is interesting to note also that the PMO model predicts the charge density at the new bond point to be given by, using the approximations mentioned above,

$$\rho^1(x^1) = \rho^0(x^1) + \delta q \rho_i(x^1)$$
$$= \rho^0(x^0) + \lambda(x^1 - x^0)^2/2 - c\delta\alpha_X\rho_i(x^1)/\lambda$$

$$\Rightarrow \quad \delta\rho = c^2\delta\alpha_X{}^2/2\lambda - c\delta\alpha_X\rho_i(x^1)/\lambda \quad (15)$$

so that no simple linear correlation between $\rho(x)$ and electronegativity of the substituent is expected. The computations show (see Figure 6) that none is found.

In summary, it has been shown that the theory of atoms in molecules based on the electron distribution provides a useful tool for investigating in a quantitative manner the extent to which the predictions of qualitative orbital models concerning the changes in the electronic structure of selected systems are realized. Conversely, it has been shown that with a little thought and the use of "back of the envelope" calculations, trends in the well-defined properties of the electron distribution arising from the theory of atoms in molecules can be accounted for in a manner consistent with current models of molecular electronic structure. Further studies will extend this approach to the analysis of trends in energies of reaction of ethylenes and to other groups.

Migratory Aptitude of Hydride and Methyl toward Carbon Monoxide, Thiocarbonyl, and Carbene in RMn(CO)₄XY (XY = CO, CS, CH₂; R = H, CH₃). A Theoretical Study by the Hartree–Fock–Slater Transition-State Method

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Contribution from the Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4. Received June 24, 1985

Abstract: A theoretical study based on the Hartree–Fock–Slater method has been carried out on the intramolecular migration of hydride and methyl toward CO, CS, and CH_2 in $RMn(CO)_4XY$ (R = H, CH_3; XY = CO, CS, CH_2). The elusive hydride migration reaction to CO with a calculated enthalpy of $\Delta H_4 = 159$ kJ mol^{-1} was found to be considerably more endothermic than the corresponding methyl migration ($\Delta H_5 = 75$ kJ mol^{-1}) as well as the migrations of H and CH_3 to CS with calculated enthalpies of $\Delta H_{6b} = 71$ kJ mol^{-1} and $\Delta H_{6a} = 20$ kJ mol^{-1}, respectively. Exploratory calculations along the paths of the four migratory reactions revealed only minor activation barriers. It is concluded that the coordinatively unsaturated 16-electron formyl and acyl complexes $RC(O)Mn(CO)_4$ (R = H, CH_3) can interconvert readily from the square pyramidal monohapto conformation initially formed in the migration process to a dihapto structure and that the dihapto geometries are 79 and 68 kJ mol^{-1} more stable for formyl and acyl, respectively. The corresponding dihapto stabilizations for the thioformyl and thioacyl complexes are 130 and 136 kJ mol^{-1}, respectively. The hydride and methyl migrations to CH_2 with $\Delta H_{7b} = -113$ kJ mol^{-1} and $\Delta H_{7a} = -71$ kJ mol^{-1} were both found to be exothermic processes.

The intramolecular migration (1) of an alkyl or aryl group R from a metal center to a cis carbon monoxide ligand
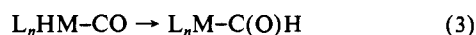
$$L_nRM\text{-}CO \rightarrow L_nM\text{-}C(O)R \quad (1)$$
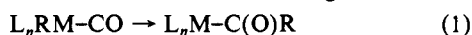
comprises among the class of organometallic shift reactions 2

$$L_nXM\text{-}Y \rightarrow L_nM\text{-}Y\text{-}X \quad (2)$$
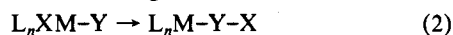
where a group X bound to the metal center migrates to an unsaturated ligand Y (Y = C_2, CO_2, C_2H_4, etc.), one of the more synthetically useful and well-studied[1,2] examples.

