A Density Functional Study on the Strength of the Metal Bonds in $Co_2(CO)_8$ and $Mn_2(CO)_{10}$ and the Metal-Hydrogen and Metal-Carbon Bonds in R-$Mn(CO)_5$ and R-$Co(CO)_4$

Elżbieta Folga and Tom Ziegler*

Contribution from the Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

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Abstract: Density functional studies have been carried out on the binuclear complexes $(CO)_4Co-Co(CO)_4$ and $(CO)_5Mn-Mn(CO)_5$ as well as the derivatives R-$Mn(CO)_5$ [R = H, CH_3, CH_2F, CHF_2, CF_3, $C(O)CH_3$, and C(O)H] and R-$Co(CO)_4$ [R = H, CH_3]. The density functional calculations were based on the local density approximation (LDA) with nonlocal corrections for exchange and correlation included self-consistently (LDA/NL). The geometries optimized by LDA/NL agrees well with experimental structures. The deviations are 0.015 Å for M-M and M-ligand distances and 2° for ligand-metal-ligand bond angles. The calculated Mn-Mn bond energy of 173 kJ/mol is in good agreement with recent experimental values. The theoretical Co-Co bond energy is 148 kJ/mol, and it is suggested that older experimental estimates (64-88 kJ/mol) for the Co-Co bond enthalpy are too low. The calculated metal-ligand bond energies are in kJ/mol: D(Mn-H) = 288; D(Mn-CH_3) = 208; D(Mn-CH_2F) = 208; D(Mn-CF_2H) = 203; D(Mn-CF_3) = 224; D(Mn-C(O)H = 196; D(Mn-C(O)CH_3) = 189; D(Co-H) = 283; D(Co-CH_3) = 198. The calculated D(Mn-H) and D(Co-H) values agree within 4 kJ mol with the most recent experimental estimates. The D(Mn-R) enthalpies are on the average 20 kJ/mol higher than experiment for R = CH_3, CF_3, CF_3, and C(O)CH_3. It is suggested that the experimental estimates for D(Mn-CFH_3) and D(Mn-CF_2H) are too low.

I. Introduction

The cleavage and formation of metal-hydrogen and metal-carbon bonds pervades organometallic chemistry, and accurate estimates of the corresponding bond energies are essential for the quantitative understanding of organometallic reaction mechanisms. The efforts to obtain accurate bond enthalpies in this field were pioneered by Skinner,[1a] Pilcher,[1b] Halpern,[1c] and Connor,[1e] and organometallic thermochemistry has since grown into a vast body of data with the aid of an impressive arsenal of experimental methods. This development has most recently been reviewed by Simoes and Beauchamp.[1d]

Theoretical methods hold, in principle, the promise to provide accurate data on bond strength. This promise has more or less been honored for small organic molecules where enthalpies of formation now can be calculated within chemical accuracy (±2 kcal/mol) in the "Gaussian-1" (G1) as well as the revised "Gaussian-2" (G2) methods due to Pople and co-workers.[2,3] Bond dissociation energies for simple diatomic metal hydrides can also be calculated to the same degree of accuracy. However, G2 calculations on larger organic molecules, let alone transition metal complexes, are still impractical.

Much interest has recently been given to methods[4] based on density functional theory[5] (DFT) as an alternative to *ab initio* schemes. This interest was initially motivated by the computational expedience since the time required in DFT methods increases as N^3 with the number of electrons, N, as opposed to N^4 (HF) or N^5 - N^7 (HF + electron correlation) for *ab initio* schemes. DFT-based methods are thus ideally suited for large size systems. Particular use has been made of the Hartree-Fock-Slater (HFS) scheme[6] as well as the local density approximation (LDA)[7] of which, at least, the LDA method includes electron correlation. Both schemes are referred to as local since the exchange (HFS) or the exchange and correlation energy (LDA) are expressed approximately as a function of the electron density. However, the extensive use of the HFS and LDA schemes has also revealed a number of shortcomings of the local methods, in particular in the calculation of bond energies which are systematically overestimated.[8]

Langreth and Mehl,[8] Becke,[9-11] Perdew,[12b,c] Wilson and Levy,[12d] Lee,[12e] *et al.* as well as DePristo and Kress[12a] have, in a series of pioneering papers, eliminated many of the shortcomings of the local approach by introducing correction terms based on electron density gradients. Correction terms dependent on the Laplacian of the density have also been suggested by Tschinke and Ziegler.[13] The nonlocal correction terms greatly improve the calculation of atomic exchange and correlation energies[7-10] and afford in addition bonding energies far superior to those obtained by local methods.[8-10,14,15]

Becke[14] has recently shown in a seminal paper that nonlocal methods afford bond energies of nearly the same quality as the

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Table I. M–M Bond Dissociation Enthalpies[a] (M = Mn, Co)

	EI/PES[b]	E/GP[c]	RCS[d]	PIMS[e]	KS[f]	PAC[g]	LP[h]
$Mn_2(CO)_{10}$	171[i]	96[j]		159 ± 21[k]	>154[l]	159 ± 21[m]	≫176[n]
$Co_2(CO)_8$		64–88[j]	86[o]				

[a] BDE's in kJ mol^{-1}. [b] EI/PES = electron impact mass spectroscopy in conjunction with photoelectron spectroscopy. [c] E/GP = equilibrium studies in gas phase. [d] RSC = reaction solution calorimetry. [e] PIMS = photoionization mass spectrometry. [f] KS = kinetic study. [g] PAC = photoacoustic calorimetry. [h] LP = laser pyrolysis. [i] Reference 30a. [j] Reference 30b. [k] Reference 30c. [l] Reference 30d. [m] Reference 30e. [n] Reference 30f. [o] Reference 31.

G2 method based on *ab initio* techniques, for the set of small molecules studied by Pople and co-workers. The nonlocal method has bee implemented at the self-consistent level[16] and applied to molecular structures[17] as well as IR studies on main group molecules[18] and transition metal complexes.[19] It was demonstrated[17] that nonlocal corrections greatly improve the accuracy of metal–ligand and metal–metal bond distances. Studies on transition state structures have also been carried out by the nonlocal method.[20]

We shall in the present investigation explore the potential of DFT as a practical tool for studies on organometallic thermochemistry. Our aim has primarily been to initialize a validation of the method, and we shall for this reason concentrate on the experimentally well-studied R–$Mn(CO)_5$ and R–$Co(CO)_4$ systems as well as the related $(CO)_4Co$–$Co(CO)_4$ and $(CO)_5Mn$–$Mn(CO)_5$ dimers. Bond energies involving transition metals have been calculated previously[15] by nonlocal methods. However, earlier studies were based on local geometries and introduced nonlocal corrections as a perturbation. The present investigation makes full use of the self-consistent implementation[17–20] of the nonlocal method in the geometry optimization[17] as well as the energy calculation.[16]

