and A. H. Cowley, *ibid.*, **97**, 5302 (1975); S. Distefano, H. Goldwhite, and E. Mazzola, *Org. Magn. Reson.*, **6**, 1 (1974).
(25) E. L. Muetterties, P. Meakin, and R. Hoffmann, *J. Am. Chem. Soc.*, **94**, 5674 (1972).
(26) R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Am. Chem. Soc.*, **94**, 3047 (1972); A. Rauk, L. C. Allen, and K. Mislow, *ibid.*, **94**, 3035 (1972); A. Stritch and A. Veillard, *ibid.*, **95**, 5574 (1973).
(27) A. C. Chapman, J. Horner, D. J. Mowthorpe, and K. T. Jones, *Chem. Commun.*, 121 (1969). The chemical shift of 85% H_3PO_4 is +112 ppm vs. P_4O_6.

Contribution No. 2592 from the Central Research and Development Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Application of Molecular Orbital Theory to Transition-Metal Complexes. 1. Fully Optimized Geometries of First-Row Metal Carbonyl Compounds

DAVID A. PENSAK* and RONALD J. McKINNEY

Received December 21, 1978

Extended Hückel theory, modified with the inclusion of two-body repulsion, has been used to reproduce and predict optimum geometries, *including bond lengths*, of some first-row transition metal carbonyl compounds.

Introduction

The application of molecular orbital (MO) techniques to transition-metal complexes is an increasingly active field.[1] In general, studies have focused on bonding in organometallic complexes and how such bonding is influenced by changes in the coordination sphere. A few papers have contained an examination of bonding changes during chemical reactions.[2]

We are interested in using MO calculations as a practical guide for laboratory studies. It is our goal to develop the capability for theoretical studies of, for example, relative rates of reaction or the comparison of first- and second-order substitution pathways. Ultimately this might facilitate the design of reagents for specific chemical transformations. Though it is widely held that only the more sophisticated nonempirical MO techniques can give reasonable results, recent work has demonstrated that semiempirical techniques can make significant contributions in this area.[3] This is important in terms of cost, computer time, and simplicity if such calculations are to become a routine tool of the experimentalist.

Throughout this work a semiempirical MO theory as derived by Anderson is used.[4] It is similar to extended Hückel theory (EHT)[5] but contains a correction for two-body repulsion. While the modified extended Hückel theory (MEHT) retains the ability of EHT to reproduce bond angles, it markedly improves bond length determinations. MEHT has been applied to the interaction of small molecules with metal clusters and surfaces as well as with a few organometallic derivatives.[6]

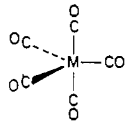
In this and future papers, we will use the MEHT approach to determine the relative energies of complexes in ground, intermediate, and transition states[7] and will be less concerned with a detailed MO analysis of the causes of geometry and bonding. We will demonstrate that for certain classes of complexes, reliable results can be obtained. In the present paper we will examine the ability of MEHT to predict correct bond distances and angles of some simple metal carbonyl derivatives and fragments and compare the results with previous EHT studies by Elian and Hoffmann[8] and by Burdett.[9] In the companion paper,[10] we will compare calculated energies against known thermodynamic values for some dissociative processes.

Results

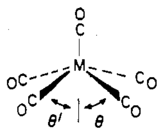
A. $M(CO)_6$. Octahedral symmetry requires that only bond lengths be optimized. The optimized metal–carbon distances for one d^5 [M = V(0)] and three d^6 [M = V(–I), Cr(0), Mn(I)] metal complexes are 1.87, 1.86, 1.86, and 1.87 Å, respectively, with corresponding optimized carbon–oxygen distances of 1.10, 1.11, 1.12, and 1.12 Å. For vandium(0) and chromium(0), both the metal–carbon and carbon–oxygen distances are shorter than those of the experimental values [V–C = 2.015 (2) Å, C–O = 1.138 (2) Å;[11] Cr–C = 1.91 (4) Å, C–O = 1.14 (4) Å[12]]. This is somewhat exceptional—more often the optimized bond lengths are longer than experimentally observed distances (vide infra).

In the d^5 vanadium(0) case, the octahedral geometry should be unstable due to first-order Jahn–Teller effects. In accordance with the distortion expected on the basis of ligand field theory, i.e., a shortening of a trans pair of metal–carbon bonds relative to the other bonds,[13] the geometry of vanadium hexacarbonyl was also optimized under D_{4h} symmetry. The axial vanadium–carbon distances shortened from 1.87 to 1.85 Å while the equatorial vanadium–carbon distances lengthened to 1.88 Å. However, the D_{4h} geometry was calculated to be only about 0.5 kcal/mol more stable than the O_h geometry. While we have not attempted to calculate a complete Jahn–Teller surface, the small energy difference between O_h and D_{4h} geometries is not inconsistent with the observation that the predicted Jahn–Teller effect is small enough to give rise, experimentally, to a dynamic effect.[9] The ability to explore Jahn–Teller distortions is a potential strength of geometry-optimized MEHT calculations.

B. $M(CO)_5$. Geometries in $M(CO)_5$ complexes were optimized under both D_{3h} (trigonal bipyramidal), **1**, and C_{4v} (square pyramidal), **2**, symmetry restrictions. In several studies using semiempirical[8,9] and ab initio[14,15] techniques, the molecular orbitals generated under these two symmetries have been detailed. In general, our results are in agreement with previous findings and, with a few exceptions, the known structural data.[16-20] The optimized bond distances and angles are presented in Table I. Demuynck, Strich, and Veillard,[14] using large basis set ab initio techniques, have also optimized metal–carbon bond lengths and angles for several of the same complexes and their results are included in Table I in brackets.