The corresponding shift reaction (3)

$$L_nHM\text{-}CO \rightarrow L_nM\text{-}C(O)H \quad (3)$$

with hydride instead of alkyl has, although inferred[3] in substituted reactions on $HMn(CO)_5$ and $HCo(CO)_4$, proven to be rather elusive, and it has in spite of considerable efforts[4] only been possible to detect a 1,2-shift rearrangement (3) in a hydrido metal carbonyl to the corresponding formyl complex conclusively in a few cases.[5]

The apparent poor migratory aptitude of hydride toward CO (3) in comparison to methyl seems surprising in view of the fact that hydride appears[6] to be on a par with methyl as a migratory group toward other ligands such as CO_2, CS_2, CS, and CH_2. Recent experimental investigations[4a,7] have indicated that (3)

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might be too endothermic compared to (1), as well as other migratory reactions (2) involving either hydride or methyl, but other explanations[2a] for the apparent inability to synthesize formyl complexes via (3) have also been given.
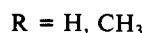
There are two main points that we have attempted to address here in our theoretical study based on the Hartree–Fock–Slater method.[8,9] The first point is concerned with whether the elusive 1,2-hydride shift reaction
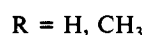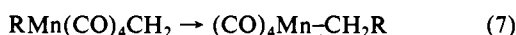
$$HMn(CO)_5 \rightarrow (CO)_4Mn-C(O)H \qquad (4)$$

in comparison with the well-studied[1] and documented 1,2-methyl shift reaction

$$CH_3Mn(CO)_5 \rightarrow (CO)_4Mn-C(O)CH_3 \qquad (5)$$

in fact has a substantially higher enthalpy. The second point is concerned with whether the apparently facile[6] hydride and methyl migration reactions to either CS or CH_2, modeled here by

$$RMn(CO)_4CS \rightarrow (CO)_4Mn-C(S) \qquad (6)$$

$$R = H, CH_3$$

and

$$RMn(CO)_4CH_2 \rightarrow (CO)_4Mn-CH_2R \qquad (7)$$

$$R = H, CH_3$$

have a smaller reaction enthalpy than (4). We have, however, also attempted to trace the energy profile for the different migration reactions in order to assess whether (4) has a substantially higher activation barrier than any of the migration reactions 5–7.

Computational Details

Our calculations were all based on the Hartree–Fock–Slater[8] (HFS) model as implemented by Baerends et al.[9] This method has been used extensively together with the generalized transition-state method[10] in calculations[11] on bond energies and bond distances of transition-metal systems.

An uncontracted triple-ζ STO basis[12] set was used for 1s on H as well as 2p and 2s on C, O, S and 3s, 3p, 3d, 4s, and 4p on the central metal M with an additional 2p polarization function on H (ζ = 1.0) and 3d polarization function on C, O, and S (ζ_C = 2.5, ζ_O = 2.0, and ζ_S = 1.5), in order to expand the molecular orbitals. The electron in shells of lower energy on C, O, S, and M were considered as core electrons and treated by the frozen-core approximation according to the procedure by Baerends et al.[9] The total molecular electron density was further fitted in each SCF iteration by s, p, f, d, and g STO's centered on each of the atoms in order to represent the Coulomb and exchange potentials accurately.

Known experimental structures were adopted for the calculations on $RMn(CO)_5$ (R = H,[13] CH_3[14]). The structures for $RMn(CO)_4CS$ and $RMn(CO)_4CH_2$ were generated from RMn-

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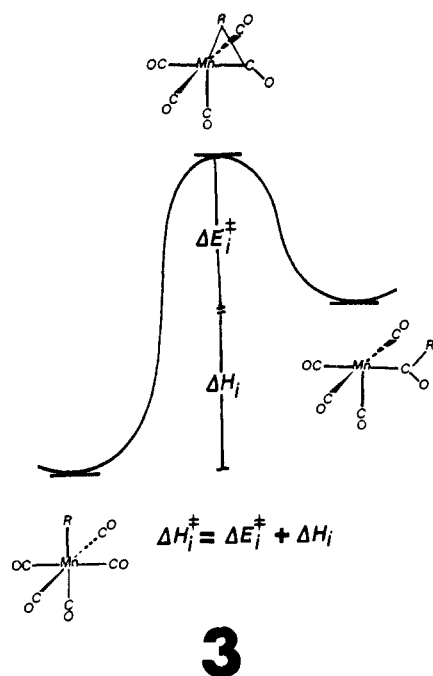
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(13) La Placa, S.; Hamilton, W. C.; Ibers, J. A.; Davidson, A. *Inorg. Chem.* **1969**, *8*, 1928. The key geometrical parameters were R(Mn–H) = 1.60 Å, R(Mn–C)$_{eq}$ = 1.85 Å, R(Mn–C)$_{ax}$ = 1.83 Å, R(C–O) = 1.13 Å, ∠C$_{eq}$–Mn–C$_{ax}$ = 96°.

