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LCAO–MO Charge Distribution and Proton Nuclear Magnetic Resonance Shifts in Transition Metal Hydride Complexes

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Received June 1, 1963

The high-field proton magnetic resonance shifts in several compounds containing the H–M (transition metal) bond are treated by combining chemical shift matrix elements for the hydrogen–metal bond with the charge distributions obtained from a one-electron LCAO–MO theory. The charge on the hydrogen, the charge in outer valence s, p, and d orbitals of the transition metal, and the effects of different ligands on the shift are discussed.

Introduction

The evaluation[1] of matrix elements related to the H–Co bond in $HCo(CO)_4$ led to a theory of the large high-field shift of the proton magnetic resonance without the assumption of an unusually short H–Co distance. The subsequent development[2,3] of a computer program for semi-empirical LCAO molecular orbital study has now made it possible to approximate molecular charge distributions in complex molecules and to compare a number of closely related chemical species. Accordingly, we combine here matrix elements of the type obtained previously[1] with these LCAO–MO charge distributions to give estimated proton shifts in a number of transition metal hydride bonds in molecules containing carbonyl, cyano, and π-cyclopentadienyl groups. The calculations of chemical shifts were carried out by the AO method[1] because it is more readily applied to a large number of examples. We find a good correlation of calculated and observed shifts and show how the shift varies as the nature of the remaining ligands is varied.

The LCAO–MO theory used here is essentially the familiar Hückel π-electron theory of aromatic systems, with several extensions[2,3]: the atoms are not confined to a plane, no nearest-neighbor approximation is made, the complete overlap matrix is used, more than one orbital per atom is considered, and the atoms are in general different, necessitating different diagonal energy matrix elements for the different types of atomic orbitals. As the atomic basis functions enter the calculation of the MO's only in terms of their overlaps, the energy matrix elements have no explicit dependence on the exact form of these functions. The assumed proportionality of the resonance integrals to the overlap integrals (eq. 2, ref. 3) then implies that the exponential distance dependence (at large distances) of the overlap integrals holds also for the resonance integrals. Finally, the semiquantitative nature of the method cannot be overstressed; if the purely qualitative aspects of the results are not insensitive to chemically reasonable variations of the atomic coordinates and AO parameters (Slater exponents and Coulomb integrals), little claim is made for the validity of the results. Fortunately, such sensitivity has not been observed for most of the properties of the various systems that have been considered so far.[2,3]

Methods and Procedures

The basis orbitals for the metal atoms in the LCAO–MO calculations were Slater orbitals of the nd, $(n + 1)$s, and $(n + 1)$p types having the value of n appropriate to the transition metal. We used Slater 2s and 2p orbitals for C, N, and O atoms, and 1s for H atoms. At present the program is limited to eleven atoms, and hence some outer atoms were omitted when the ligands were polynuclear. Thus, only the π-system of the π-cyclopentadienyl was included when this ligand was present. Similarly, when more than four CO or CN^- groups occur, only the C atom was included in such a way that CO or CN^- was replaced by C^{-4}, thus increasing the negative charge on M and H by an amount which, we hope, only compensates for the tendency of this method to exaggerate charge transfer.

The LCAO–MO calculations yield approximate one-electron energies and wave functions. However, only the wave functions are considered in the present application. From them, a molecular charge distribution is calculated by the use of a population analysis scheme. The particular scheme[4] used here assumes that the occupancy of the ith AO in a molecule is given by

$$N_i = \sum_j n_j C_{ij} \left(\sum_k S_{ik} C_{kj} \right) \qquad (1)$$

where C_{kj} is the coefficient of the kth AO in the jth MO, S_{ik} is the overlap integral of the ith and kth AO's and n_j is the occupation number of the jth MO. Thus the overlap terms have been split equally between atoms of the appropriate atomic pairs. If σ_i is defined as the contribution to the shielding of one electron in the ith AO (Table I), then the total shielding is

$$\sigma = \sum_i N_i \sigma_i \qquad (2)$$

where this sum is limited to the contributions (Table I)

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(1) R. M. Stevens, C. W. Kern, and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 279 (1962); also see C. W. Kern and W. N. Lipscomb, *ibid.*, **37**, 260 (1962).

