observed metal–hydrogen stretching frequencies given in Table II.

Results

Calculations were performed as described in the previous paper, using Clementi's wave functions.[11-13]

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[12] E. Clementi, *J. Chem. Phys.*, **41**, 303 (1964), and previous papers referenced therein.

[13] E. Clementi, *IBM J. Res. Develop. Suppl.*, **9**, 2 (1965).

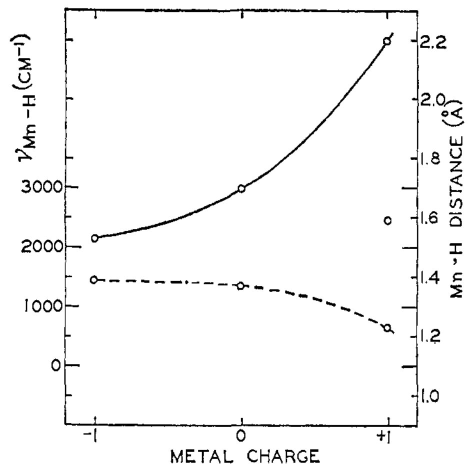

Figure 1. Calculated equilibrium distance and stretching frequency for the Mn–H bond in $HMn(CO)_5$, as a function of metal charge.

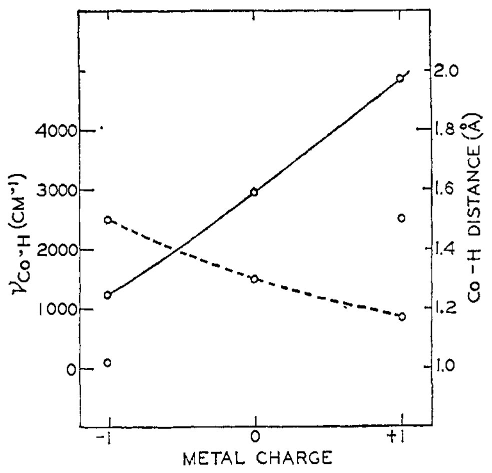

Figure 2. Calculated equilibrium distance and stretching frequency for the Co–H bond in $HCo(CO)_4$, as a function of metal charge.

$Mn(CO)_5H$. Calculations were carried out for $Mn(CO)_5H$ assuming a +1, 0, and −1 charge on the Fe in the united molecule. Wave functions for the configurations $4s^23d^n$ are available for these three charges. When the charge on the metal is different from zero, it has been assumed that the charge of opposite sign is distributed equally among the five CO groups. The results were not affected by assuming that the axial CO group carries a slightly different charge than the radial. The bond angles and distances observed in solid $HMn(CO)_5$[7] were employed in the calculation. The resulting equilibrium Mn–H distance as a function of metal charge is shown as the solid line in Figure 1. There is only one other configuration available for testing, namely $4s^03d^7$ for Fe^+, for which the calculated equilibrium Mn–H distance is shown as the single point on the figure. This configuration represents an unlikely extreme in terms of s character. It is generally assumed from theoretical considerations that the first-row transition metals do employ considerable 4s orbital character in metal carbonyl compounds. The solid curve in Figure 1 is therefore probably satisfactory from the standpoint of s orbital character. The effect of 4p character on the equilibrium Mn–H distance is an important question, which we cannot test for a lack of the appropriate atomic wave functions. Although 4p orbital functions of high accuracy are not available for the first-row transition elements, it is quite clear that the 4p charge densities lie outside the 3d. Richardson and co-workers[14] report that in the neutral atoms the 3d distribution completely screens nuclear charge from the 4p, to within 1%. We may state with confidence, therefore, that the assumed $4s^23d^n$ configuration will lead to a *lower bound* estimate of the Mn–H distance for the model chosen. Part of the error resulting from failure to include 4p occupation is cancelled by the assumption of a full two-electron occupation of the 4s.[15] The 4s and 4p have similar radial charge-density dependences.