1, D_{3h}



2, C_{4v} $\theta = \theta'$
3, C_{2v} $\theta \neq \theta'$

0020-1669/79/1318-3407$01.00/0

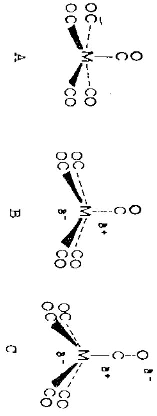
Table I. Optimized Geometries of $M(CO)_5$[i]

	d^5	d^6			d^7		d^8			
	M = V	V^-	Cr	Mn^+	Cr^-	Mn	Cr^{2-}	Mn^-	Fe	Co^+
					D_{3h}					
M–C(ax), Å	1.84 [1.99]	1.85	1.85	1.87	1.87	1.86 [1.95]	1.85	1.85 (1.82)[c] [1.86]	1.86 (1.81)[b] [1.98]	1.88 [1.80]
M–C(eq), Å	1.87 [2.10]	1.85	1.86	1.87	1.84	1.85 [1.85]	1.82	1.83 (1.80) [1.79]	1.84 (1.83) [1.85]	1.84 [1.82]
C–O(ax), Å	1.12	1.12	1.13	1.13	1.12	1.13	1.13	1.14 (1.15)	1.13 (1.15)	1.12
C–O(eq), Å	1.10	1.12	1.13	1.13	1.17	1.15	1.18	1.17	1.16	1.14
energy, eV	−955.06	−964.93	−959.30	−958.13	−969.00	−967.83	−978.93	−977.67	−978.10	−979.37
					C_{4v}					
θ, deg	87 [88]	87	87 [88]	87	79	81 [81]	72	74 [75]	75 [75]	76 [75]
M–C(ax), Å	1.85 [1.93]	1.82	1.83	1.84	1.80	1.82 [1.83]	1.78	1.81 [1.77]	1.83 [1.88]	1.85 [1.85]
M–C(eq), Å	1.87 [2.03]	1.86	1.87	1.88	1.85	1.86 [1.92]	1.84	1.85 [1.83]	1.85 [1.90]	1.86 [1.81]
C–O(ax), Å	1.11	1.14	1.14	1.14	1.20[a]	1.16	1.20[a]	1.20[a]	1.16	1.13
C–O(eq), Å	1.11	1.11	1.14	1.12	1.13	1.14	1.14	1.14	1.14	1.13
energy, eV	−955.55	−966.28	−960.21	−958.98	−969.33	−968.09	−978.86	−977.61	−978.03	−979.31
optimum geom	C_{4v}[g]	C_{4v}	C_{4v}[f]	C_{4v}	C_{4v}[e]	C_{4v}[d]	D_{3h}	D_{3h}[c]	D_{3h}[b]	D_{3h}
ΔE,[h] kcal/mol	11.3 [6.3]	31.0	20.9 [>10]	19.6	7.6	6.0 [10]	1.6	1.4 [0.6]	1.6 [0.6]	1.4 [3.8]

[a] Maximum allowed value, see text for discussion. [b] Reference 16. [c] Reference 17. [d] Reference 18. [e] Reference 19. [f] Reference 20. θ Estimated between 86 and 90°; also $[Co(CN)_5{}^{2-}]$ is C_{4v}, θ = 82°, L. D. Brown and K. N. Raymond, *J. Chem. Soc., Chem. Commun.*, 910 (1974). [g] See Table IV of ref 18 or Table I of ref 23. [h] Energy difference between C_{4v} and D_{3h} geometries. [i] Values in brackets are optimization results from ref 14.

In C_{4v} symmetry, the two techniques give very similar values of θ. MEHT, in most cases, reproduces the relationship between axial and equatorial metal–carbon distances found in the ab initio study, but MEHT gives smaller, more realistic differences. The calculated energy differences between the two geometries for each case are found to be of similar magnitude with the two computational techniques. Experimental bond length data are available for trigonal-bipyramidal complexes $[Mn(CO)_5]^-$ and $Fe(CO)_5$. In both cases the calculated metal–carbon distances are longer than those for the observed values (in contrast to the $M(CO)_6$ cases described above). The carbon–oxygen distances are in good agreement with the average observed values. For $[Mn(CO)_5]^-$, the relationship between the axial and the equatorial bond lengths (ax > eq) is correctly reproduced by both MEHT and the ab initio study; for Fe the same relationship is calculated but the opposite is observed. Frenz and Ibers[17] have rationalized the observed values as a balance between ligand–ligand repulsion (which lengthens the metal to axial ligand bond) and d electron–ligand repulsion (which lengthens the metal to equatorial ligand bond). Note that in the calculated series of neutral D_{3h} complexes (see Table I) the equatorial M–C bond lengths decrease in going from V to Fe (in parallel with the decrease in the atomic radius of the metals), while the axial M–C bond length increases. The calculated nuclear repulsion energy between equatorial carbons remains zero throughout the series, while nuclear repulsion between axial and equatorial carbons increases slightly (despite a lengthening of the axial M–C bonds to relieve the pressure). This is consistent with the first part of Frenz and Ibers' argument; each axial nucleus is repulsed by three equatorial nuclei whereas each equatorial nucleus is repelled primarily by the two axial nuclei; therefore the axial nuclei are squeezed out as the metal radius shrinks. That MEHT appears to incorrectly deal with d electron–ligand repulsion might be attributed to improper parameterization for an approximation of electron correlation in this case were it not that the ab initio study comes to the same conclusion (see Table I). The reasons for this discrepancy remain unclear.

A limitation of MEHT (and EHT) is an overestimation of intramolecular charge transfer. For example, in the negatively charged species Cr^-, Cr^{2-}, and Mn^-, if as the angle θ decreases the atomic charges remained the same, a change in molecular dipole would be expected as shown schematically in the diagram (A → B). Optimizations with MEHT compensate for



this by increasing the length of the axial carbon–oxygen bond and transferring more negative charge to the oxygen (B → C). In one case the bond lengthens to 1.41 Å, almost a carbon–oxygen single bond. In these, and succeeding cases where noted, specific carbon–oxygen bond lengths were restricted to 1.20 Å. This allowed realistic values for the other variables to be obtained through optimization. For example, with $[Mn(CO)_5]^-$, permitting optimization of the axial carbon–oxygen bond resulted in the C_{4v} geometry being the most stable geometry. Restricting the bond length to 1.20 Å makes the D_{3h} geometry more stable, similar to that found for the iron and cobalt(I) cases (in agreement with the observed structure). It should be remembered that we have ignored the role of a counterion but these results point out that one must be very careful when applying MEHT to polar systems.