(2) T. Jordan, H. W. Smith, L. L. Lohr, Jr., and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 846 (1963); also see L. L. Lohr, Jr., and W. N. Lipscomb, *ibid.*, **85**, 240 (1963).

(3) L. L. Lohr, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **38**, 1607 (1963).

(4) R. S. Mulliken, *ibid.*, **23**, 1833 (1955).

TABLE I

ORBITAL CONTRIBUTIONS[a] TO SHIFT

Orbital	Cr	Mo	W	Co[b]	Rh[b]	Ir[b]
$1s_H$	31.22	28.69	26.85	32.85	30.74	28.61
$(n + 1)s$	2.73	3.13	3.45	2.09	2.74	3.40
$(n + 1)p_\sigma$	3.55	4.57	5.24	2.18	3.71	5.16
$(n + 1)p_\pi$	2.32	2.41	2.56	2.05	2.26	2.53
nd_σ	−1.50	−1.75	−1.42	−1.24	−1.67	−1.93
nd_π	0.10	0.32	0.86	−0.01	0.14	0.51
nd_δ	0.86	1.07	1.43	0.71	0.92	1.25

[a] In p.p.m. per electron in the AO method (ref. 1) for exponents given in Table II and M–H distances given in the text. The contributions listed in Table II of ref. 1 are for two electrons per orbital, except those for $1s_H$ and $3d_{\sigma Co}$, which are for one electron each. In addition, the listed $4p_{AV}$ value of 2.209 in the AO column should read 4.418. [b] Exponent of nd = 2.7.

from the atomic orbitals of hydrogen and the heavy metal. In the AO method[1] of calculating chemical shifts, the atomic orbital contributions σ_i for AO's other than the $1s_H$ orbital are merely diagonal matrix elements of the shift, given (in p.p.m.) by

$$\langle i|\sigma_H|i\rangle = 3^{-1}c^{-2}\langle i|r_H^{-1} - Rz_H r_H^{-3}|i\rangle \times 10^6 \qquad (3)$$

where all quantities, including the velocity of light c and the M–H distance R, are in dimensionless atomic units. However, the $1s_H$ contribution is taken to be the contribution from a $1s_H$ orbital which has been orthogonalized with respect to all σ-type metal atom orbitals, namely $3d_\sigma$, 4s, and $4p_\sigma$. All inner-shell orbitals are neglected here. The contribution σ_{1s_H} then contains not only a term in $\langle 1s_H|\sigma|1s_H\rangle$, but also terms of the types $\langle 1s_H|\sigma|4s\rangle$ and $\langle 4s|\sigma|4p_\sigma\rangle$, for example. The sizes of the contributions of the latter types of elements depend upon the degree of overlap of the $1s_H$ orbital and the various σ-type metal orbitals. Thus the σ_{1s_H} contribution for a given number of electrons depends upon the particular molecular system in which the H atom is incorporated (Table I) and is in general much larger than the contribution of 23.075 p.p.m. per electron in a nonorthogonalized $1s_H$ orbital (with an orbital exponent of 1.3). As has been pointed out,[1] the AO method is considerably simpler than the valence bond and MO methods used in considering $HCo(CO)_4$, but yet gives proton shifts not greatly different from them. The various components of σ_{1s_H} in the AO method represent roughly the off-diagonal contributions arising from the use of a valence bond or MO wave function that are otherwise neglected in the simple orbital sum.