II. Computational Details

The reported calculations were all carried out by utilizing the HFS-LCAO program system A-MOL, developed by Baerends *et al.*[21,22] and vectorized by Ravenek. The numerical integration procedure applied for the calculations was developed by Boerrigter *et al.*[23] The geometry optimization procedure was based on the method developed by Versluis and Ziegler.[24] Vibrational frequencies were evaluated from force constants calculated by numerical differentiation of the energy gradients.[25] The electronic configurations of the molecular systems were described by an uncontracted triple-ζ STO basis set[26] on manganese (3d, 4s, and 4p) and cobalt (3d, 4s, and 4p) as well as a double-ζ STO basis set[8] on oxygen (2s, 2p), carbon (2s, 2p), and hydrogen (1s). Oxygens, carbons and hydrogens were given an extra polarization function: $3d_O$ ($\zeta_{3d} = 2.0$), $3d_C$ ($\zeta_{3d} = 2.5$); $2p_H$ ($\zeta_{2p} = 2.0$). The $1s^22s^22p^6$ configuration on manganese and cobalt and the $1s^2$ configuration on carbon, oxygen, and fluorine were assigned to the core and treated by the frozen-core approximation. A set of auxiliary[27] s, p, d, f, and g STO functions, centered on all nuclei, was used to fit the molecular density and present Coulomb and exchange potentials accurately in each SCF cycle. Energy differences were calculated by including the local exchange-correlation potential by Vosko *et al.*[28] with Becke's[11a] nonlocal exchange corrections and Perdew's[12c] nonlocal correlation correction. Geometries were optimized including nonlocal corrections. The application of approximate density functional theory to organometallic chemistry has been reviewed recently.[4,29]

III. Results and Discussion

The D(M–R) bond dissociation energies in R–$Mn(CO)_5$ and R–$Co(CO)_4$ can be determined from the equation

$$D(\text{M–R}) = \Delta H_f{}^\circ[\text{L}_n\text{M,g}] + \Delta H_f{}^\circ[\text{R,g}] - \Delta H_f{}^\circ[\text{L}_n\text{MR,g}] \quad (1a)$$

corresponding to the homolytic dissociation process

$$\text{L}_n\text{M–R} \rightarrow \text{L}_n\text{M} + \text{R} - D(\text{M–R}) \quad (1b)$$

It is relatively easy to measure $\Delta H_f{}^\circ$[R,g] and $\Delta H_f{}^\circ[L_nMR,g]$ representing respectively the energy of formation of the undissociated complex L_nM–R and that of the departing radical R. The free energy of formation, $\Delta H_f{}^\circ[L_nM,g]$, for the metal radical L_nM is on the other hand difficult to obtain. An estimate of $\Delta H_f{}^\circ[L_nM,g]$ can be obtained from the free energy of formation, $\Delta H_f{}^\circ[L_nM\text{–}ML_n,g]$, for the dimer L_nM–ML_n as well as the metal–metal bond dissociation D(M–M) corresponding to the process

$$\text{L}_n\text{M–ML}_n \rightarrow 2\text{ML}_n - D(\text{M–M}) \quad (2)$$

by making use of the relation

$$\Delta H_f{}^\circ[\text{L}_n\text{M,g}] = {}^1/_2\Delta H_f{}^\circ[\text{L}_n\text{MR,g}] + {}^1/_2 D(\text{M–M}) \quad (3)$$

It is thus finally possible to write the dissociation energy D(M–R) as

$$D(\text{M–R}) = {}^1/_2 D(\text{M–M}) + {}^1/_2\Delta H_f{}^\circ[\text{M}_2\text{L}_{2n}\text{,g}] + \Delta H_f{}^\circ[\text{R,g}] - \Delta H_f{}^\circ[\text{L}_n\text{MR,g}] \quad (4)$$

It follows from eq 4 that accurate absolute values for D(M–R) depend on how well the metal–metal bond energy D(M–M) is determined. The experimental[30] values for D(Mn–Mn) published between 1970 and today range from 96 to more than 176 kJ mol^{-1}, Table I. The spread in the measured metal–metal bond energies D(M–M) leads to a considerable uncertainty in the values for the metal–ligand dissociation energies, D(M–R). We shall discuss calculations on the metal–metal bond energies D(M–M) for $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ in Section IIIa along with an evaluation of the experimental[30,31] data.

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Table II. Experimental Bond Dissociation Enthalpies for M–R Bonds

R	electrochem[b]	CMC[c,n]	RSC[d,n]	PIMS[e,n]	others
		M = Mn			
H	284.5[i]	245 ± 10[j]			263.7[f]
CH_3		187 ± 4[j]		192 ± 11[l]	
CH_2F				139 ± 11[l]	
CF_2H				144 ± 11[l]	
CF_3		203 ± 6[j]		182 ± 11[l]	
$C(O)CH_3$		160 ± 10[j]	185 ± 8[k]		182[g]
		M = Co			
H	280.1 ± 4[i]				227,[g] 213[h] 243[m]

[a] BDE's in kJ mol^{-1}. [b] Electrochemical in conjunction with acidity measurement. [c] CMC = Calvet microcalorimetry. [d] RSC = reaction solution calorimetry. [e] PIMS = photoionization mass spectrometry. [f] Kinetic study. [g] Equilibrium studies in solution, ref 1e. [h] Kinetic study, ref 1e. [i] Reference 32. [j] Reference 54b. [k] Reference 54a. [l] Reference 30c. [m] Kinetic study, ref 1f. [n] Assumed D(M–M) values are the following: $D(\text{Mn–Mn})^{30c}$ = 159 kJ/mol (Mn^{30c}) and $D(\text{Co–Co})^{1d}$ = 64 kJ mol^{-1}.

Table II summarizes some of the experimental D(M–R) enthalpies obtained by different experimental techniques. In columns 3–5 are collected the results from calorimetric experiments in which D(M–R) depends on the metal–metal bond strength through eq 4. For these enthalpies the assumed values for D(M–M) are equal to 159 ± 21 kJ/mol (Mn^{30c}) and 64 kJ/mol (Co^{1b}). Column 6 of Table II gives estimates for D(M–R) from kinetic studies. Kinetic values are independent of D(M–M) but offer only rough estimates. A recent study by Tilset and Parker[32] demonstrate that various M–H bond dissociation enthalpies can be determined utilizing electrochemical methods in conjunction with Brønsted acidity measurements. The authors estimate that their D(M–H) values are accurate to within 4 kJ mol^{-1}. The study covers a variety of carbonyl hydride complexes of transition metals, among them Mn and Co (column 2, Table II). The D(M–H) enthalpies are independent of estimates for D(M–M). We shall compare our calculated D(M–R) values with experimental estimates in Sections IIIb and IIIc.

Bond dissociation enthalpies, D(M–R), are not a direct measure of the M–R bond strength since they include the energy required to snap the bond, i.e. the bond snapping enthalpy E(M–R), as well as the energy gained when the R and ML_n fragments relax to their ground state structures from the conformations they assumed in L_nM–R. The relaxation energies are given as ER_2 and ER_3 for ML_n and R, respectively (Scheme I; M = Mn). In our discussions of the Mn–R bond strengths in Section IIIb and the Co–R bond strengths in Section IIIc, we shall present calculations on D(M–R) as well as E(M–R).