In the d^8 cases, the D_{3h} structure is calculated to be only about 1.5 kcal/mol more stable than the C_{4v} geometry. Elian and Hoffmann also found a small energy difference and noted

Table II. Optimized Geometries of $M(CO)_4$

	d^7	d^8				d^9		d^{10}		
	M = Mn	Mn^-	Fe	Co^+	Fe[a]	Fe^-	Co	Fe^{2-}	Co^-	Ni
C_{2v} (D_{2d})[f]										
θ, deg	90	120	126 (120)[b]	135	102	124	130			
M–C(θ), Å	1.84	1.79	1.80	1.85	1.83	1.82	1.84			
C–O(θ), Å	1.17	1.20[e]	1.20[e]	1.15	1.16	1.18	1.16			
φ	150	154.4	154 (145)	160.5	138					
M–C(φ)	1.85	1.88	1.89	1.87	1.84					
C–C(φ)	1.15	1.10	1.10	1.12	1.18					
energy, eV	−787.50	−797.12	−797.81	−799.36	−797.43	−807.13	−808.66			
C_{2v}										
θ deg	83.5	84	84	84		74	76 (80)[c]			
M–C(ax), Å	1.81	1.81	1.84	1.85		1.80	1.83			
M–C(eq), Å	1.85	1.83	1.84	1.84		1.83	1.84			
C–O(ax), Å	1.20	1.20	1.15	1.13		1.20[e]	1.16			
C–O(eq), Å	1.15	1.18	1.17	1.15		1.18	1.16			
energy, eV	−787.32	−797.13	−797.80	−799.25		−807.16	−808.65			
D_{4h}										
M–C, Å	1.84	1.83	1.83	1.88		1.83	1.86	1.84	1.85	1.87
C–O, Å	1.15	1.19	1.18	1.11		1.17	1.13	1.18	1.16	1.15
energy, eV	−787.23	−796.54	−797.02	−799.18		−805.93	−804.04	−814.84	−817.14	−817.51
T_d										
M–C, Å	1.84	1.83	1.84	1.85		1.82		1.81	1.82	1.86 (1.84)[d]
C–O, Å	1.16	1.18	1.16	1.14		1.19		1.21	1.18	1.15 (1.15)
energy, eV	−786.87	−796.55	−797.22	−798.66		−807.05	−808.51	−817.01	−818.47	−818.42
optimum geom[g]	C_{2v}	C_{3v} (C_{2v})	C_{2v} (C_{3v})	C_{2v}		C_{3v} (D_{2d}) (T_d)	D_{2d} (C_{3v}) (T_d)	T_d	T_d	T_d

[a] High spin. [b] Reference 27. [c] Reference 25. [d] Reference 24. [e] Maximum allowed value, see text for discussion. [f] $D_{2d} = C_{2v}$ ($\theta = \phi$); $T_d = C_{2v}$ ($\theta = \phi = 109.5°$); $T_d = C_{3v}$ ($\theta = 70.5°$). [g] Symmetries in parentheses are of very similar energy.

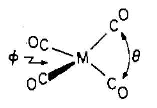
that it is consistent with the fluxional behavior observed for $Fe(CO)_5$.[21]

In the d^7 case, the C_{4v} structure is about 6 kcal/mol more stable than the D_{3h}, the latter being subject to Jahn–Teller distortions.

For d^6 metals, D_{3h} structures are Jahn–Teller stable but would be paramagnetic having two unpaired electrons in a doubly degenerate MO. The calculations clearly suggest a preference (about 20 kcal/mol) for the C_{4v} structure. The D_{3h} complex has apparently been made with Cr by matrix isolation techniques[20] but irreversibly isomerizes to the C_{4v} structure, even at very low temperatures.

In the d^5 case, both the D_{3h} and C_{4v} structures are Jahn–Teller unstable. Burdett has predicted that the D_{3h} is the most stable geometry and cited a matrix isolation study[22] as corroboration. Elian and Hoffmann predicted a C_{4v} structure by using different matrix isolation results for corroboration.[18,23] Our results agree with the latter, C_{4v} being 11 kcal/mol more stable than D_{3h}. Burdett has claimed that the dynamic Jahn–Teller effect suggested for $V(CO)_6$ may also be applied to $V(CO)_5$. A slight bond length distortion of two of the equatorial carbonyls could remove this Jahn–Teller instability. An examination of the reduced overlap population matrix reveals that the equatorial bonds are not equivalent and should be optimized as opposing independent pairs of CO's. Accordingly, when this molecule was optimized with C_{2v} restrictions (**3**), one opposing pair of V–C distances shrank from 1.87 Å to 1.85 Å while the other lengthened to 1.88 Å. The angles θ and θ′ were found to be 87.8 and 85.5°, respectively. This C_{2v} geometry is about 0.7 kcal/mol more stable than C_{4v}. Again, calculation of a complete Jahn–Teller surface was not attempted.

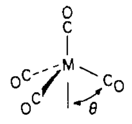
C. $M(CO)_4$. Geometries of tetracarbonyl complexes were optimized under several symmetry restrictions. Under the C_{2v} (**4**) restriction the angles θ and φ were optimized initially while holding bond lengths constant. In those cases where θ and φ equalized (d^9 and d^{10}), further optimizations were carried out with a higher symmetry restriction (D_{2d}, θ = φ, **5**, and T_d, θ = φ = 109.5°, **7**). All complexes were also optimized with C_{3v} (**6**), T_d (**7**), and D_{4h} (square planar) (**8**) symmetry restrictions even though the latter two are special cases of C_{2v} and C_{3v} symmetry.



4, C_{2v}

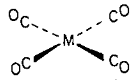
5, D_{2d} (θ = φ)

7, T_d (θ = φ = 109.5°)



6, C_{3v}

7, T_d (θ = 70.5°)



8, D_{4h}

In the d^{10} cases, the angles θ and φ optimized between 109 and 110°. Further optimization carried out with T_d constraints produced the bond lengths shown in Table II, which for $Ni(CO)_4$ agree well with the X-ray structural results.[24] The other two cases are also known from spectral measurements to be of T_d symmetry. The shortening of the metal–carbon bond and the lengthening of the carbon–oxygen bond as the negative charge increases is explained by increasing retrodative bonding. T_d is favored over D_{4h} symmetry by at least 20 kcal/mol (Table II).

In the d^9 cases Elian and Hoffmann and Burdett found the D_{2d} symmetry to be optimum. We find that D_{2d} (**5**) and C_{3v} (**6**) are energetically equivalent (Table II). This is consistent with reports that matrix isolation studies performed under several different conditions have found both D_{2d}[25] and C_{3v} (θ = 80°)[26] species. In addition, T_d is only about 3.5 kcal/mol less favorable, suggesting the possibility of an easily accessible

Table III. Metal–Metal Bonded Species

	$Mn_2(CO)_{10}$, **12**	$Co_2(CO)_8$, **13**	$Fe_2H_2(CO)_8$, **14**[b]	$Fe_3(CO)_{12}$, **15**
M–M, Å	3.02 [2.94][a]	2.86	3.00	2.81
θ, deg	80 [86]	76	87	87
ϕ, deg			123	113
Mn–C(θ), Å	1.86 [1.85]	1.84	1.86	1.85
M–C(ϕ or ax), Å	1.80 [1.80]	1.82	1.82	1.85
C–O(θ), Å	1.13 [1.15]	1.16	1.13	1.15
C–O(ϕ or ax), Å	1.19	1.17	1.18	1.15

[a] Average of values quoted in ref 32. [b] Fe–H = 1.73 Å; H–Fe–H = 59.4°.

transition state for a dynamic equilibrium between the two.