Parameters (Table II) for the LCAO–MO program are the Slater exponents and the Coulomb integrals which are taken in general as valence state ionization potentials. Separate calculations on the CO molecule were made in order to find Coulomb integrals which gave essentially zero charge on C and O at the observed[5] C–O distance of 1.128 Å. These values are listed in Table II below the corresponding reported[6] valence state ionization potentials, which were used in several calculations for $HCo(CO)_4$. The Coulomb integrals for the various metal atoms were estimated either from the ionization potentials[7] or from one-electron atomic SCF energies.[8] For d-orbitals, these latter values are significantly lower than the former, but the calculated shifts (Table III) for $HCo(CO)_4$ and $HCo(CN)_5^{-3}$ were relatively insensitive to choice of the 3d Coulomb integral at −9.0, −11.0, or −17.9 e.v.; this last value is the atomic SCF one-electron energy.[8]

Although the standard Slater rules[9] were used to obtain exponents for C and O, the metal atom d-orbital exponents used here are in general larger than the Slater rule values for neutral atoms. The exponents, 2.4 for the Cr series and 2.7 for the Co series, correspond nearly to an average of the exponents for the two 3d-type basis functions having the largest coefficients in neutral atom SCF calculations[8] for $d^{n-2}s^2$ configurations. Indeed, the Cr exponent is identical with that used in recent LCAO–MO calculations[3] for Cr^{+3} complexes. The consequences of using the neutral atom Slater rule Co (3d) exponent of 2.0 for the Co, Rh, and Ir systems are discussed below, while the problem of choosing exponents for the $(n + 1)s$ and $(n + 1)p$ metal orbitals and the 1s hydrogen orbital has been considered previously.[1] Essentially the same choices which were made earlier are also made here.

Results and Discussion

The calculated shifts (Table III) were obtained for the following molecular structures (Fig. 1):

(1) $HCo(CO)_4$, symmetry C_{3v}, tetrahedral C–Co–C angles,[1] Co–H = 1.53 Å. (varied), Co–C = 1.81 Å., C–O = 1.16 Å.

(2) $H_2Fe(CO)_4$, symmetry C_{2v}, H–H[10] = 1.88 Å., Fe–H = 1.5 Å., Fe–C = 1.8 Å., ∠C–Fe–C = 77 and 90°.

(3) $HCo(CN)_5$,$^{-3}$ symmetry C_{4v} (assumed), ∠C–Co–C = 90°, Co–H = 1.53 Å., Co–C = 1.81 Å. (this ion is isoelectronic with $HMn(CO)_5$).

(4) $HRh(CN)_5^{-3}$ and $HIr(CN)_5^{-3}$ as above, but with distances M–H = 1.62 Å. and M–C = 1.90 Å.

(5) $HCr(CO)_3(\pi\text{-}C_5H_5)$, symmetry C_s, tetrahedral OC–Cr–CO angles, Cr–H = 1.53 Å., Cr–C = 1.81 Å. (carbonyl),[11,12] Cr–C = 2.04 Å. (ring), C–C = 1.40 Å. (ring).

(6) $HMo(CO)_3(\pi\text{-}C_5H_5)$ and $HW(CO)_3(\pi\text{-}C_5H_5)$ as above, but with distances[11,12] M–H = 1.64 Å., M–C = 1.95 Å. (carbonyl), M–C = 2.20 Å. (ring).

The calculated shifts (Table III) are comparable with observed shifts only when the H atom has an excess negative charge, corresponding to about 1.1 to 1.4 electrons around the proton. This electronic contribution is, of course, responsible for the greater part of the high-field chemical shift. The number of excess electrons on the metal atom is always less than four, and in certain instances the metal atom is positive. Even so,

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(5) O. R. Gilliam, C. M. Johnson, and W. Gordy, *Phys. Rev.*, **78**, 140 (1950); the observed C–O distance is not at the simple LCAO–MO energy minimum, which is is at 0.8 Å. if 1s orbitals are omitted or at 0.5 Å. if they are included.

(6) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

(7) C. E. Moore, "Atomic Energy Levels," National Bureau of Standards, Circular No. 467, 1949.

(8) R. E. Watson, *Phys. Rev.*, **119**, 1934 (1960).

(9) J. C. Slater, *ibid.*, **36**, 57 (1930).

(10) E. O. Bishop, J. L. Down, P. R. Emtage, R. E. Richards, and G. Wilkinson, *J. Chem. Soc.*, 2484 (1959).

(11) For bond lengths in Cr, Mo, and W hexacarbonyls, see L. O. Brockway, R. V. G. Ewens, and M. Lister, *Trans. Faraday Soc.*, **34**, 1350 (1938).