Finally, in Section IIId we shall perform an internal check on our calculated values for D(M–M) and D(M–H) by evaluating the reaction enthalpy, ΔH_5, for the hydrogenation reactions

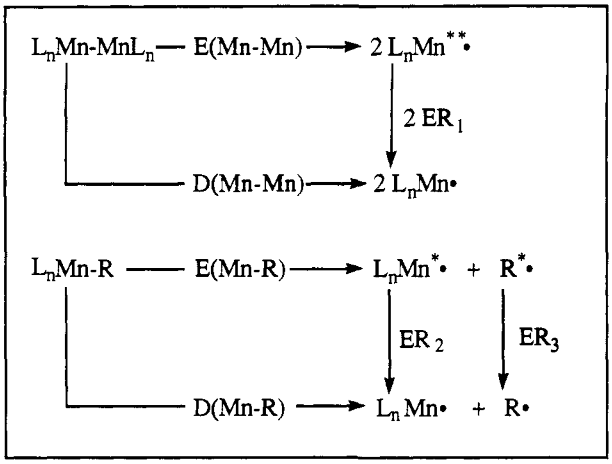
$$M_2L_{2n} + H_2 \rightarrow HML_n + \Delta H_5 \qquad (5)$$

involving $Mn_2(CO)_{10}$ and $Co_2(CO)_8$. The reaction enthalpy ΔH_5 is known[37] with high accuracy for the two processes. It can further be written as

$$\Delta H_5 = D(\text{M–M}) + D(\text{H–H}) - 2D(\text{M–H}) \qquad (6)$$

and can thus be obtained from calculated values of D(M–M), D(H–H), and D(M–H).

Scheme I



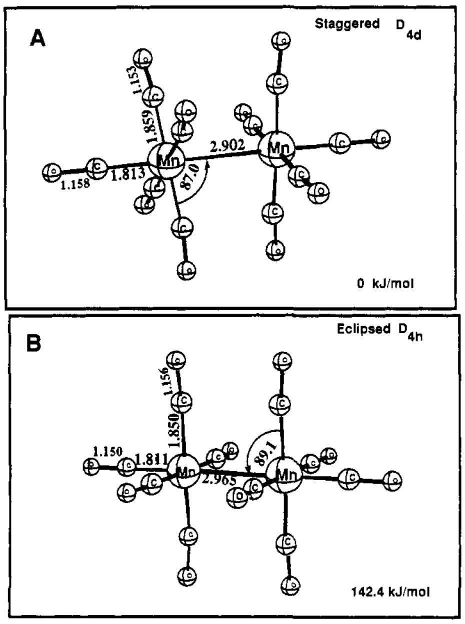


Figure 1. Optimized structures of $Mn_2(CO)_{10}$: (A) staggered conformation of D_{4d} symmetry; (B) eclipsed conformation of D_{4h} symmetry.

(a) The Geometrical and Thermodynamic Properties of $Mn_2(CO)_{10}$ and $Co_2(CO)_8$. We have carried out a complete geometry optimization on two conformations of $Mn_2(CO)_{10}$, corresponding to the staggered structure of D_{4d} symmetry, Figure 1A, as well as the eclipsed structure of D_{4h} symmetry, Figure 1B. In both the staggered and the eclipsed conformations, each manganese center has a pseudooctahedral coordination, with four carbonyl groups in equatorial positions, and a remaining CO group as well as another manganese atom in axial positions.

The X-ray diffraction data[33] for the dimanganese decarbonyl complex indicate a near-D_{4d} symmetry (the torsion angle of the two $Mn(CO)_5$ fragments is 50.2° rather than 45°). Table III collects the structural data from the cited crystallographic study along with the results of our SCF calculation. The experimental parameters shown in Table III are averaged over assumed-to-be-equivalent bond lengths and bond angles corresponding to D_{4d} symmetry. The uncertainties are given in brackets. All calculated bond distances differ from the crystallographic data by a maximum of 0.01 Å. The highest deviation in the bond angles comes from the C_{ax}–Mn–Mn′ angle, which we have assumed to be 180°. All other angles are within 2°.

Structural parameters for the eclipsed conformation of $Mn_2(CO)_{10}$ are shown in the last column in Table III. It is evident that the large Mn–Mn separation of 2.965 Å in D_{4h} structure, Figure 1B, compared to 2.902 Å in the staggered conformation, Figure 1A, is dictated by the repulsive interactions between the

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Table III. Structural Parameters for $Mn_2(CO)_{10}$

	exptl (D_{4d})[a]	calcd[b] (D_{4d})	calcd[c] (D_{4h})
	Interatomic Distances (Å)		
Mn–Mn′	2.895(1)	2.902	2.965
Mn–C_{ax}	1.820(3)	1.813	1.812
Mn–C_{eq}	1.859(3)	1.859	1.850
C_{ax}–O_{ax}	1.150(4)	1.158	1.157
C_{eq}–O_{eq}	1.140(4)	1.153	1.156
	Bond Angles (deg)		
C_{ax}–Mn–Mn′	175.33(6)	180.00	180.00
C_{eq}–Mn–Mn′	86.12(4)	87.00	89.10
C_{ax}–Mn–C_{eq}	93.94(10)	93.00	90.90
O_{ax}–C_{ax}–Mn	178.27(26)	180.00	180.00
O_{eq}–C_{eq}–Mn	177.77(19)	175.87	174.39

[a] Reference 33. [b] This work, D_{4d} symmetry constraints. [c] This work, D_{4h} symmetry constraints.

Table IV. Calculated M–M Bond Energies[a] (M = Mn, Co)

	D_e(M–M)	D_0(M–M)	E_e(M–M)	ER_1
$Mn_2(CO)_{10}$	174.2	173.3	193.4	–9.6
$Co_2(CO)_8$	148.0		295.0	–73.5

[a] All energies are in kJ mol^{-1}.

two eclipsed $Mn(CO)_5$ moieties. The same effect is also reflected in the larger Mn′–Mn–C_{eq} angle (89° vs 87°). We found that the eclipsed structure (D_{4h}) is higher in energy by 142.4 kJ mol^{-1} than the staggered geometry (D_{4d}). We have calculated the bond dissociation enthalpy, D_e(M–M), for the Mn–Mn′ bond in the D_{4d} dimanganese carbonyl complex to be 174.2 kJ mol^{-1} (NL/LSD), Table IV. A proper estimate of D_0(Mn–Mn) requires a zero-point energy correction. The frequency corresponding to the Mn–Mn bond stretch was measured[34] to be 160 cm^{-1}, thus the corrected value for D_0(Mn–Mn) amounts to 173.3 kJ mol^{-1}. This estimate compares well with most of the relatively recent experimental values obtained using EI/PES techniques[30a] (171 kJ mol^{-1}), PAC[30e] (159 ± 21), and LP[30f] ($\gg$176 kJ mol^{-1}); see Table I for a more complete listing of experimental data on D(Mn–Mn).

In order to evaluate the bond snapping enthalpy for the Mn–Mn linkage, the relaxation energy, ER_1, of Scheme I must be calculated, Table IV. The ER_1 relaxation energy represents the amount of energy released when the $L_nM^{\bullet}$ radical reorganizes itself from the geometry taken up in M_2L_{2n} complex to the geometry of a free radical. Since the $(CO)_5Mn^{\bullet}$ radical is only slightly distorted from its equilibrium geometry, the calculated ER_1 value amounts to only –9.6 kJ mol^{-1}, Table IV. The resulting Mn–Mn bond snapping enthalpy (D_e(Mn–R) – $2ER_1$) amounts to 193.4 kJ mol^{-1}, Table IV.

We shall now turn our discussion to the $Co_2(CO)_8$ system. It has been established by studies based on X-ray diffraction[35a,b] and vibrational spectroscopy that $Co_2(CO)_8$ possesses more than one isomer. In principle, six different geometrical isomers could exist: with respectively C_{2v}, D_{3d},[36] D_{3h}, D_{2h}, D_{2d}, and C_{2h} symmetries. Among them, the C_{2v} structure is the most stable. It has been crystallographically proven to have two CO groups bridging between the two cobalt centers. There are five carbonyl groups arranged in square-pyramidal fashion about each cobalt atom. The two $Co(CO)_3$ moieties are mutually eclipsed.