(14) Seip, H. M.; Seip, R. *Acta Chem. Scand.* **1970**, *24*, 3431. The key geometrical parameters were R(Mn–CH$_3$) = 2.19 Å, R(Mn–C)$_{eq}$ = 1.85 Å, R(Mn–C)$_{ax}$ = 1.83 Å, R(C–O) = 1.13 Å, ∠C$_{eq}$–Mn–C$_{ax}$ = 96°.

$(CO)_5$ by replacing a cis CO ligand with CS and CH_2, respectively, using the optimized distances R(M–CS) = 1.83 Å and R(M–CH$_2$) = 1.95 Å, with R(CS) = 1.54 Å, R(CH) = 1.12 Å and HCH = 120°. For $RC(O)Mn(CO)_4$, $RC(S)Mn(CO)_4$, and $RCH_2Mn(CO)_4$, the $Mn(CO)_4$ framework was taken to be the same as in the parent hydride and methyl systems with the RCO and RCS angles fixed at 120°. In $RCH_2Mn(CO)_4$ all HCH angles were tetrahedral with R(CH) = 1.08 Å. All complexes had a low-spin electron configuration with a singlet ground-state.

Migratory Aptitude of Hydride and Methyl toward Carbon Monoxide in $RMn(CO)_5$ (R = H, CH_3), and the Structure of $RC(O)Mn(CO)_4$

The carbonylation process (8)

$$CH_3Mn(CO)_5 + CO \rightarrow CH_3C(O)Mn(CO)_5 \qquad (8)$$
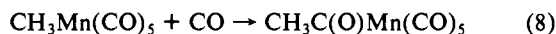
in which one carbon monoxide molecule is inserted into the $Mn-CH_3$ bond is facile and exothermic with an enthalpy[7b] of ΔH_8 = -54 kJ mol^{-1}. The rate-determining step in (8) is assumed[1] to be the intramolecular migration of the methyl groups 1a to one

1a   1b   2a   2b
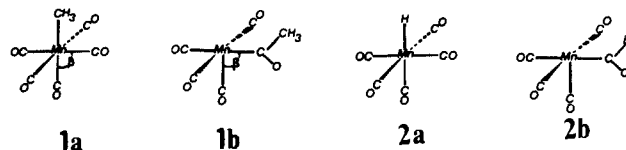
of the cis CO ligands, affording the coordinatively unsaturated 16-electron acyl complex $CH_3C(O)Mn(CO)_4$ **1b**, which then subsequently will bind the incoming CO at the site vacated by the migrating CH_3 group.

The observed activation energy[1e] for the migratory step 1a → 1b is ΔH_5 = 59 kJ mol^{-1}. The carbonylation reaction where carbon monoxide is alkylated to form an acyl group (8) is a key step in several[6] catalytic processes.

The carbonylation process (9) where a carbon monoxide molecule is inserted into the Mn–H bond

$$HMn(CO)_5 + CO \rightarrow HC(O)Mn(CO)_5 \qquad (9)$$

to form a formyl complex appears on the other hand not to be viable except in a few cases,[5] and most formyl complexes have in fact been prepared[4a] by intermolecular hydride transfer rather than by (9) where the intramolecular hydride migration 2a → 2b would be involved.

The apparently poor migratory ability of hydride toward CO (4) in comparison with methyl (5) is, as already mentioned, somewhat surprising since hydride is known to be as good a migratory group as methyl toward other ligands,[6] notably C_2H_4, CS, and CH_2. Berke and Hoffmann have[2a] in their general study on the migratory insertion process addressed this problem by calculating, at least in part, the reaction profile 3 for (4) as well as (5) within the extended Hückel approximation. Berke and Hoffmann found that a calculated activation energy of ΔH_4^* = 67 kJ mol^{-1} for the hydride migration (4) and ΔH_5^* = 82 kJ mol^{-1} for the methyl migration (5) that hydride might be a better migratory group than methyl toward CO and suggested that the formyl intermediate **2b**, after in fact being formed, suffers a rapid homolytic or heterolytic decomposition in contrast to the methyl intermediate **1b**.