(12) For related structure of Mo dimer see F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, **27**, 809 (1957).

TABLE II

ATOMIC ORBITAL PARAMETERS

Slater exponents

	H	Fe	Co	Rh	Ir	Cr	Mo	W	C	O
s	1.3	1.6	1.6	1.6	1.6	1.4	1.4	1.4	1.62	2.28
p	...	1.6	1.6	1.6	1.6	1.4	1.4	1.4	1.62	2.28
d	...	2.7	2.7	2.7	2.7	2.4	2.4	2.4	...	...
			2.0	2.0	2.0					

Coulomb Integrals, e.v.

	H	Fe	Co	Rh	Ir	Cr	Mo	W	C	O
		−6.9	−7.2						−21.0	−36.1
s	−13.6	−10.0	−8.0	−9.0	−9.0	−8.0	−8.0	−8.0	−23.0	−33.9
			−10.0							
p	...	−5.5	−6.0	−7.0	−7.0	−7.0	−7.0	−7.0	−11.3	−18.5
		−8.0	−8.0						−13.4	−16.4
d	...	−11.0	−9.0	−12.0	−12.0	−9.0	−9.0	−9.0	...	...
			−11.0							
		−17.3	−17.9							

TABLE III

PROTON CHEMICAL SHIFTS[a] AND CALCULATED CHARGES

Compound	Exptl. shift	Calcd. shift	Q (H)[b]	Q (M)	M–H overlap pop.[b]
$HCo(CO)_4$	45.3[c]	37.5[g,i,k]	+0.01	−1.95	0.427
		31.4[g,i,l]	+0.11	−1.34	0.178
		32.6[h,i,m]	+0.13	+1.85	0.308
		52.5[g,j,k]	−0.22	−1.75	0.634
		50.1[g,j,l]	−0.21	−1.28	0.420
		37.7[h,j,m]	+0.10	+2.31	0.410
		44.5[h,j,n]	−0.13	+3.28	0.284
		47.5[h,j,n,o]	−0.11	+3.25	0.288
$H_2Fe(CO)_4$	46.1[d]	48.3[g,i,k]	−0.35	−1.64	0.620
		53.8[g,j,p]	−0.40	−0.60	0.508
$HCo(CN)_5^{-3}$	47.2[e]	48.7[i,k]	−0.37	−0.31	0.601
		53.2[j,k]	−0.31	−0.24	0.709
		53.0[j,l]	−0.38	+0.42	0.530
$HRh(CN)_5^{-3}$	45.4[e]	46.9[i]	−0.39	+0.22	0.592
		55.9[j]	−0.36	+0.32	0.680
$HIr(CN)_5^{-3}$	49.0[f]	47.8[i]	−0.44	+0.40	0.574
		58.6[j]	−0.40	+0.49	0.650
$HCr(CO)_3(\pi\text{-}C_5H_5)$	40.46[d]	37.2	−0.12	−0.76	0.298
$HMo(CO)_3(\pi\text{-}C_5H_5)$	40.52[d]	41.8	−0.33	+0.14	0.416
$HW(CO)_3(\pi C_5H_5)$	42.52[d]	44.1	−0.38	+0.92	0.462

[a] In p.p.m. relative to bare proton. [b] For definition, see ref. 2. [c] R. A. Friedel, I. Wender, S. L. Shufler, and H. W. Sternberg, *J. Am. Chem. Soc.*, **77,** 3951 (1955). [d] A. Davison, private communication; also see ref. 15. [e] J. S. Griffith and G. Wilkinson, *J. Chem. Soc.*, 2757 (1959). [f] M. L. H. Green, *Angew. Chem.*, **72,** 719 (1960). [g] Oxygen atoms omitted. [h] Oxygen atoms included. [i] Exponent of *n*d = 2.7. [j] Exponent of *n*d = 2.0. [k] Coulomb integrals are Co (4s) = −10.0, Co (4p) = −8.0, Co (3d) = −11.0, C (2s) = −23.0, C (2p) = −13.4 e.v. [l] Coulomb integrals are Co (4s) = −7.2, Co (4p) = −6.0, Co (3d) = −17.9, C (2s) = −23.0, C (2p) = −13.4 e.v. [m] Coulomb integrals as in *k*, with O (2s) = −33.9, O (2p) = −16.4 e.v. [n] Coulomb integrals are Co (4s) = −8.0, Co (4p) = −6.0, Co (3d) = −9.0, C (2s) = −21.0, C (2p) = −11.3, O (2s) = −36.1, O (2p) = −18.5 e.v. [o] Co–H = 2.6 a.u. [p] Coulomb integrals are Fe (4s) = −6.9, Fe (4p) = −5.5, Fe (3d) = −17.3, C (2s) = −23.0, C (2p) = −13.4 e.v.