In the d^8 systems the T_d structure should be unstable with respect to first-order Jahn–Teller effects but the C_{2v}, C_{3v}, and D_{4h} structures are Jahn–Teller stable. We found that while a C_{2v} structure is favored for $[Co(CO)_4]^+$, the C_{3v} and C_{2v} structures are energetically equivalent for the Mn^- and Fe cases. In contrast, Elian and Hoffmann claimed that D_{2d} should be optimum, while Burdett claimed D_{4h}. Matrix isolation studies have established that $[Fe(CO)_4]$ is C_{2v}.[27] While different matrices seem to cause variation in the angles, they have been estimated as $\theta = 145°$ and $\phi = 120°$. A very recent report[28] has determined by magnetic circular dichroism that this fragment is paramagnetic. Consistent with this, Burdett found an optimum C_{2v} geometry ($\theta = 135°$, $\phi = 110°$) for the high-spin case (2 unpaired electrons). With similar high-spin C_{2v} restrictions, we obtained comparable angles ($\theta = 138°$, $\phi = 102°$). It should be noted that in the low-spin case, we again had to restrict two of the CO bond lengths to 1.20 Å. However, the restriction was not necessary in the high-spin case.

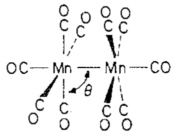
Since the C_{2v} and C_{3v} symmetries are of similar energy in the low-spin case, it is interesting that recent studies of infrared excitation of matrix-isolated $Fe(CO)_4$ suggest an intramolecular isomerization with a C_{3v} species in the transition state.[29]

It is disturbing that Elian and Hoffmann found low-spin $Fe(CO)_4$ to prefer D_{2d}, Burdett D_{4h}, and this work C_{2v}. To test if the bond lengths used could account for the differences, we carried out optimizations fixing the bonds at the values they cited. With Elian and Hoffmann's bond lengths, a C_{2v} ($\theta = 154°$, $\phi = 123°$) geometry was found to be optimum, as it was with Burdett's values ($\theta = 156°$, $\phi = 128°$). The differences therefore lie either in the calculation procedures themselves or in the atomic parameters used. Further investigation is planned.

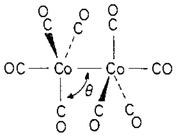
In the d^7 case, both we and Elian and Hoffmann found C_{2v} to be the most stable geometry whereas Burdett predicted D_{4h} for the low-spin cases. Elian and Hoffmann predict angles of $\theta = 150°$, $\phi = 90°$. No structural data are available for comparison.

D. $M(CO)_3$. While a thorough investigation of the metal tricarbonyl fragments was not carried out, optimization reproduced two known tricarbonyl geometries, i.e., $Ni(CO)_3$,[30] D_{3h}, and $Fe(CO)_3$, C_{3v} ($\theta = 72° + 3°$).[31] The latter is calculated to have two unpaired electrons populating doubly degenerate MO's.

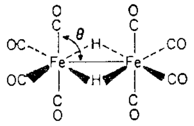
E. Metal–Metal Bonded Species. A few representative members of this class were examined, $[Mn_2(CO)_{10}]$ (**9**), $[Co_2(CO)_8]$ (**10**), $[Fe_2H_2(CO)_8]$ (**11**), and $[Fe_3(CO)_{12}]$ (**12**). In each case only non-carbonyl-bridged isomers were calculated. The results are given in Table III. The experimental values for $Mn_2(CO)_{10}$[32] are in brackets. For **9** and **10**, the D_{4h} and D_{3h} (eclipsed) geometries were found to be higher in energy. Interestingly, the calculated geometrical parameters for **9** and **10** do not vary appreciably from those calculated for the isolated halves, $Mn(CO)_5$ and $Co(CO)_4$ (see Tables I and II). In **9**, the angle $\theta = 80°$ is very similar to that found for the C_{4v} geometry of $Mn(CO)_5$ ($\theta = 80.7°$) while the experimentally determined angle for **9** is 86°. The failure to reproduce this value may stem from an inability of MEHT to draw electron population away from the metal centers into the bonding area between them. The reduced overlap population matrix gives support to the notion by showing very little electron population in the overlap region between metals. The apparent charge-transfer problem and its relationship to θ are further illustrated and discussed in the following section. For both **11** and **12** the relative geometry of the $[Fe(CO)_4]$ units is similar to that calculated for the low-spin monomer (Table II).



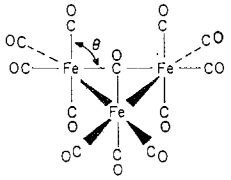
9, D_{4d}



10, D_{3d}



11, D_{2h}



12, D_{3h}

The metal–metal bonds, the major points of interest, are found to be uniformly lengthened beyond that which is expected. The calculated Mn–Mn bond (3.02 Å) is 0.1 Å longer than that of the experimental value.[32] The calculated Co–Co length at 2.68 Å is more than 0.3 Å longer than that found for the carbonyl-bridged isomers,[33a] but 0.2 Å longer than in the more applicable $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ (D_{3d}),[33b] and is less than 0.1 Å longer than found for the isoelectronic $[Fe_2(CO)_8]^{2-}$ (D_{3d}).[34] The metal–metal distances calculated for the iron cases **11** (3.00 Å) and **12** (2.81 Å) also appear to be long when compared with $Fe_2(CO)_9$ (Fe–Fe = 2.56 and 2.67 Å)[36] as well as $[Fe_2(CO)_8]^{2-}$ (Fe–Fe = 2.79 Å).[34] According to our calculations, the metal–metal bonds have very shallow potential wells. Therefore small errors in the repulsive energy may be magnified when compared with the same error in carbon monoxide which has a very deep potential well. The lengthening of bonds between homoatoms appears to be general so that carbon–carbon bonds are always calculated to be from 0.1 to 0.2 Å too long. Similar problems occur with N–N and O–O bonds. For that reason, we do not optimize the latter distances, using instead known experimental values.