We have at the HFS level of approximation calculated the energy of **1b** relative to **1a** as well as the energy of **2b** relative to **2a** while optimizing some of the unknown key geometrical parameters for the acyl and formyl complexes **1b** and **2b** with β fixed at 90°; see Figure 1. We find the hydride migration 2a → 2b with a calculated enthalpy of ΔH_4 = 159 kJ mol^{-1} to be considerably more endothermic than the corresponding methyl migration 1a → 1b for which the calculated enthalpy is ΔH_5 = 75 kJ mol^{-1} and attribute, based on an analysis of the calculated results, the order $\Delta H_5 < \Delta H_4$ found here to the Mn–H bond in **1a** being stronger (by 49 kJ mol^{-1}) than the Mn–CH$_3$ bond in **2a**.

The apparently poor migratory aptitude of hydride can thus in view of our HFS calculations partly be rationalized in terms of the unfavorable overall energetics (ΔH_4) for the hydride mi-

3

Figure 1. Structures and energies of $CH_3C(O)Mn(CO)_4$ and $HC(O)$-$Mn(CO)_4$. The energies (kJ mol^{-1}) are relative to the parent CH_3Mn-$(CO)_5$ and $HMn(CO)_5$ molecules, respectively. Optimized bond distances in Å. Assumed bond distances are indicated by parenthesis. The $Mn(CO)_4$ framework for all four structures was the same as for HMn-$(CO)_5$, and the HCO and CH_3–CO angles are all 120°: (A) monohapto structure of $CH_3C(O)Mn(CO)_4$; (B) monohapto structure of $HC(O)$-$Mn(CO)_4$; (C) dihapto structure for $CH_3C(O)Mn(CO)_4$; (D) dihapto structure for $HC(O)Mn(CO)_4$ with all geometrical parameters except $R(C–H)$ taken from the optimized dihapto structure of $CH_3C(O)Mn$-$(CO)_4$.

gration reaction (4). Whether the hydride migration is disfavored even further by an activation barrier, ΔE^* of 3, can only be assessed tentatively here as we, in spite of considerable efforts[15] in that direction, are unable, efficiently, to evaluate a minimum energy reaction path where all degrees of freedom are optimized along the reaction coordinate. We have, however, calculated the energy profiles for the two migration reactions along the paths traced by Berke and Hoffmann in ref 2a. The activation barriers ΔE^* calculated along the two paths are, as in the extended Hückel study, modest, 6 kJ mol^{-1} for (4) and 11 kJ mol^{-1} for (5), and the fact that we in (4) and (5) can proceed along the continuous paths of ref 2a from **1a, 2a**, to **1b, 2b** without significant activation barriers leads us to believe that the actual activation barriers along the minimum energy paths too must be small.
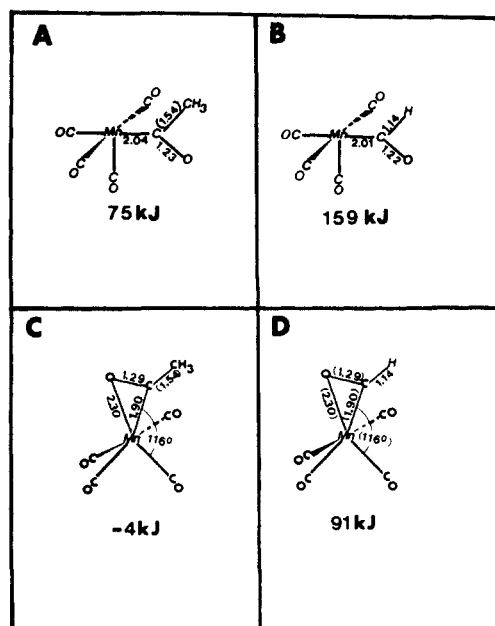
The degree to which the 16-electron acyl complex $CH_3C(O)$-$Mn(CO)_4$ rearranges once it is formed in the rate-determining migratory step (5) of (8) prior to the coordination of the incoming CO ligand has obvious implications for the stereochemistry of the overall carbonylation process (8). Kinetic investigations[1] in THF/acetone solution, including an elegant ^{13}C NMR experiment by Flood et al.,[1d] indicate that the incoming CO ligand is coordinated at the site vacated by the migrating CH_3 group without isomerization of $CH_3C(O)Mn(CO)_4$.