We have optimized two structures for the $Co_2(CO)_8$ complex, the bridged geometry of C_{2v} symmetry, Figure 2A, as well as the staggered conformation of D_{3d} symmetry with an unsupported Co–Co bond, Figure 2B. The calculated structural parameters for the bridged C_{2v} conformation, Table 2A, were compared with the crystallographic data of Leung and Coppens *et al.*,[35] Table V. The experimental structure finds the $(C–O)_{terminal}$ distance at 1.136 Å and the $(C–O)_{bridge}$ distance at 1.167 Å. The corresponding theoretical values are in good agreement at 1.149 and 1.169 Å, respectively. Also, in agreement with the experimental data by Leung and Coppens, the $C_{terminal}$–Co–C_{bridge} angle was calculated to be ~94°. A substantial difference of 0.06 Å was found between the experimental and theoretical values of the Co–Co′ distance, Table V.

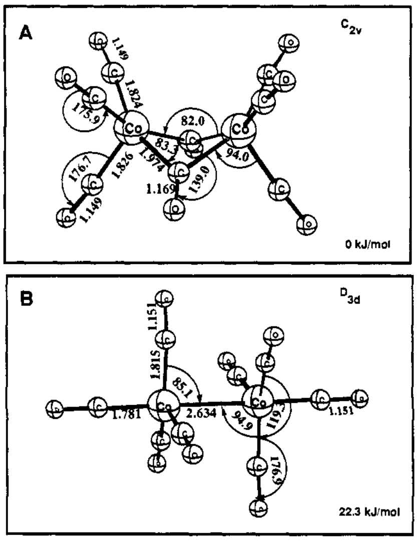

Figure 2. Optimized structures of $Co_2(CO)_8$: (A) C_{2v} conformation; (B) D_{3h} conformation.

Table V. Structural Parameters for $Co_2(CO)_8$

	exptl (C_{2v})[a]	calcd[b] (C_{2v})	calcd[c] (D_{3d})
	Interatomic Distances (Å)		
Co–Co′	2.528(1)	2.592	2.634
Co–$C_{terminal}$	1.827(2)	1.825[d]	
Co–C_{bridge}	1.939(2)	1.974	
$(C–O)_{terminal}$	1.136(3)	1.149	
$(C–O)_{bridge}$	1.167(3)	1.169	
Co–C_{eq}			1.815
Co–C_{ax}			1.781
C–O_{eq}			1.151
C–O_{ax}			1.151
	Bond Angles (deg)		
Co–C_{bridge}–Co′	81.4(1)	82.0	
C_{bridge}–Co–C_{bridge}	86.8(1)	83.3	
$C_{terminal}$–Co–C_{bridge}	93.5(1)	94.0	
O–$C_{terminal}$–Co	174.9(1)–178.9(1)	175.9–176.7	
C_{ax}–Co–Co′			180.0
C_{eq}–Co–Co′			85.1
C_{ax}–Co–C_{eq}			119.3
O_{ax}–C_{ax}–Co			180.0
O_{eq}–C_{eq}–Co			176.9

[a] Reference 35b. [b] This work, C_{2v} symmetry constraints. [c] This work, D_{3d} symmetry constraints. [d] Average value for all six terminal CO groups in $Co_2(CO)_8$.

We have also optimized the alternative structure with an unsupported Co–Co bond, Figure 2B. Geometry optimization has been carried out within D_{3d} symmetry constraints. Each cobalt center is pentacoordinated. The four carbonyl groups and another Co atom form approximately a trigonal bipyramid around the reference cobalt center. The two bipyramids are mutually staggered. The CO groups are slightly bent away from the center of mass of the molecule. The distance for the unsupported Co–Co bond in the D_{3d} conformation is 2.634 Å. This separation is 0.042 Å longer than the Co–Co distance in the bridged $Co_2(CO)_8$ complex of C_{2v} symmetry, Figure 2A. For the more complete collection of parameters for the calculated D_{3d} structure, see Table V.

We have calculated the D_{3d} conformation of Figure 2B to be 22.3 kJ mol^{-1} higher in energy than the C_{2v} bridged structure of Figure 2A. The calculated order of stability between the C_{2v} and D_{3d} conformations is in agreement with IR evidence.[31] The absolute energy difference has been previously determined experimentally by Noack,[36b] who found the C_{2v} bridged structure to be 5.44 kJ mol^{-1} more stable than the D_{3d} structure. Our calculation shows that the D_{3d} conformation is energetically accessible. It is gratifying to find that the LDA/NL method is able to provide the correct order of stability for two conformations of $Co_2(CO)_8$ with vastly different Co–Co and Co–CO bonding pictures.

We have calculated the amount of energy necessary to dissociate the C_{2v} bridged complex into two $Co(CO)_4$ fragment radicals by breaking the two equivalent $Co–C_{bridge}$ bonds. The homolytic dissociation of $Co_2(CO)_8$ requires 147.97 kJ mol^{-1} (NL/LSD) and is lower then the calculated D(Mn–Mn) value by only 25 kJ mol^{-1}. This finding contradicts most of the up-to-date experimental estimates for the D(Mn–Mn) - D(Co–Co) difference, with values ranging from 50 to 90 kJ mol^{-1}, Table I. On the other hand, a very recent analysis[37] of the hydrogenation energies for both $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ indicates that D(Co–Co) and D(Mn–Mn) differ by a maximum of 25 kJ mol^{-1}. We suggest that the experimental D(Co–Co) estimates of Table I are too low.

In the case of the C_{2v} structure of $Co_2(CO)_8$, the term "bond snapping enthalpy" refers to the snapping of the two $Co–C_{bridge}$ bonds, rather than the fracture of a single Co–Co linkage. The calculated ER_1 value of Scheme I for M = Co adopts a large value of 73.5 kJ mol^{-1}. Consequently, the bond snapping enthalpy (D_e(Co–Co) - $2ER_1$) equals 295 kJ mol^{-1}.

(b) The Geometrical and Thermodynamic Properties of R–Mn(CO)$_5$. In this section, we present results from DFT calculations on the geometry and thermochemistry of hydride, alkyl, and acyl derivatives of pentacarbonylmanganese(I), R–Mn(CO)$_5$. This family of compounds has been studied both theoretically[38–47] and experimentally. In recent theoretical investigations, emphasis has been put on the group migration reactions and the qualitative effects caused by different alkyl and acyl groups. In particular, the effects of hydride,[38,40] methyl,[38–40] ethyl,[46] trifluoromethyl,[38] difluoromethyl,[38,46] fluoromethyl,[38], phenyl,[38] and several larger alkyl groups were studied.[41–47] The relative strength of the M–H and M–CH_3 bonds in coordinatively saturated carbonyls of group 6 to 12 transition metal complexes has been studied previously by members of our group.[40b,c] The bond energies for the important hydride and methyl complexes of the R–$(CO)_4$M (M = Co, Rh, Ir, Ni$^+$) and R–$(CO)_5$M (M = Mn, Tc, Re, Fe$^+$) type have been calculated. In the above study, for the methyl complexes, the structures of $(CO)_4M^\bullet$ and $(CO)_5M^\bullet$ have been assumed to be isostructural with the hydrides. The calculated structural parameters of the $Mn(CO)_5H$ and $Co(CO)_4H$ complexes have been reported[17,48] and compared with the existing experimental values.