Table II

	ν_{M-H}, cm^{-1}		ν_{M-H}, cm^{-1}
$Mn(CO)_5H^a$	1775	Mn–H	1548
$Co(CO)_4H^b$	1934	CoH	1890
$Fe(CO)_4H^-$	1900	FeH^-	. . .

[a] Reference 10. [b] W. F. Edgell and R. Summitt, *J. Am. Chem. Soc.*, **83**, 1772 (1961).

The dotted line shows the calculated Mn–H stretching frequency, in the harmonic oscillator approximation, as a function of metal charge, for the assumed $4s^23d^n$ configurations. As the metal charge becomes more negative, there is an asymptotic approach to a frequency of about 1500 cm^{-1}, somewhat below the observed frequency of 1775 cm^{-1}. Frequency decreases quite rapidly with increase in charge above zero. The model is in best accord, therefore, with a metal charge of about −0.5; the predicted Mn–H stretching frequency is in the range 1350 to 1450 cm^{-1}; and the predicted Mn–H bond distance is 1.60 ± 0.07 A.

$Co(CO)_4H$. The procedure described above was followed also for $Co(CO)_4H$. Unfortunately, the only configuration of Ni^- for which the wave function is available is $4s^13d^{10}$; this was used along with the wave function of the $4s^23d^8$ and $4s^23d^7$ configurations for Ni and Ni^+, respectively. The results are graphed in Figure 2. For Ni^+ the configuration $4s^03d^9$ is also available. The result of using the wave function for this configuration is shown as the single point. We take half the difference between this point and the point corresponding to the $4s^23d^7$ configuration as a correction to the $4s^13d^{10}$ point at −1 charge, to make it correspond approximately to a $4s^23d^9$ configuration. This point is used in constructing the solid line in Figure 2.

The calculated equilibrium Co–H distance was found to be quite insensitive to the assumed C–Co–C angles. The data are shown for tetrahedral disposition of the CO groups. Variation of up to 10° in the H–Co–C angles produced a change of less than 0.02 A in the calculated Co–H distance, even when the charge on the metal is assumed to be +1 or −1.

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(14) J. W. Richardson, R. R. Powell, and W. C. Nieuwpoort, *J. Chem. Phys.*, **38**, 796 (1963).

(15) An extensive approximate Roothaan SCF MO calculation on $Ni(CO)_4$, using approximate SCF metal atomic orbitals[14] in the basis set, has been carried out by W. C. Nieuwpoort, *Philips Res. Rept. Suppl.*, **6**, 1 (1965). He obtains a net metal charge, based on a conventional population analysis, of −1. The total Ni orbital populations are $4s^{0.84}4p^{1.93}3d^{8.3}$.

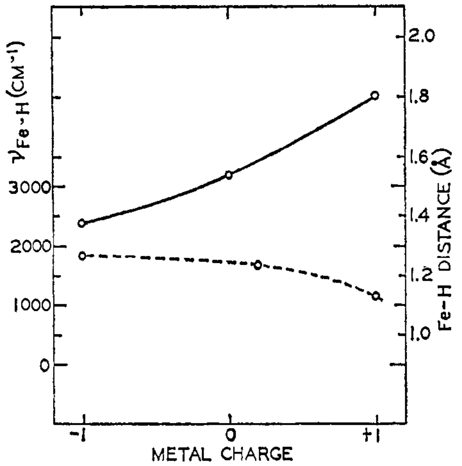

Figure 3. Calculated equilibrium distance and stretching frequency for the Fe-H bond in $HFe(CO)_4^-$, as a function of metal charge.