The ground-state equilibrium structure of $CH_3C(O)Mn(CO)_4$ is not known with certainty although McHugh and Rest[1c] from IR measurements on $CH_3C(O)Mn(CO)_4$, generated a photolysis of $CH_3C(O)Mn(CO)_5$ in the gas phase, tentatively inferred that $CH_3C(O)Mn(CO)_4$ had a pseudo-C_{2v} bipyramidal structure with the acyl group either equatorial **4b** or in a dihapto conformation

4e   **4a**   **4b**   **4c**   **4d**
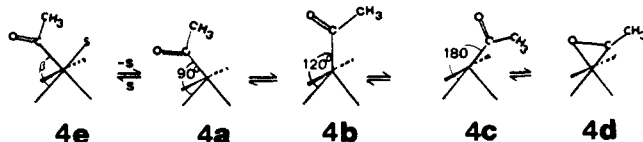
4d, and it is not clear whether the kinetic solution experiments[1d] indicate that $CH_3C(O)Mn(CO)_4$ as its equilibrium geometry has the square pyramidal structure **4a** (**1a**) or whether in fact the acyl complex once formed in conformation **4a** is prevented from further rearrangement to more favorable structures, **4b** or **4d**, by high isomerization barriers or the blocking of incoming solvent molecules, S, **4a** → **4e**.

We have, in some detail, studied the relative energies of conformation **4a** through **4d** as well as the energetics of their in-

terconversion. The energy profile for the path along **4a** → **4b** → **4c** where β gradually is changed from 90° to 180° is shown in Figure 2A. The bipyramidal structure **4b** is 13 kJ mol^{-1} above **4a** in energy whereas the square pyramidal structure **4c**, where the acyl oxygen points toward the vacant site, is 20 kJ mol^{-1} below **4a** in energy. The interconversion between the structures **4a, 4b**, and **4c** is seen in Figure 2A to be relatively facile. The structure **4c** can further, as shown in Figure 2B, relax to the dihapto conformation **4d** without any barrier, and **4d** is a full 79 kJ mol^{-1} below **4a** in energy. The corresponding dihapto stabilization for $HC(O)Mn(CO)_4$ was 68 kJ mol^{-1}; see Figure 1D.
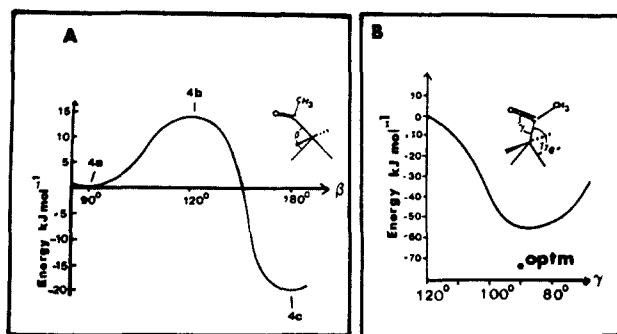
The present set of HFS calculations would indicate that $CH_3C(O)Mn(CO)_4$ as its equilibrium structure has the dihapto geometry **4d** and that there is a low energy path **4a** → **4b** → **4c** → **4d** from **4a** to **4d**. The observation that the $CH_3C(O)Mn(CO)_4$ framework in solution retains the conformation **4a** prior to the coordination of an incoming CO ligand must thus, in our opinion, be explained by the blocking of a solvent molecule, **4a** → **4e**. We note in support for our conclusion concerning the equilibrium geometry of $CH_3C(O)Mn(CO)_4$ that Roper et al.[16] have determined the 16-electron d^6 acyl complex $CH_3C(O)RuI(CO)(PPh_3)_2$ to have a dihapto structure. The metal to acyl oxygen distances in $CH_3C(O)Mn(CO)_4$ (see Figure 1C) as well as $CH_3C(O)$-$RuI(CO)(PPh_3)_2$ are much longer than the metal to acyl carbon distances, suggesting relatively weak dihapto interactions ($\sim$80 kJ mol^{-1}) in comparison to the interactions in η^2-acyl complexes[17] of zirconium, where the two distances are nearly the same.