We have optimized fully the geometries of seven structures: hydride (Figure 3A), methyl (Figure 4A), fluoromethyl (Figure 5A), difluoromethyl (Figure 5B), trifluoromethyl (Figure 6A), formyl (Figure 7A), and acetyl (Figure 7B). Where available, selected structural parameters determined through electron diffraction studies are shown in Figure 3B ($HMn(CO)_5$), Figure 4B ($CH_3Mn(CO)_5$), and Figure 6B ($CF_3Mn(CO)_5$).

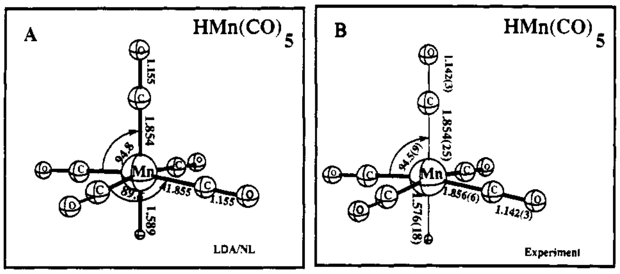

Figure 3. Molecular structure for $HMn(CO)_5$: (A) from LDA/NL calculations; (B) from electron diffraction.

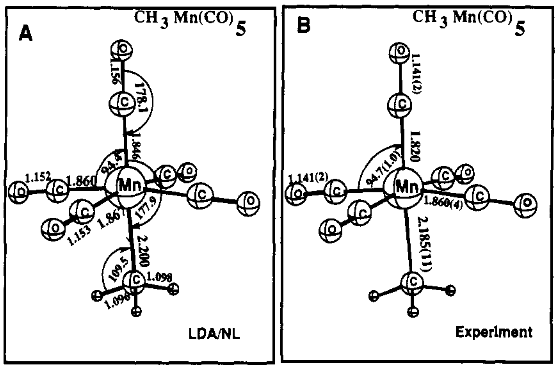

Figure 4. Molecular structure for $CH_3Mn(CO)_5$. (A) from LDA/NL calculations; (B) from electron diffraction.

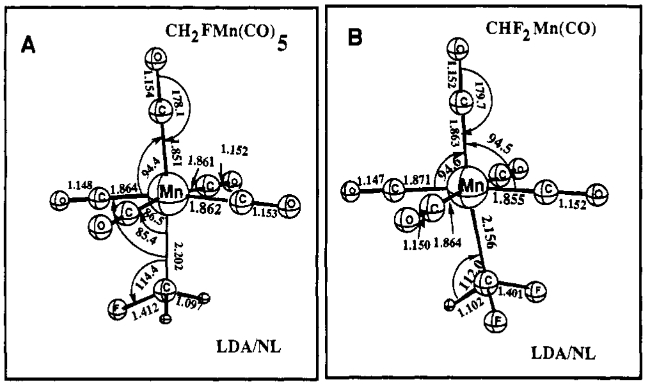

Figure 5. Molecular structures of $CH_2FMn(CO)_5$ and $CHF_2Mn(CO)_5$ from LDA/NL calculations: (A) $CH_2FMn(CO)_5$; (B) $CHF_2Mn(CO)_5$.

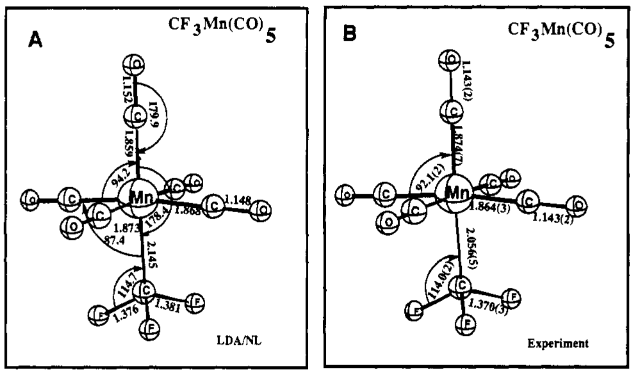

Figure 6. Molecular structure of $CF_3Mn(CO)_5$: (A) from LDA/NL calculations; (B) from electron diffraction.

The geometry of H–Mn(CO)$_5$ has been optimized within D_{4v} symmetry constraints, Figure 3A. The molecule adopts a distorted square-bipyramidal structure, with equatorial CO groups slightly bent toward the axial hydrogen atom. All bonding distances are calculated within 0.015 Å from those obtained by electron diffraction,[49] Figure 3B. In particular, the Mn–H distance of 1.589 Å was found to be 0.013 Å longer than the experimental value. Also, the theoretical estimate of the C_{eq}–Mn–C_{ax} angle agrees with experimental data to within 0.3°.

The geometry of H_3C–Mn(CO)$_5$ has been optimized within C_s symmetry constraints, Figure 4A. The Mn–CH_3 bond length is

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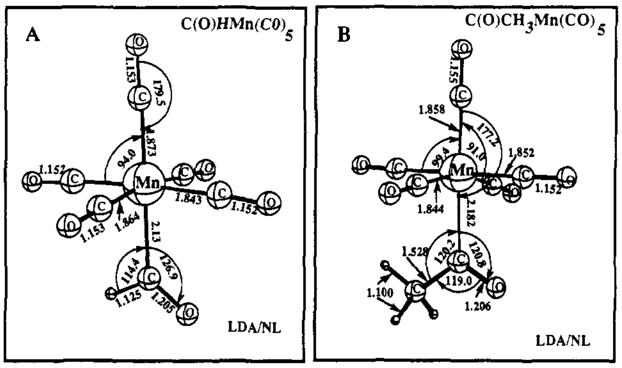

Figure 7. Molecular structure of $C(O)R–Mn(CO)_5$ from LDA/NL calculations: (A) $C(O)H–Mn(CO)_5$; (B) $C(O)CH_3–Mn(CO)_5$.

Table VI. Theoretical and Experimental R–Mn Bond Distances[a] for $R–Mn(CO)_5$

R	this work	*ab initio*[f]	PRDDO[f,g]	exptl
H	1.589	1.658	1.560	1.576[b]
CH_3	2.200	2.176	2.028	2.185(11)[c]
CH_2F	2.202		2.022	
CHF_2	2.156		2.023	
CF_3	2.145	2.126	2.012	2.056[d]
C(O)H	2.130			
$C(O)CH_3$	2.182		2.020	2.05[e]

[a] Bond lengths are in Å. [b] Reference 49. [c] Reference 50. [d] Reference 51. [e] Reference 52. This value refers to (acetyl)(benzoyl)tetracarbonylmanganate(I). [f] Reference 38. [g] Reference 39.

calculated to be 0.015 Å longer than the value of 2.185(11) Å determined by a gas-phase electron-diffraction study,[50] Figure 4B. The average $Mn–C_{eq}$ bond distance of 1.864 Å is in excellent agreement with the experimental value of 1.860(4) Å, see Figure 4B. The $Mn–C_{ax}$ separation is calculated to be 0.018 Å smaller than that of the average $Mn–C_{eq}$. The C–H bonds of the methyl group are all of normal length, ~1.1 Å. There is a slight, 4.4° tilt of the axial CO group away from the in-plane methyl hydrogen atom, probably due to the steric congestion.