The errors in optimizing homoatomic bond lengths, in particular in the metal–metal bonds, can be traced in part to the portion of the two-body repulsion calculation which requires assignment of electron occupancy of the atomic orbitals. Only the occupancy of the most electronegative atom is used in the calculation (hence the need for Pauling electronegativities in the parameter input), except where both atoms are the same. When ligands completely surround the metal, the occupancy of the donor atoms is important because they are more electronegative than the metal (the occupancy of the metal does not matter). However, when metal–metal interactions are involved, the metal occupancy is important. Anderson has suggested[37] the following occupations: Mn, 2 s, 0 p, 5 d electrons; Co, 1 s, 0 p, 8 d; Fe, 1 s, 0 p, 7 d. We have tried both one and two s electrons for Mn and Co and found that using one s electron for Mn caused drastic shortening of the Mn–Mn bond while use of two s electrons for Co resulted in a Co–Co bond length which was much too long. It appears that fractional electron occupation would be needed to get

Table IV. Hydrido Metal Carbonyls

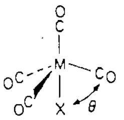
	$HCo(CO)_4$	$HFe(CO)_4^-$	$HMn(CO)_5$
M-H, Å	1.58 [1.56 (2)][a]	1.59 [1.57 (12)][b]	1.60 [1.60 (2)][c] [1.58 (2)][a]
θ, deg	81 [80.3 (6)]	81 [81]	84 [84 (1)] [85.5 (9)]
M-C(ax), Å	1.85 [1.76 (1)]	1.84 [1.72]	1.84 [1.82 (1)] [1.85 (2)]
M-C(eq), Å	1.83 [1.82 (1)]	1.81 [1.75]	1.86 [1.85 (2)] [1.86 (1)]
C-O(ax), Å	1.13 [1.14 (1)]	1.14 [1.18]	1.16 [1.14 (2)] [1.14 (1)]
C-O(eq), Å	1.16 [1.14 (1)]	1.18 [1.15]	1.12

	cis-$H_2Fe(CO)_4$	*trans*-$H_2Fe(CO)_4$		*cis*-$H_2Fe(CO)_4$	*trans*-$H_2Fe(CO)_4$
M-H, Å	1.59 [1.56 (2)][a]	1.59	Fe-C(ax), Å	1.85 [1.83 (1)][a]	
HFeH, deg	81 [100 (10)]		Fe-C(eq), Å	1.84 [1.80 (1)]	1.85
C-Fe-C(ax), deg	151 [148.5 (1.5)]		C-O(ax), Å	1.13 [1.15 (1)]	
C-Fe-C(eq), deg	96.4 [96.0 (6)]		C-O(eq), Å	1.16	1.13

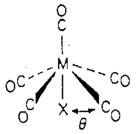
[a] Reference 38. [b] Reference 39. [c] Reference 40.

proper bond lengths. We have not as yet compensated for this in a wholly satisfactory manner.

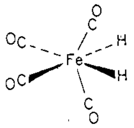
F. Hydrido Metal Carbonyls. MEHT is successful in reproducing correct geometries of some simple hydridometal carbonyl complexes. The optimized geometries are compared with experimental results[38-40] in Table IV. The angles and distances refer to the geometries **13**–**15**. Good agreement with bond angles is obtained except for the angle H–Fe–H of $FeH_2(CO)_4$. However, given the accuracy with which the other angles were reproduced (in contrast to the large standard deviation on the experimental angle H–Fe–H, 10°!), the calculated result is not necessarily wrong. This geometry is calculated to be more stable (9 kcal/mol) than that of the trans isomer. The relatively small difference in energy may be pertinent to the stereochemical nonrigidity observed in $FeH_2(CO)_4$.[41]



13, C_{3v}



14, C_{4v}



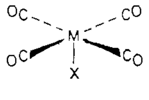
15, C_{2v}

The above calculations were carried out with an abnormal hydrogen 1s orbital energy value (−10.0 eV). The use of the more common energy parameter (−13.6 eV) caused overestimation of charge transfer from metal to hydrogen and for **13** (X = H) and **14** (X = H) resulted in values of θ near 90° and metal–hydrogen distances near 1.7 Å. The amount of charge transfer between atoms is related to the relative energy levels of the interacting orbitals (the basis for Hoffmann's charge iteration process). Raising the energy of the hydrogen 1 s orbital therefore causes a decrease in the charge transfer from metal to hydrogen. The resulting geometrical changes are a shortening of the metal–hydrogen bond and a decrease in the value of θ. For example, when a low value for the hydrogen orbital energy (<-13.6 eV) is used for the optimization of **13**, extreme charge transfer from cobalt to hydrogen occurs, best represented as $[H^- \cdots Co(CO)_4^+]$, with $\theta = 90°$. At the opposite extreme the use of very high values (the hydrogen energy parameter (>-7.0 eV)) in the optimization of **13** results in a species $[H^+ \cdots Co(CO)_4^-]$ with $\theta = 70.5°$ (T_d symmetry if the proton is ignored). These observations suggest a direct relationship between θ and the acidity of the metal hydride. An intermediate value of the hydrogen 1 s orbital energy parameter (−10.0 eV) gives good geometrical results.

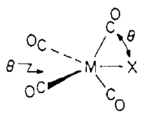
In the previous section it was noted that for $Mn_2(CO)_{10}$ (**9**), the angle θ was smaller than that experimentally observed. The above discussion on the relationship between θ and charge transfer suggests that both of the $Mn(CO)_5$ units need to transfer charge toward each other to reproduce θ. That MEHT places little electron population in the overlap region between the metals was noted above and thus probably accounts for the incorrect θ.

G. $MnX(CO)_5$ and $MnX(CO)_4$. In an effort to determine the sensitivity of MEHT toward subtle changes in ligands, a series of $MnX(CO)_5$ (**14**) complexes were calculated. The results are shown in Table VI and compared with experimental data where possible.[42-45] It is readily apparent that the choice of X affects the Mn–C and C–O distance very little. For this reason, the Mn–C–O distances in several cases were held constant during optimization at the values obtained for the case X = PH_3. Aside from the Mn–X distance the greatest geometrical variation is in θ, which is not unexpected. Though all the M–X bonds optimized somewhat long (based on reasonable estimates where no data are known), the worst offenders are the halogens; the chloride anion very nearly dissociates (see values in parentheses, Table V). This may be an indication of the relative ionic character of these bonds. However, holding the bond lengths constant at reasonable values lets us obtain satisfactory values of θ.