Our HFS calculations suggest further that the overall carbonylation reaction (8) in weakly coordinating solvents might be less stereospecific than[1d] in THF/acetone with isomerization of the $Mn(CO)_4$ framework prior to the coordination of an incoming CO ligand and that labeling experiments in "inert" solvents might be of interest. It should, however, be noted that coordinatively

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Migratory Aptitude of Hydride and Methyl

J. Am. Chem. Soc., Vol. 108, No. 4, 1986 615

Figure 2. (A) Energy of $CH_3C(O)Mn(CO)_4$ (kJ mol^{-1}) as a function of the C–Mn–C deformation angle β, with the energy zero point at $\beta = 90°$. (B) Energy of $CH_3C(O)Mn(CO)_4$ (kJ mol^{-1}) as a function of the Mn–C–O deformation angle γ, with the energy zero point at $\gamma = 120°$. Bond distances are those optimized for the monohapto structure. The point indicated by "optm" corresponds to the energy of the fully optimized dihapto structure.

unsaturated 16-electron ML_5 complexes have been predicted[1f] to bind even rare-gas atoms (Ar) with an estimated bond energy of 40 kJ mol^{-1}.

## Migratory Aptitude of Hydride and Methyl toward Thiocarbonyl in $RMn(CO)_4CS$ (R = H, CH_3), and the Structure of $RC(S)Mn(CO)_4$

Thiocarbonyl is in contrast to carbon monoxide quite susceptible to reductive hydrogenation by intramolecular hydride migration as demonstrated by Roper et al.[18a] in the carbonylation reaction 10

$$CO + HOs(CO)Cl(PPh_3)_2CS \rightarrow HC(S)Os(CO)_2Cl(PPh_3)_2 \tag{10}$$
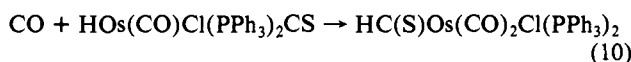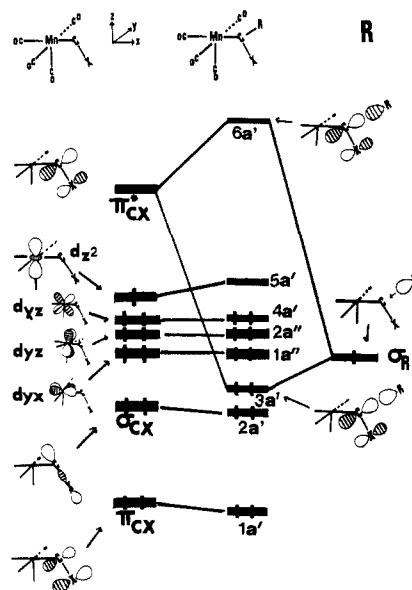
and analogous migration reactions with acyl groups are also known.[18b]

We have, in order to study this apparent disparity between CO and CS, calculated the enthalpies ΔH_{6a} and ΔH_{6b} for the two migration reactions **5a → 5b** and **6a → 6b**, respectively, optimizing
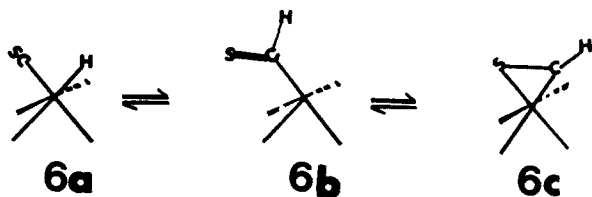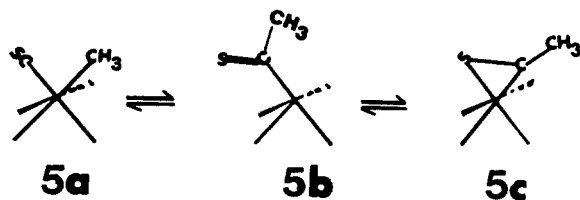
in the course some of the key geometrical parameters for HC-$(S)Mn(CO)_4$ and $CH_3C(S)Mn(CO)_4$; see Figure 3. We find that the thioformylation process **6a → 6b** interestingly enough with $\Delta H_{6b} = 71$ kJ mol^{-1} is considerably less endothermic than the elusive formylation reaction 4 with $\Delta H_4 = 159$ kJ mol^{-1}. The methyl migration in the thioacylation process **5a → 5b** with $\Delta H_{6a} = 20$ kJ mol^{-1} is likewise calculated to be more favorable than the corresponding methyl migration in the acylation process 5 with an enthalpy of $\Delta H_5 = 75$ kJ mol^{-1}. The considerably smaller enthalpy for the hydride migration **6a → 6b** toward CS compared to the hydride migration toward CO (4) does not reflect any