We have also optimized a series of fluoromethyl complexes of pentacarbonylmanganese(I). Similarly to their methyl analogue, all three fluoromethyl complexes are characterized by an octahedral coordination about manganese. The Mn–R bond length does not seem to be affected by a substitution of a single methyl hydrogen by a fluorine atom. However, there is a noticeable bond shortening on going from $R = CH_2F$ to CHF_2, and then further to $R = CF_3$, see Figures 5A, 5B, and 6A. We calculate the $Mn–CH_3$ distance to be 0.055 Å longer than the $Mn–CF_3$ bond. A recent *ab initio* study affords a similar value of 0.05 Å,[38] Table VI. A survey[38] indicates that $M–CH_3$ bonds are between 0.05 and 0.08 longer than $M–CF_3$ bonds for a number of metals. However, in the present case, experiment[51] finds the $Mn–CF_3$ bond to be 0.13 Å longer than the $Mn–CH_3$ distance, Table VI. We are not able to rationalize the large deviation between experiment and theory for this $Mn–CF_3$ distance, Table VI. There is no available experimental data for the geometries of either $CH_2F–Mn(CO)_5$ or $CHF_2–Mn(CO)_5$. The results from the gas-phase electron-diffraction study[51] on the structure of $CF_3–Mn(CO)_5$ are summarized in Figure 6B.

Up to date, there have been *ab initio*[38] (Hartree–Fock) and PRDDO theoretical studies[38,39] on $R–Mn(CO)_5$. We compare theoretical and experimental Mn–R distances in Table VI. *Ab initio* calculations are only available for the two alkyls $R = CH_3$ and CF_3. However, our Mn–R distances compare well with the *ab initio* values for these two groups, Table VI. The PRDDO distances appear consistently to be too short by 0.1 Å to 0.15 Å.

We have calculated Mn–R bond dissociation enthalpies for all the systems in Figures 3–7. The results are summarized and compared to experiment in Table VIII. We have also been able to evaluate the relaxation energies, ER_2 and ER_3 in Scheme I. The term ER_2 represents the energy gain when the $(CO)_5Mn^\bullet$ radical rearranges from the geometry taken up in the $R–Mn(CO)_5$ complex into its equilibrium structure. Similarly, the ER_3 term corresponds to the amount of energy gained due to the reorganization of $R^\bullet$. Combining bond dissociation enthalpies, *D*(Mn–R), and ERs yields the bond snapping enthalpies, *E*(Mn–R), of Table VIII.

Table VII. Relaxation Energies[a] for $(CO)_5Mn^\bullet$ and $R^\bullet$ Radicals Calculated at LDA and LDA/NL Levels of DF Theory

	LDA		LDA/NL		
R	$(CO)_5Mn^\bullet$	$R^\bullet$	$(CO)_5Mn^\bullet$	$R^\bullet$	EHM[b] $R^\bullet$
H	–44.64	0.00	–36.13	0.00	0.0
CH_3	–5.86	–28.60	–4.78	–28.55	–24
CH_2F	–0.21	–30.08	–0.14	–24.45	–9
CF_2H	–1.16	–31.98	–0.28	–23.20	–3
CF_3	–9.46	–26.58	–10.74	–32.62	–26
C(O)H	–5.90	–3.20	–6.15	–1.58	
$C(O)CH_3$	–1.11	–6.16	–1.00	–4.89	–68

[a] Energies are in kJ mol^{-1}. [b] From extended Hückel method of ref 52.

Table VII collects the calculated ER's for the homolytic dissociation of $R–Mn(CO)_5$. The relaxation energies are not available experimentally. A previous study based on the extended Hückel method[52] has estimated ER_3 of R, and the EHM values are in reasonable agreement with our results for $R = CH_3$ and CF_3. It is interesting to note that the relaxation of the $Mn(CO)_5$ fragment (ER_2) is largest for R = H. The large value can be attributed to the large elongation of the $Mn–CO_{tr}$ bond trans to the hydride, Figure 3A. In fact, the ER_2 values correlate well with the $Mn–CO_{tr}$ distances and the trans-directing ability of R. ER_2 values have not been calculated by any other method.

The calculated values in Table VIII come from two levels of density functional theory corresponding to the simple local density approximation[7a] (LDA) and the more involved scheme in which nonlocal corrections[11a,12c] are added to LDA (LDA/NL). Clearly, the LDA values greatly overestimate most of the BDEs in comparison with experiment, column 4 of Table VIII. This observation is in accordance with all previous experience.[4a] Accordingly, in our quantitative discussion, we shall use the results from the LDA/NL calculations, column 5 of Table VIII.

The theoretical bond dissociation enthalpies are compared with the best available experimental data in Table VIII. The body of *D*(Mn–R) bond energies quoted in columns 7–11 of Table VIII relies on *D*(Mn–Mn) = 159 ± 21 kJ mol^{-1}, as established by Goodman *et al.*[53] in a photoacoustic calorimetry experiment. They are referred to as dependent estimates. We present in addition experimental *D*(Mn–R) enthalpies that are obtained without assuming a value for *D*(Mn–Mn). These independent estimates are given in column 6.

The calculated *D*(Mn–H) bond energy is higher than the dependent estimates by respectively 43 (CMC) and 22 kJ/mol (PIMS), but it agrees within the experimental accuracy of ±4 kJ mol^{-1} with the independent value due to Tilset and Parker.[32] The calculated $D(Mn–CH_3)$ and $D(Mn–CF_3)$ values are also seen to be higher than the corresponding dependent estimates. The average deviation is 20 kJ mol^{-1}. Independent estimates are not available for this series. One would expect the $D(Mn–CFH_2)$ and $D(Mn–CF_2H)$ enthalpies to fall in the range between $D(Mn–CH_3)$ and $D(Mn–CF_3)$. This is in fact roughly the case for our LDA/NL results, Table VIII. However, the experimental PIMS values for $D(Mn–CFH_2)$ and $D(Mn–CF_2H)$ are 40 kJ mol^{-1} lower than the corresponding PIMS estimates for $D(Mn–CH_3)$ and $D(Mn–CF_3)$. We are not able to understand this trend from our calculations or general chemical considerations and suggest that

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Table VIII. Calculated M–H and M–C Bond Snapping Enthalpies *E*(M–R) and Calculated and Experimental Bond Dissociation Enthalpies, *D*(M–R),[a] for M = Mn and Co

	calcd *E*(M–R)		calcd *D*(M–R)		exptl *D*(M–R)					
molecule	LDA	NL/LDA	LDA	NL/LDA	El-chem[c]	equil	RCS[d]	PIMS[e]	CMC[f]	KS[g]
$(CO)_5MnH$	368.32[b]	324.26[b]	323.68[b]	288.13[b]	284.2 ± 4				245 ± 10	264
$(CO)_5MnCH_3$	356.19	241.26	321.76	207.93				192 ± 11	187 ± 4	
$(CO)_5MnCH_2F$	300.51	220.90	270.21	196.30				139 ± 11		
$(CO)_5MnCHF_2$	309.00	226.03	275.95	202.55				144 ± 11		
$(CO)_5MnCF_3$	347.26	260.00	303.91	223.96				182 ± 11	203 ± 6	
$(CO)_5MnC(O)H$	279.96	204.35	270.86	196.62						
$(CO)_5MnC(O)CH_3$	276.07	194.64	271.02	188.75		182[h]	185 ± 8		160 ± 10	
$(CO)_4CoH$	333.01[b]	281.23[b]	331.63[b]	282.03[j]	280.1 ± 4	227[i]				213
$(CO)_4CoCH_3$	319.76	233.03	286.77	197.63						

[a] BDE's in kJ mol^{-1}. [b] Zero point energy correction included based on the frequency of the Mn–H bond of 1775 cm^{-1}. [c] Electrochemical in conjunction with acidity measurement. [d] RSC = reaction solution calorimetry. [e] PIMS = photoionization mass spectrometry. [f] CMC = Calvet microcalorimetry. [g] KS = kinetic study. [h] Equilibrium studies in solution. [i] Equilibrium studies in the gas phase. [j] Zero point energy correction included based on the frequency of the Co–H bond of 1956 cm^{-1}, ref 60.

the *D*($Mn-CFH_2$) and *D*($Mn-CF_2H$) enthalpies should be measured by alternative techniques.