For purposes of the thermodynamic calculations in the succeeding paper,[10] the geometries of a similar series of $MnX(CO)_4$ complexes were also optimized. Optimizations were carried out with the restrictions of C_{3v} (**13**), C_{4v} (**16**), and C_{2v} (**17**) symmetry, the latter being at least 20 kcal/mol more stable in each case. The optimized C_{2v} geometrical parameters are given in Table V. Note again the effect of allowing the M–X bond to optimize vs. holding it constant at a reasonable value.



16, C_{4v}



17, C_{2v}

Conclusion

We have demonstrated that while MEHT is in many ways comparable to EHT, it has the advantage of giving some reasonable bond lengths. It successfully reproduces optimum geometries for metal carbonyl derivatives which have little or no dipole moment and allows comparison of relative energy differences of less stable isomers. It begins to fail as the dipole moment is increased, presumably because of the overestimation of charge transfer. In contrast to EHT, the relative effects of varying substituents on the other bond distances may be studied as well as Jahn–Teller distortions. The technique is

Table V. $MnX(CO)_5$ and $MnX(CO)_4$

	X = Cl	Br	I	CH_3[a]	GeH_3[a]	SnH_3[a]	(PH_3)[a]	SH[a]	$CH_3C{=}O$
$MnX(CO)_5$, **17**									
θ, deg	(86.2)[b] 89.5[c] [88.3][d]	(86.3) 88.7	(85.5) 86.5	88.9 [85 (1)][e]	81 [85][f]	77.8 [86.7][g]	87.4	87	90.4
Mn–X, Å	(3.14) 2.37 [2.37]	(2.84) 2.50	(2.95) 2.70	2.15 [2.18]	2.60 [2.44]	2.81 [2.68]	2.41	2.52	2.00
Mn–C(ax), Å	1.84 [1.81]	1.84	1.83	1.84 [1.82]			1.84		
Mn–C(eq), Å	1.88 [1.89]	1.88	1.87	1.87 [1.86]			1.87		
C–O(ax), Å	1.15 [1.11]	1.16	1.16	1.15 [1.14]			1.16		
C–O(eq), Å	1.12 [1.12]	1.12	1.12	1.12			1.12		
energy, eV	(−1086.04) −1085.68	(−1077.46) −1077.21	(−1063.15) −1063.03	−1087.25	−1072.95	−1067.90	−1081.61	−1070.61	−1266.08
$MnX(CO)_4$, **20**									
θ, deg	(84.8) 89.5	(86.1) 88.6	(84.9) 84.9	88.7	71.2	67	86.7	88.3	83
φ, deg	90	90	90	90	90	90	90	90	90
Mn–X, Å	(3.11) 2.37	(2.81) 2.50	(2.76) 2.70	2.14	2.61	2.81	2.40	2.32	1.92
Mn–C(θ), Å	1.87	1.87	1.87	1.87					
Mn–C(φ), Å	1.84	1.83	1.82	1.84					
C–O(θ), Å	1.13	1.13	1.12	1.12					
C–O(φ), Å	1.16	1.17	1.17	1.17					
energy, eV	(−905.71) −905.57	(−897.15) −897.09	(−882.87) −882.86	−907.04	−892.53	−887.50	−901.27	−890.57	−1086.24

[a] M–E–H = 110°, E = C, Ge, Sn; 115°, E = P; 90°, E = S; C–H = 1.10 Å, Ge–H = 1.55 Å, Sn–H = 1.75 Å, S–H = 1.35 Å, P–H = 1.40 Å; $C(H_3)$–C–O = 120°, C–O = 1.21 Å, C–C = 1.54 Å. [b] Fully optimized. [c] M–X bond held constant. [d] Reference 42. [e] Reference 43. [f] For X = $GeBr_3$.[45] [g] For X = $SnPh_3$.[44]

Table VI. Atomic Orbital Energies (eV)

atom	s	p	d
H	−13.60 (−10.00)[a]		
C	−16.6	−11.3	
O	−28.5	−13.6	
P	−16.1	−10.5	−3.0
Cl	−24.5	−13.0	−5.0
V	−6.74	−3.6	−9.0
Cr	−6.77	−3.7	−8.3
Mn	−7.43	−3.8	−8.5
Fe	−7.87	−3.87	−9.0
Co	−7.86	−3.94	−9.6
Ni	−7.63	−4.0	−10.0
Br	−23.8	−11.8	
I	−20.61	−10.45	

[a] Used for M–H calculations.

sensitive to rather subtle changes in ligands, for example, Cl vs. Br vs. I.

Anderson has suggested[37] many of the inconsistencies between calculated and experimental geometries would be removed by adjustment of atomic parameters. However, we feel that the use of a single set of atomic parameters is important for simplicity sake if this computational technique is to gain widespread use among experimentalists. Therefore, we have chosen to explore the limitations of a set of parameters which was derived from experimental data (see computational details). Further studies on the limits of reliability of the MEHT computational technique are underway.

Computational Details

Molecular structures were encoded by internal coordinates (bond length, bond angles, and dihedral angles). Optimization was carried out with a modified Davidon–Fletcher–Powell technique. The energies of each geometry were evaluated by using FORTICON-8 (Quantum Chemistry Program Exchange No. 344) modified at Du Pont to include the two-body repulsions of Anderson. All these routines were combined into one interactive program which permits a sequence of optimizations to be performed without manual intervention. This program is one module of the TRIBBLE SYSTEM—An Interactive Computing System for Chemical Research (to be submitted for publication).

The atomic parameters used in this study were obtained from literature sources where they had been determined from experimental data. The atomic screening constants (exponents and coefficients of Slater-type wave functions) for nontransition elements are those of Clementi and Raimondi,[46] while those of the first-row transition metals are from Richardson et al.[47] Valence orbital ionization potentials (VOIP) were used for orbital energies from the work of Lotz;[48] an exception is the value for hydrogen in metal hydrides (see text). The orbital energies are given in Table VI.

Acknowledgment. We thank Dr. A. Anderson for providing details of the modified extended Hückel theory (MEHT) and for many suggestions. We also thank Dr. F. Van Catledge for helpful discussions and a referee for many constructive comments.