the second largest contribution to the chemical shift comes from the electrons in the 4s and 4p orbitals of the metal, but in the present calculation this contribution is about 10% of the total shift, rather than the 20–30% estimated previously! Thus we feel that in the previous study[1] the H atom was assumed to be too nearly neutral and the Co atom taken as too negative (−4), perhaps more negative than necessary to compensate for the omission of electrons in the orbitals of the C atom, which is presumably only about 2 Å. away from H in $HCo(CO)_4$.

Explicit inclusion of the O atoms of the CO groups, or the N of CN^-, produces proton chemical shifts which are quite low, but also the excess charge on O is −1 in units of electronic charge. This pile-up of negative charge on O seems excessive, and hence CO has been replaced in these calculations by C^{-4}, which compensates, we hope, for the omission of direct contributions of the ligand electrons to the proton chemical shift. Certainly, our results suggest that the H atom is more hydridic in nature than we had assumed in the previous study.

The Co, Rh, Ir and Cr, Mo, W series of complexes are especially interesting. The last member of the group has the highest shift. The structural assumptions made here seem reasonable, and it is expected that the

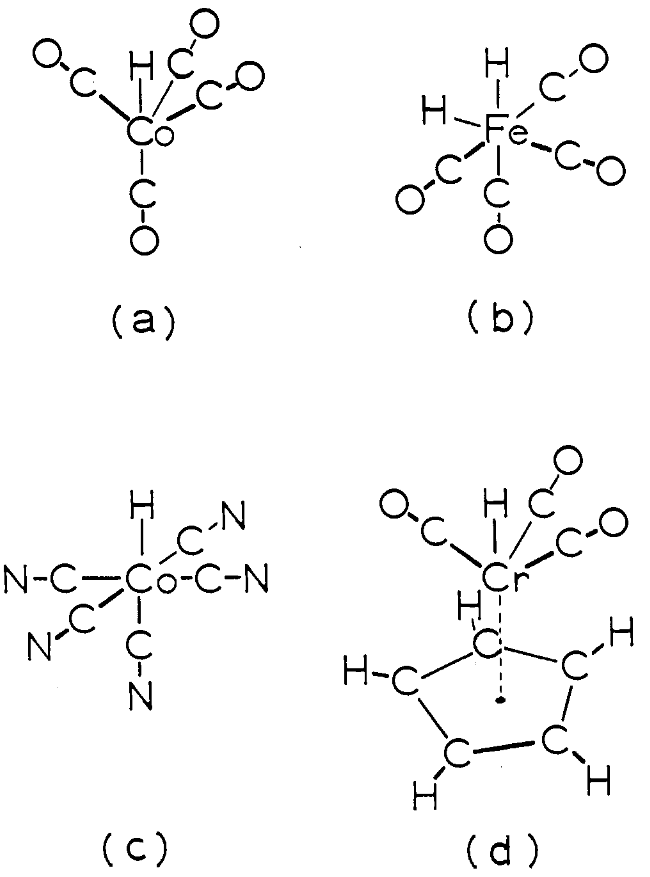

Fig. 1.—Assumed structures for (a) cobalt tetracarbonyl hydride, (b) iron tetracarbonyl dihydride, (c) pentacyanohydridocobaltate(III), and (d) chromium π-cyclopentadienyltricarbonyl hydride.

shifts are not greatly sensitive to minor changes in ligand positions. Slater exponents for the second- and third-row elements are taken to be the same as those used for the corresponding first-row elements, the basis orbitals then differing only in their principal quantum numbers. In addition, the M–H distance for the third-row complex was taken to equal that of the second-row complex, a reasonable assumption in the light of the well-known lanthanide contraction. The relatively large shifts for complexes of the last member of the group then arise from the increased negative charge on H, despite the increased positive charge on M. Table I shows that an electron on H has an order-of-magnitude greater contribution to the chemical shift of H than an electron in any M orbital.