Finally, we have calculated bond dissociation enthalpies for the two Mn–C(O)R complexes, where R = H and CH_3. There is no experimental data available for the formyl complex. The calculated *D*($Mn-C(O)CH_3$) enthalpy of 189 kJ mol^{-1} is in excellent agreement with values from both the RCS experiment[54a] (185 ± 8 kJ mol^{-1}) and equilibrium studies in solution (182 kJ mol^{-1}). Also, the agreement with the CMC value[54b] of 160 ± 10 kJ mol^{-1} is reasonably good, Table VIII.

The comparison between theory and the available body of experimental data indicates that the LDA/NL method is capable of estimating Mn–R bond energies for R = H, CH_3, CF_3, C(O)-CH_3 to within 20 kJ mol^{-1}. In fact, the agreement between theory and the dependent estimates for *D*(Mn–R) might be even better if one adopts a value for *D*(Mn–Mn) that is higher than the photoacoustic estimates of 159 ± 21 kJ mol^{-1}. Our calculations would suggest a *D*(Mn–Mn) enthalpy of 173 kJ mol^{-1}, Table IV, which is close to the experimental EI/PES energy of 171 kJ mol^{-1}, Table I. The current cost of frequency calculations from finite differences[18,19,25] of the energy gradients prohibits the evaluation of zero point corrections to *D*(Mn–R). The low experimental $Mn-CH_3$ frequency[55] of ~416 cm^{-1} would indicate that zero point corrections should be marginal, ~3 kJ mol^{-1} for R = CH_3, CF_3, and $C(O)CH_3$. The larger Mn–H frequency of 1775 cm^{-1} points to a more substantial zero point correction of ~10 kJ mol^{-1}.

The bond snapping energies, *E*(Mn–R), follow roughly the same trend as the bond dissociation enthalpies, *D*(Mn–R). We note that the strength of the Mn–H bond is much larger than that of the other Mn–R bonds. We have previously rationalized[15b,c] this by observing that the Mn–R alkyl bonds are weakened by repulsive 4-electron two-orbital interactions between 3d, 3s, and 3p metal orbitals on the one hand and C–H and C–C bonding pairs on the other. This type of destabilization is absent in hydrides since hydrogen is a single electron ligand.

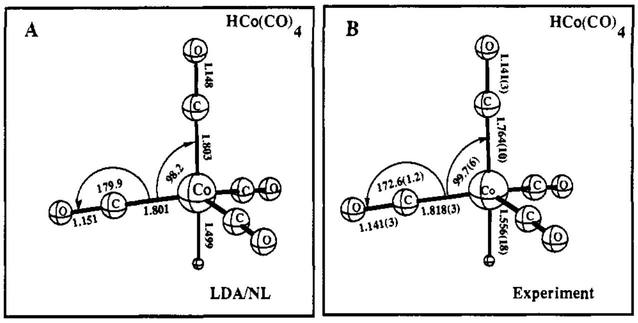

Figure 8. Molecular structure for $HCo(CO)_4$: (A) from LDA/NL calculations; (B) from electron diffraction.

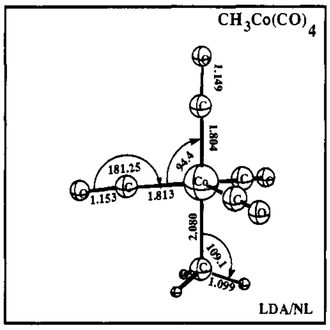

Figure 9. Molecular structure for $CH_3Co(CO)_4$ from LDA/NL calculations.

(c) The Geometrical and Thermodynamic Properties of R–Co-$(CO)_4$. We have fully optimized the structures of $H-Co(CO)_4$, Figure 8A, and $CH_3Co(CO)_4$, Figure 9. The geometry of H–Co-$(CO)_4$ has been optimized within the constraints of the C_{3v} symmetry point group. The molecule adopts a pseudo-trigonal-bipyramidal structure, with three carbonyl groups in the equatorial plane and the forth CO group and the hydride ligand in the axial positions. Other conformations with the hydride in an equatorial position are of higher energy[15g,56] by 60 kJ mol^{-1} or more. The equatorial CO groups are further seen to be leaning toward the hydride. The optimized structural parameters compare well with the data obtained from the electron diffraction study by McNeill and Scholer,[38] Figure 8B. The only exception is the *d*(Co–H) distance which we calculate to be 1.499 Å as opposed to the experimental value of 1.556(18) Å. We expect that at least some of the deviation might be due to experimental uncertainties in the Co–H distance. It is in general difficult to locate hydrogens next to a metal center in electron diffraction experiments. Previous *ab initio* HF studies of Antolovic and Davidson[57] in general generated too long bond distances (*d*(Co–H) = 1.71 Å, *d*($Co-C_{ax}$) = 2.02 Å, *d*($Co-C_{eq}$) = 1.96 Å).

The geometry of $H_3C-Co(CO)_4$ was optimized within C_s symmetry constraints. The $Co-CH_3$ bond distance was calculated to be 2.080 Å. The average *d*($Co-C_{eq}$) distance is 0.01 Å longer than the $Co-C_{ax}$ separation of 1.804 Å. There are no available experimental data, neither structural nor thermochemical, for $CH_3Co(CO)_4$. The calculated *d*($Co-CH_3$) distance of 2.080 Å is 0.581 Å longer than the *d*(Co–H) distance for $HCo(CO)_4$. This value is consistent with the experimental and theoretical difference between *d*(Mn–H) and *d*($Mn-CH_3$) of 0.609 and 0.611 Å, respectively. The available experimental data concern sub-

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Table IX. Relaxation Energies[a] for the $Co(CO)_4^{\bullet}$ and $R^{\bullet}$ Radicals Calculated at LDA and NL/LDA Levels of DF Theory

	LDA		NL/LDA	
R	$(CO)_4Co^{\bullet}$	$R^{\bullet}$	$(CO)_4Co^{\bullet}$	$R^{\bullet}$
H	−1.98	0.00	−1.86	0.00
CH_3	−4.70	−28.29	−7.15	−28.26

[a] Energies are in kJ mol^{-1}.

stituted $RH_2C–Co(CO)_4$ complexes, where R is a bulky ligand such as η^1-[η^6-(4-$MeC_6H_4CH_2$)]$Cr(CO)_3$.[58] The reported Co–$C(H_2R)$ bond length of 2.126(7) Å is somewhat longer than the Co–CH_3 separation of 2.08 Å calculated in this work. Some theoretical aspects of $H_3C–Co(CO)_4$ were analyzed by means of EHT by Cser *et al.*[59] The Co–CH_3 bond distance was calculated[59] to be 2.06 Å while the Co–C_{ax} and Co–C_{eq} bond lengths were reported at 1.74 and 1.80 Å, respectively.