Registry No. $V(CO)_5$, D_{3h}, 59982-54-6; $V(CO)_5^-$, D_{3h}, 71564-14-2; $Cr(CO)_5$, D_{3h}, 54822-35-4; $Mn(CO)_5^+$, D_{3h}, 71564-15-3; $Cr(CO)_5^-$, D_{3h}, 71564-16-4; $Mn(CO)_5$, D_{3h}, 71564-17-5; $Cr(CO)_5^{2-}$, D_{3h}, 71518-79-1; $Mn(CO)_5^-$, D_{3h}, 35816-56-9; $Fe(CO)_5$, D_{3h}, 13463-40-6; $Co(CO)_5^+$, D_{3h}, 71564-18-6; $V(CO)_5$, C_{4v}, 71564-19-7; $V(CO)_5^-$, C_{4v}, 71564-20-0; $Cr(CO)_5$, C_{4v}, 42386-76-5; $Mn(CO)_5^+$, C_{4v}, 71563-56-9; $Cr(CO)_5^-$, C_{4v}, 39586-86-2; $Mn(CO)_5$, C_{4v}, 54882-42-7; $Cr(CO)_5^{2-}$, C_{4v}, 71564-21-1; $Mn(CO)_5^-$, C_{4v}, 71564-22-2; $Fe(CO)_5$, C_{4v}, 71564-23-3; $Co(CO)_5^+$, C_{4v}, 71564-24-4; $Mn(CO)_4$, C_{2v}, 71518-80-4; $Mn(CO)_4^-$, C_{3v}, 71564-25-5; $Fe(CO)_4$, C_{2v}, 71564-26-6; $Co(CO)_4^+$, C_{2v}, 70002-18-5; $Fe(CO)_4^-$, C_{3v}, 71564-27-7; $Co(CO)_4$, D_{2d}, 58207-38-8;

$Fe(CO)_4^{2-}$, T_d, 22321-35-3; $Co(CO)_4^-$, T_d, 14971-27-8; $Ni(CO)_4$, T_d, 13463-39-3; $Mn(CO)_4$, D_{4h}, 71564-28-8; $Mn(CO)_4^-$, D_{4h}, 71564-29-9; $Fe(CO)_4$, D_{4h}, 71564-30-2; $Co(CO)_4^+$, D_{4h}, 71564-31-3; $Fe(CO)_4^-$, D_{4h}, 71564-32-4; $Co(CO)_4$, D_{4h}, 71564-33-5; $Fe(CO)_4^{2-}$, D_{4h}, 71564-34-6; $Co(CO)_4^-$, D_{4h}, 71564-35-7; $Ni(CO)_4$, D_{4h}, 71564-36-8; $Mn_2(CO)_{10}$, 10170-69-1; $Co_2(CO)_8$, 10210-68-1; $Fe_2H_2(CO)_8$, 71500-60-2; $Fe_3(CO)_{12}$, 17685-52-8; $HCo(CO)_4$, 64519-62-6; $HFe(CO)_4^-$, 18716-80-8; $HMn(CO)_5$, 16972-33-1; *cis*-$H_2Fe(CO)_4$, 22763-20-8; *trans*-$H_2Fe(CO)_4$, 71564-37-9; $MnCl(CO)_5$, 14100-30-2; $MnBr(CO)_5$, 14516-54-2; $MnI(CO)_5$, 14879-42-6; $Mn(CH_3)(CO)_5$, 13601-24-6; $Mn(GeH_3)(CO)_5$, 25069-08-3; $Mn(SnH_3)(CO)_5$, 71500-59-9; $Mn(PH_3)(CO)_5$, 71500-58-8; $Mn(SH)(CO)_5$, 59390-73-7; $Mn(CH_3C{=}O)(CO)_5$, 13963-91-2; $MnCl(CO)_4$, 71518-81-5; $MnBr(CO)_4$, 71518-82-6; $MnI(CO)_4$, 71518-83-7; $Mn(CH_3)(CO)_4$, 71518-84-8; $Mn(GeH_3)(CO)_4$, 71518-85-9; $Mn(SnH_3)(CO)_4$, 71518-86-0; $Mn(PH_3)(CO)_4$, 71518-87-1; $Mn(SH)(CO)_4$, 71518-88-2; $Mn(CH_3C{=}O)(CO)_4$, 71518-89-3; $V(CO)_6$, 14024-00-1; $V(CO)_6^-$, 20644-87-5; $Cr(CO)_6$, 13007-92-6; $Mn(CO)_6^+$, 21331-06-6.