The effect of decreasing the *n*d exponent for Co, Rh, and Ir from 2.7 to the Slater rule[9] value of 2.0 is quite striking (Table III). The greater increased shifts result not so much from changes in the calculated charge distributions as from changes in the atomic orbital contributions[1] to the shift. For example, the $1s_H$ contributions for Co, Rh, and Ir are increased by 5.0, 3,5, and 2.1 p.p.m., respectively, over the values in Table I. In addition, the *n*d contributions, not significant for an exponent of 2.7, are approximately 5 to 10 p.p.m., the latter value being that for Ir, where the 5d contribution is positive for an exponent of 2.0, but negative for a value of 2.7. However, the shifts computed using 2.7 not only agree better with experiment, but are based on an orbital exponent more nearly like that in the neutral atom SCF wave functions.[8]

TABLE IV

CALCULATED SHIFT FOR CoH[a]

R, a.u.	Q_H	Overlap pop.	No. electrons in 4s	4pσ	3dσ	Shift
2.27	−0.23	0.812	0.412	0.206	0.154	50.9
2.65	−0.26	.768	.400	.229	.116	47.8
3.02	−0.29	.708	.384	.242	.082	45.4
3.40	−0.34	.630	.360	.242	.056	42.3

[a] The d_π, d_δ orbitals assumed filled and the p_π assumed vacant, with exponent of 3d = 2.7.

Calculations were also made (Table IV) in a four-orbital, one-electron pair approximation for the diatomic molecule CoH, with an observed[13] internuclear distance of 3.0 a.u. As a result of the neglect of nuclear repulsions in the LCAO–MO method, no minimum in the total orbital energy[14] is found for a diatomic molecule with only one occupied MO, such as CoH in the present approximation of nonbonding inner orbitals and π- or δ-type outer orbitals. Thus the LCAO–MO method cannot be used here to give an equilibrium internuclear distance. The calculated shift at the observed distance is 45.4 p.p.m.; however, the shift decreases greatly with distance as a result of changes in the matrix elements (eq. 1) despite an increasing negative charge on H as the distance increases. This result is identical with that found (Table III) for $HCo(CO)_4$ at distances of 2.6 and 2.9 a.u. For the diatomic CoH, the H (1s) and Co (4p) orbitals gain electrons as the distance increases, while the Co (4s) and Co (3d) lose electrons over the distance range considered. The Co Coulomb integrals (4s = −10.0, 4p = −8.0, 3d = −11.0 e.v.) are above H (1s), hence the molecule becomes Co^{+1}, H^{-1} at infinite separation.[15] This diatomic system corresponds to the system HML_n, with $n = 0$; the presence of ligands (other than the hydrogen) may reduce the shift by the withdrawal of electrons from the hydrogen atom. At best, the electrons go into ligand orbitals that appreciably overlap the H (1s) orbital, which receives just one-half of all overlap populations involving it. For example, typical $HCo(CO)_4$ results, including O atoms, give a M–H overlap population of 0.284, while the total C–H population for the three nearest C atoms is 0.330, giving contributions to the H charge of 0.142 and 0.165, respectively. In cases where the ligands lose electrons upon compound formation, as in $HCo(CO)_4$ calculations not including O atoms, the shift will increase because not only the metal atom but also the H atom may gain electrons. The *trans* ligands are then the more positive as their overlap with H is negligible. However, in $HCo(CO)_4$ calculations in-

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[13] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 257.