(18) (a) Collins, T.; Roper, W. R. *J. Organomet. Chem.* **1978**, *73*, 159. (b) Clark, G. B.; Collins, T. J.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1983**, *259*, 215.

Figure 3. Diagram for the interaction between the orbitals of C(X)-$Mn(CO)_4$, shown schematically to the left and σ_R and the σ_{CH_3} or $1s_H$ orbital shown to the right. The orbital levels of $RC(X)Mn(CO)_4$, shown in the middle, are labeled according to the C_s symmetry of $RC(X)Mn$-$(CO)_4$ as a' or a''.

Table I. Calculated C–H Bond Dissociation Energies (kJ mol^{-1}) for $HC(O)Mn(CO)_4$, $HC(S)Mn(CO)_4$, and $CH_3Mn(CO)_4$

	$HC(O)Mn(CO)_4$	$HC(S)Mn(CO)_4$	$CH_3Mn(CO)_4$
D(C–H)	78[a]	160[a]	341[b]

[a] Difference in energy between $HC(X)Mn(CO)_4$ (X = O, S) and the two fragments H and $Mn(CO)_4CX$, where the geometry of Mn-$(CO)_4CX$ was the same as the $Mn(CO)_4CX^-$ framework in HMn-$(CO)_4CX$. The calculations on H and $Mn(CO)_4CX$ were spin-unrestricted. [b] Difference in energy between $CH_3Mn(CO)_4$ and the two fragments H and $Mn(CO)_4CH_2$, where the geometry of $Mn(CO)_4CH_2$ was the same as the $Mn(CO)_4CH_2$ framework in $HMn(CO)_4CH_2$. The calculations on H and $Mn(CO)_4CH_2$ were spin-unrestricted. [c] Deformation of $Mn(CO)_4CX$ from the geometry of the $Mn(CO)_4CX$ framework in $HMn(CO)_4CX$ (assumed to be the ground-state geometry of $Mn(CO)_4CX$) to the geometry of the $Mn(CO)_4CX$ framework in $RC(X)Mn(CO)_4$ was calculated to require 110 kJ mol^{-1} for X = O and 136 kJ mol^{-1} for X = S. Deformation of $Mn(CO)_4CH_2$ from the geometry of the $Mn(CO)_4CH_2$ framework in $HMn(CO)_4CH_2$ (assumed to be the ground-state geometry of $Mn(CO)_4CH_2$ to the geometry of the $Mn(CO)_4CH_2$ framework in $Mn(CO)_4CH_3$ was calculated to require 77 kJ mol^{-1}.

substantial difference in the manganese–hydrogen bond strength between $HMn(CO)_5$ and $HMn(CO)_4CS$ but rather a stronger hydrogen–carbon bond in $HC(S)Mn(CO)_4$ compared to HC-$(O)Mn(CO)_4$ (Table I). The methyl–carbon bond is also stronger in $CH_3C(S)Mn(CO)_4$ compared to $CH_3C(O)Mn(CO)_4$, whereas the manganese–methyl bond strength roughly is the same in $CH_3Mn(CO)_5$ and $CH_3Mn(CO)_4CS$. We can readily understand the enhanced strength of the C–R bond in $RC(S)Mn(CO)_4$ compared to $RC(O)Mn(CO)_4$ by noting that the main stabilizing interaction in the C–R bond is between the vacant π^*_{CX}-type orbital **7a** of $C(X)Mn(CO)_4$ (X = O, S) (see Figure 3) and the σ_R-orbital, **7b**, consisting of 1s on H or the σ-orbital of CH_3, where π^*_{CX} and σ_R in **7a** and **7b**, respectively, are shown in the xz plane. The orbital **7a** is for X = S 1.3 eV lower in energy than for X = O and thus in the first case capable of a stronger interaction with σ_R, according to simple arguments[19] based on perturbational molecular theory, since the energy gap (see Figure 3) between π^*_{CX} and σ_R is smaller for X = S than for X = O.