References and Notes

(1) D. M. P. Mingos, *Adv. Organomet. Chem.*, **15** (1976).
(2) For example see (a) D. R. Armstrong, P. G. Perkins, and J. J. P. Stewart, *J. Chem. Soc., Dalton Trans.*, 1972 (1972); (b) D. R. Armstrong, R. Fortune, and P. G. Perkins, *J. Catal.*, **45**, 339 (1976); (c) V. D. Sutula, A. P. Zeif, B. I. Popov, and L. I. Chernyauskii, *React. Kinet. Catal. Lett.*, **4**, 359 (1976); (d) J. P. Grima, F. Chaplin, and Gr. Kaufmann, *J. Organomet. Chem.*, **124**, 315 (1977); (e) K. Ohkubo, H. Kanaeda, and K. Tsuchihashi, *Bull. Chem. Soc. Jpn.*, **46**, 3095 (1973).
(3) For example see (a) D. L. Lichtenberger and T. L. Brown, *J. Am. Chem. Soc.*, **100**, 366 (1978); (b) J. K. Burdett, *Inorg. Chem.*, **16**, 3013 (1977); (c) D. L. Thorn and R. Hoffmann, *J. Am. Chem. Soc.*, **100**, 2079 (1978); (d) H. Berke and R. Hoffmann, *ibid.*, **100**, 7224 (1978).
(4) A. B. Anderson, *J. Chem. Phys.*, **62**, 1187 (1975).
(5) R. Hoffman, *J. Chem. Phys.*, **39**, 1397 (1963); R. Hoffman and W. N. Lipscomb, *ibid.*, **36**, 2179, 3489 (1962); **37**, 2872 (1962).
(6) A. B. Anderson, *J. Am. Chem. Soc.*, **100**, 1153 (1978), and references cited therein; A. B. Anderson, *Inorg. Chem.*, **15**, 2598 (1976).
(7) A referee has noted that parameterization which reproduces ground-state geometries is not necessarily applicable to transition-state species (see G. Klopman, P. Andreozzi, A. J. Hopfinger, O. Kikuchi, and M. J. S. Dewar, *J. Am. Chem. Soc.*, **100**, 6267 (1978)).
(8) M. Elian and R. Hoffmann, *Inorg. Chem.*, **14**, 1058 (1975).
(9) J. K. Burdett, *J. Chem. Soc., Faraday Trans. 2*, **70**, 1599 (1974).
(10) Ronald J. McKinney and David A. Pensak, *Inorg. Chem.*, following paper this issue.
(11) D. G. Schmidling, *J. Mole. Struct.*, **24**, 1 (1975).
(12) A. Whitaker and J. W. Jeffrey, *Acta Crystallogr.*, **23**, 977 (1967).
(13) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed., Interscience, New York, 1972, p 590.
(14) J. Demuynck, A. Strich, and A. Veillard, *Nouv. J. Chim.*, **1**, 217 (1977).
(15) P. Jeffrey Hay, *J. Am. Chem. Soc.*, **100**, 2411 (1978).
(16) B. Beagley, D. W. J. Cruickshank, P. M. Pinder, A. G. Robiette, and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, **25**, 737 (1969).
(17) B. A. Frenz and J. A. Ibers, *Inorg. Chem.*, **11**, 1109 (1972).
(18) H. Huber, E. P. Kundig, G. A. Ozin, and A. J. Poë, *J. Am. Chem. Soc.*, **97**, 308 (1975).
(19) P. A. Breeze and J. J. Turner, *J. Organomet. Chem.*, **44**, C7 (1972).
(20) R. Perutz and J. J. Turner, *Inorg. Chem.*, **14**, 262 (1975).
(21) F. A. Cotton, A. Danti, J. S. Waugh, and R. W. Fessenden, *J. Chem. Phys.*, **29**, 1427 (1958); R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, **58**, 1893 (1962); O. A. Gansow, A. R. Burke, and W. D. Vernon, *J. Am. Chem. Soc.*, **94**, 2552 (1972).
(22) M. A. Graham, Ph.D. Thesis, University of Cambridge, 1971.
(23) E. P. Kündig and G. A. Ozin, *J. Am. Chem. Soc.*, **96**, 3820 (1974), Table I.
(24) J. Ladell, B. Post, and I. Faukuchen, *Acta Crystallogr.*, **5**, 795 (1952).
(25) G. A. Ozin and A. Vander Voet, *Acc. Chem. Res.*, **6**, 313 (1973).
(26) O. Crichton, M. Poliakoff, A. J. Rest, and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 1321 (1973).
(27) M. Poliakoff and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 2276 (1974).
(28) Cited as unpublished work in ref 29.
(29) B. Davies, A. McNeish, M. Poliakoff, and J. J. Turner, *J. Am. Chem. Soc.*, **99**, 7573 (1977).
(30) R. L. DeKock, *Inorg. Chem.*, **10**, 1205 (1971).
(31) M. Poliakoff, *J. Chem. Soc., Dalton Trans.*, 210 (1974).
(32) (a) L. F. Dahl and R. E. Rundle, *Acta Crystallogr.*, **16**, 419 (1963); (b) N. I. Gapotchenko, N. V. Alekseev, K. N. Anisimov, N. E. Kolobova, and I. A. Ronova, *Zh. Strukt. Khim.*, **9**, 892 (1968); (c) A. Almenningen, G. G. Jacobsen, and H. M. Seip, *Acta Chem. Scand.*, **23**, 685 (1969).
(33) (a) G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Crystallogr.*, **17**, 732 (1964); (b) J. A. Ibers, *J. Organomet. Chem.*, **14**, 423 (1968).
(34) H. B. Chin, M. B. Smith, R. D. Wilson, and R. Bau, *J. Am. Chem. Soc.*, **96**, 5285 (1974).
(35) H. M. Powell and R. V. G. Ewens, *J. Chem. Soc.*, 286 (1939).
(36) C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **91**, 1351 (1969).
(37) A. Anderson, private communication.
(38) E. A. McNeill and F. R. Scholer, *J. Am. Chem. Soc.*, **99**, 6243 (1977).
(39) M. B. Smith and R. Bau, *J. Am. Chem. Soc.*, **99**, 2388 (1977).
(40) S. J. La Placa, W. C. Hamilton, J. A. Ibers, and A. Davison, *Inorg. Chem.*, **8**, 1928 (1969).
(41) L. Vancea and W. A. G. Graham, *J. Organomet. Chem.*, **134**, 219 (1977).
(42) P. T. Greene and R. F. Bryan, *J. Chem. Soc. A*, 1559 (1971).
(43) H. M. Seip and R. Seip, *Acta Chem. Scand.*, **24**, 3431 (1970).
(44) H. P. Weber and R. F. Bryan, *Chem. Commun.*, 443 (1966).
(45) N. I. Gapotchenko, N. V. Alekseev, A. B. Antonova, K. N. Anisimov, N. E. Kolobova, I. A. Ronova, and T. Yu. Struchkov, *J. Organomet. Chem.*, **23**, 525 (1970).
(46) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963); E. Clementi, D. L. Raimondi, and W. P. Reinhardt, *ibid.*, **46**, 1300 (1967).
(47) J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962); J. W. Richardson, R. R. Powell, and W. C. Nieuwpoort, *ibid.*, **38**, 796 (1963).
(48) W. Lotz, *J. Opt. Soc. Am.*, **60**, 206 (1970).

Contribution No. 2595 from the Central Research and Development Department,
Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Application of Molecular Orbital Theory to Transition-Metal Complexes. 2. Calculation of Enthalpies of Activation for Dissociative Processes[1]

RONALD J. McKINNEY and DAVID A. PENSAK*

Received December 21, 1978

Molecular energies calculated with a modified extended Hückel theory are used to calculate enthalpies of activation and/or reaction for a number of dissociative processes involving transition metal carbonyl compounds. Metal–carbonyl, metal–hydride, and metal–metal bond dissociations are examined as well as the interaction of metal hydride with water to give $M^- + H_3O^+$. The effects of a series of ligands, X, on cis CO labilization in $MnX(CO)_5$ are examined and compared with similar calculations by other workers by use of the Fenske–Hall method.

Introduction

In the preceding paper,[1] we demonstrated that extended Hückel theory modified by the inclusion of two-body repulsion can successfully reproduce ground-state geometries, including bond lengths, for a number of transition metal carbonyl compounds. In principle, the molecular energies calculated therefrom may be compared to give internal energy (ΔE) of reaction (or activation).[2] For example, for eq 1, ΔE can be calculated by adding the molecular energies of B and C (E_B and E_C) and subtracting that of A (E_A). The change in

$$A \rightarrow B + C \qquad (1)$$

$$\Delta E = E_B + E_C - E_A \qquad (2)$$

enthalpy (ΔH) is more commonly determined experimentally,

0020-1669/79/1318-3413$01.00/0 © 1979 American Chemical Society