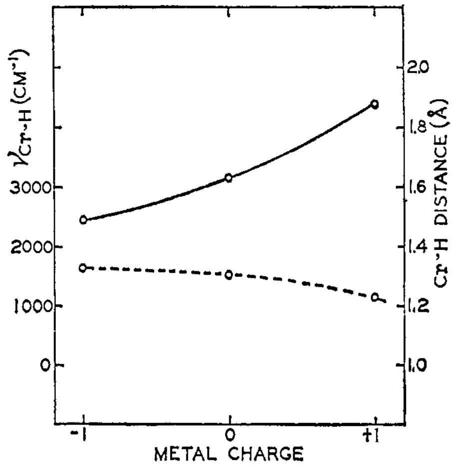

Figure 4. Calculated equilibrium distance and stretching frequency for the Cr-H bond in $HCr(CO)_5^-$, as a function of metal charge.

The variation in Co-H stretching frequency as a function of assumed metal charge, for the $4s^23d^n$ configuration, is shown as the dashed line in Figure 2. The value for -1 charge is only approximate, since the $4s^23d^9$ wave function is not available. The observed frequency intersects the line at a metal charge of about -0.5. For this charge the equilibrium Co-H bond distance is calculated to be about 1.40 ± 0.1 A.

$Fe(CO)_4H^-$. Wave functions for $4s^23d^n$ configurations of Co^-, Co^0, and Co^+ are available. The results of the calculations are as shown in Figure 3. The observed Fe-H stretching frequency is approached in the calculations for a rather negative charge on the metal, in the range from -0.5 to -1. The calculated Fe-H distance based on this range of charge is 1.40 ± 0.05 A.

$HCr(CO)_5$ and $HCr_2(CO)_{10}^-$. The calculations for $HCr(CO)_5^-$ were carried out as described above for the other cases, using Mn wave functions for $4s^23d^n$ configurations (Figure 4). For a metal change of about -0.75, the Cr-H frequency is calculated as 1600 cm^{-1}, the Cr-H distance as 1.50 ± 0.05 A.

Certain aspects of the structure of $HCr_2(CO)_{10}^-$ have recently been described.[16] The hydrogen is presumably located along the Cr-Cr axis and separates two $Cr(CO)_5$ units. If we assume that each unit carries a -0.5 charge, the charge on the Cr in $HCr_2(CO)_{10}^-$ should be slightly less negative, by perhaps 0,25 e, than in $HCr(CO)_5^-$. Assuming that the charge on the Cr in $HCr_2(CO)_{10}^-$ is -0.5, a Cr-H distance of 1.54 A is estimated from Figure 4. This leads to a predicted Cr-Cr distance of about 3.1 A, as compared with the experimental value of 3.41 A.[16] The comparison is rather tenuous, but the agreement is encouraging.

Discussion

There is an unfortunate paucity of data regarding metal-hydrogen distances in metal carbonyl hydrides. The results obtained here are in good agreement with expectations based on somewhat empirical covalent radii.[16] Thus a value of about 1.65 is expected for the Mn-H distance, as compared with our calculated value of 1.60 ± 0.07 A.

The only experimental data which relate directly to the M-H distances are the broad-line proton nmr studies of Farrar, Davison, *et al.*[17] These authors conclude that the Mn-H distance in $HMn(CO)_5$ is 1.28 A. The Co-H distance in $HCo(CO)_4$ is estimated on the basis of line-shape data as 1.2 ± 0.1 A.[18]

Both these results are shorter than the estimates from the present calculations. No reasonable modification which retains the simplicity of the model could appreciably shorten the calculated M-H distances. Indeed, the calculated values are probably lower bounds, in view of our neglect of the 4p orbital occupations.

Even if the estimates of metal-hydrogen distances from the nmr studies are subsequently corroborated by neutron diffraction or other data, the results obtained are quite good for such a simple model. The approach is of value in suggesting how the transition metal hydride structures relate to known organometallic structures.[2,19] It provides a nice rationale for the observation that the M-H stretching frequencies are close to those for the corresponding diatomic metal hydrides. Extension to calculation of other expectation values, notably chemical shift[20] and electric field gradient,[21] would not be difficult.

Acknowledgment. Calculations were performed at the University of Illinois Digital Computer Laboratory.

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