[14] For a discussion of the use of the total orbital energy as an energy to be minimized with respect to molecular geometry, see L. L. Lohr, Jr., and W. N. Lipscomb, *Inorg. Chem.*, **2**, 911 (1963).

[15] This result is incorrect, of course, as the first ionization potential of Co is greater than the electron affinity of H. Neither the simple LCAO–MO method nor the atomic orbital parameters used here are adequate at large internuclear distances.

cluding O atoms, the withdrawal of electrons from H and Co orbitals by the ligands led to reduced shifts and a more negative charge for the *trans* ligand. In the series $HM(CO)_3(\pi\text{-}C_5H_5)$, the charges on the $\pi\text{-}C_5H_5$ ring are −0.90, −1.41, and −2.41 e for Cr, Mo, and W, respectively, suggesting successively greater ring-proton shifts to high field in accord with observed[16] absolute chemical shifts for the ring protons of 29.78, 30.30, and 30.35 p.p.m. for Cr, Mo, and W, respectively.

Finally, the matrix elements for the shifts in CoH (Table IV) and in $HCo(CO)_4$ with Co–H = 2.6 a.u. were evaluated at the appropriate distances. The distance dependence of the $HCo(CO)_4$ shift in the previously reported[1] AO method, with fixed atomic charges, is nearly linear, with

$$\frac{d\sigma}{dr} \cong -3.6 \text{ p.p.m./0.1 Å.} \qquad (4)$$

As the atomic charges are not independent of the M–H distance in the present model, the distance dependence of the individual AO shift contributions was considered and found to depend on the AO being considered, although all slopes had the sign of eq. 4 except that of the $3d_\sigma$ contribution. Thus the $3d_\sigma$ contribution is negative (Table I), with a positive slope, while the remaining AO contributions are positive (the $3d_\pi$ contribution is very slightly negative at distances greater than 2.8 a.u.), with negative slopes.

In summary, the trends in the calculated proton shifts and the observed proton shifts shown in Table III for $HCo(CO)_4$, $H_2Fe(CO)_4$, $HCo(CN)_5^{-3}$, $HRh(CN)_5^{-3}$, $HIr(CN)_5^{-3}$, $HCr(CO)_3(\pi\text{-}C_5H_5)$, $HMo(CO)_3(\pi\text{-}C_5H_5)$, and $HW(CO)_3(\pi\text{-}C_5H_5)$ compare well and do not conflict with the theory that these H–M distances are normal covalent distances.[17] The agreement, certainly within the limits of the approximations of both the theories of charge distribution and chemical shift, lends further support to the general nature of the explanation of the completely consistent high-field shift of the proton resonance in the H–M (transition metal) bond. Finally, we can only urge that these distances be studied by neutron diffraction techniques,[18] because the only distances known so far are in the diatomic hydrides, for which normal covalent radii are applicable,[13] except for MnH which has an anomalously *long* distance in the $^7\Sigma$ ground state.

Acknowledgments.—We wish to thank Mr. Richard M. Stevens for the use of his molecular integral programs and for valuable discussions, and the National Science Foundation and the Office of Naval Research for support of this research.

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(16) A. Davison, J. A. McCleverty, and G. Wilkinson, *J. Chem. Soc.*, 1133 (1963).

(17) For a simple treatment suggesting a Co–H distance of 1.2 Å. in $HCo(CO)_4$, see F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 4425 (1958).

(18) On the basis of a recent neutron diffraction study of a single crystal of K_2ReH_9 (K. Knox and S. C. Abrahams, Abstracts of the Am. Cryst. Assoc. Annual Meeting, 1963), the ReH_9^{-2} ion has a staggered D_{3h} structure (a face-centered trigonal prism). This structure has a lower total orbital energy than any of the several other possible structures of this ion for which we carried out LCAO–MO calculations, all structures having a single Re–H distance of 1.64 Å. In addition, a single proton resonance shift of 42.5 p.p.m. for the ReH_9^{-2} ion in solution was reported. Calculated atomic charges are −0.27 for each of the six apical hydrogens and −0.36 for each of the three equatorial hydrogens and, if averaged, would lead us to expect a shift roughly equal to the observed value.