We have calculated the Co–R bond dissociation enthalpies for both $HCo(CO)_4$ and $CH_3Co(CO)_4$. Calculated D(Co–R) values for the Co–H and Co–CH_3 bonds are shown in Table VIII. The theoretical bond dissociation enthalpy for the hydride complex of 293 kJ mol^{-1} compares well with the independent experimental estimate of 280 kJ mol^{-1} obtained by Tilset and Parker.[32] The D(Co–Co) dependent[30b] results from kinetic measurements (227 kJ mol^{-1}) and equilibrium studies in the gas phase (213 kJ mol^{-1}) are considerably lower. Thus our theoretical study and the work by Tilset and Parker[32] indicate that the Co–H bond is stronger than previously assumed, and quite similar to the Mn–H bond in $HMn(CO)_5$. Zero point energy correction of −11.68 kJ mol^{-1}, based on the experimental[60] vibrational frequency of 1956 cm^{-1} for the Co–H bond stretch, decreases the theoretical D(Co–H) value to 282.03 kJ mol^{-1} (Table VIII). With the use of the self-consistent modified extended Hückel (SC-MEH) MO method, Boudreaux[61] evaluated the Co–H bond dissociation enthalpy at 233.3 kJ mol^{-1} which, in the light of the most recent experiment[32] and this work, seems to be underestimated.

As for the $H_3C–Co(CO)_4$ complex, we have calculated the Co–CH_3 bond dissociation enthalpy to be 198 kJ mol^{-1}. It is thus 86 kJ mol^{-1} lower in energy than the Co–H bond energy. This calculated difference exhibits the same trend as observed for the manganese systems, where D(Mn–H) − D(Mn–CH_3) = 80.2 kJ mol^{-1}. The evaluation of the ER_2 and ER_3 relaxation energies of Scheme I enables us to calculate bond snapping energies. The modest ER values for $Co(CO)_4^{\bullet}$ and $R^{\bullet}$ are presented in Table IX and the E(Co–R) enthalpies in Table VIII.

(d) Hydrogenation of $Mn_2(CO)_{10}$ and $Co_2(CO)_8$. In order to check the results of our theoretical thermochemical work, we have performed a calculation on the reaction enthalpy for the hydrogenation of both $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ according to the reactions

$$Mn_2(CO)_{10} + H_2 \rightarrow 2(CO)_5Mn\text{–}H \qquad (7)$$

$$Co_2(CO)_8 + H_2 \rightarrow 2(CO)_4Co\text{–}H \qquad (8)$$

The corresponding expression for the reaction enthalpy is given by

$$\Delta H_{\text{hydrogenation}} = D(\text{M–M}) + D(\text{H–H}) - D(\text{M–H}) \qquad (9)$$

The reaction enthalpy, $\Delta H_{\text{hydrogenation}}$, is known experimentally with high accuracy for both $Mn_2(CO)_{10}$ and $Co_2(CO)_8$. It depends in addition according to eq 9 on the very quantities D(M–M) and D(M–H) which we have attempted to evaluate theoretically. It is thus clear that a comparison between the well-established experimental $\Delta H_{\text{hydrogenation}}$ values and theoretical estimates of $\Delta H_{\text{hydrogenation}}$ based on our calculated D(M–M) and D(M–R) values would afford an independent evaluation of the accuracy of the latter.

Table X. Calculated and Experimental Enthalpies of Hydrogenation of $Mn_2(CO)_{10}$ and $Co_2(CO)_8$

	calcd BDE[a]	exptl[f]
Mn–Mn	173.3[b]	
Mn–H	288.1[c]	
H–H	443.4[d]	
$\Delta H_{\text{hydrogenation}}$	40.5	34.6 ± 1
Co–Co	148.0	
Co–H	282.0[d]	
H–H	443.4[e]	
$\Delta H_{\text{hydrogenation}}$	27.4	19.7 ± 1

[a] BDEs in kJ mol^{-1}. [b] Based on empirical ν(Mn–Mn) = 160 cm^{-1}. [c] Based on empirical ν(Mn–H) = 1775 cm^{-1}. [d] Based on empirical ν(Co–H) = 1956 cm^{-1}. [e] Based on empirical ν(H–H) = 4401 cm^{-1}. [f] Reference 46.

The bond dissociation enthalpies used in this evaluation come from the LDA/NL calculations in Table VIII, and we have in addition carried out LDA/NL calculations on D(H–H). The D(M–H) and D(H–H) enthalpies have been corrected for the zero-point energy, based on the empirical vibrational frequency of 1775 cm^{-1} for the Mn–H bond in $(CO)_5Mn–H$ and 4401 cm^{-1} for the H–H bond stretch. Finally, the D_e(Mn–Mn) enthalpy of 174.2 kJ mol^{-1} has been corrected to D_0(Mn–Mn) = 173.3 kJ mol^{-1} according to the low-frequency vibration at 160 cm^{-1} for the Mn–Mn bond in the decacarbonyldimanganese complex.[21] We calculate the $\Delta H_{\text{hydrogenation}}$ of the $Mn_2(CO)_{10}$ complex to be 40 kJ mol^{-1}. The theoretical hydrogenation enthalpy $\Delta H_{\text{hydrogenation}}$ is close to the value of 34.7 ± 1 kJ mol^{-1} obtained in the recent experimental study by Klingler and Rathke,[37] Table X. Similarly, our theoretically determined $\Delta H_{\text{hydrogenation}}$ for the $Co_2(CO)_8$ complex of 27.4 kJ mol^{-1} agrees reasonably well with the empirical value[37] of 19.7 kJ mol^{-1}, Table X. The internal test performed here indicates at least that the LDA/NL method is capable of calculating reaction enthalpies for organometallic reaction steps.

IV. Concluding Remarks

The present investigation seems to indicate that the LDA/NL method is capable of calculating metal–carbon and metal–hydrogen bond energies with an accuracy of at least 20 kJ mol^{-1}. A more accurate assessment of the error limit was not possible due to the uncertainty in the experimental data. The present investigation favors a dissociation energy of 173 kJ mol^{-1} for the Mn–Mn bond in $Mn_2(CO)_{10}$. This value is in line with a more recent experimental estimate based on EI/PES techniques,[30a] Table I, but somewhat higher than older experimental values. The LDA/NL calculations indicate that the Co–Co bond in $Co_2(CO)_8$ should be considerably stronger (~148 kJ mol^{-1}) than previously suggested (64–88 kJ mol^{-1}). The geometries optimized by LDA/NL agree well with experimental structures. The deviations are 0.015 Å for M–M and M–ligand distances and 2° for ligand–metal–ligand bond angles. The calculated reaction enthalpies for the hydrogenation of $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ are within 4 kJ mol^{-1} of the experimental values. Thus, the LDA/NL method should be of use in estimating enthalpies for organometallic reactions. It is finally gratifying to find that the LDA/NL method is able to provide the correct order of stability for the two conformations of $Co_2(CO)_8$ with vastly different Co–Co and Co–CO bonding pictures. We have previously[15] made use of nonlocal calculations in thermochemical studies. However, these studies did not include the nonlocal correction[12c] to the LDA correlation energy. We attribute the improved agreement with experiment to the inclusion of nonlocal correlation corrections.

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