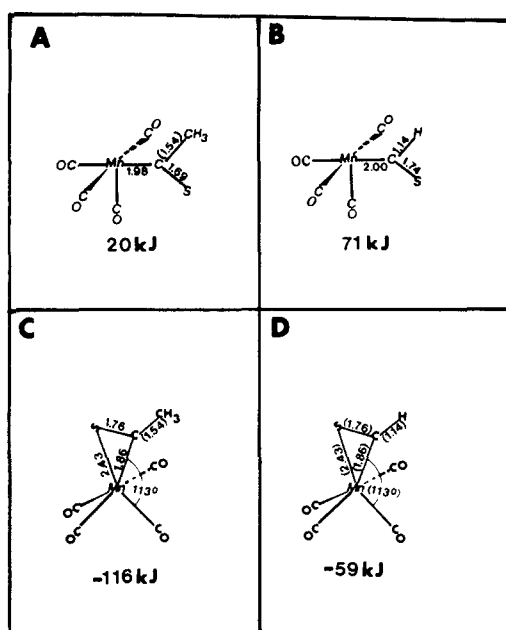The rationalization given here for the experimental observation that CS is more susceptible to reductive hydrogenation (and

(19) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. "Orbital Interactions in Chemistry"; Wiley: New York, 1985; pp 12–38.

7a   7b   7c   7d

7e   7f   7g   7h   7i
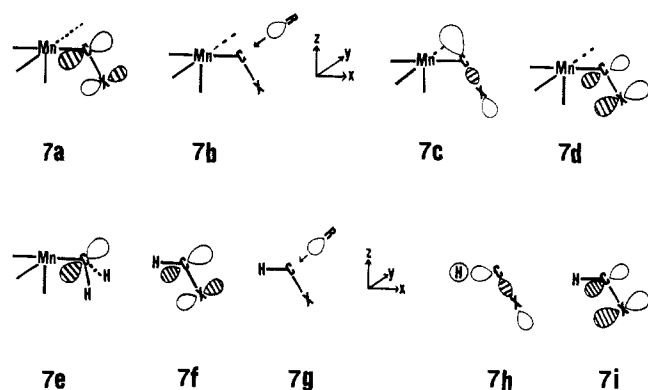
alkylation) by intramolecular migration than CO is based on calculated differences in the enthalpies (and activation energies[20]) of the migration reactions toward respectively CS and CO. It has, however, been proposed[21] that the facile reduction of CS compared to CO should be associated with an ability of the RCS groups to form stronger dihapto bonds to the metal center than the corresponding RCO groups. Dihapto structures such as **4d**, **5c**, and **6c** can, in our opinion, first be reached in an intramolecular migration reaction after the formation and subsequent rearrangement of a square pyramidal **4a** or bipyramidal **4b** intermediate and should thus not have any influence on the rate of the forward migration reaction, $RMn(CO)_4CX \rightarrow RC(X)Mn(CO)_4$. The dihapto formation might, however, to the extent that it can compete in solution with a solvent molecule for the vacant site, stabilize the intermediate $RC(X)Mn(CO)_4$ and influence the rate of the back-reaction $RC(X)Mn(CO)_4 \rightarrow RMn(CO)_4CS$ as well as the $RC(X)Mn(CO)_4/RMn(CO)_4CX$ equilibrium.

Few experimental data are available on the relative energies of monohapto and dihapto conformations, and we have, in order to gauge the ability of the thioformyl and thioacyl groups to form dihapto structures in comparison to the homologous formyl and acyl systems, calculated the stability of $CH_3C(S)Mn(CO)_4$ in conformation **5c** relative to **5a** and **5b** as well as the stability of $HC(S)Mn(CO)_4$ in **6c** relative to **6a** and **6b**; see Figure 4. The calculated dihapto stabilization for $HC(S)Mn(CO)_4$, **6b** → **6c**, was 130 kJ mol^{-1} and that of $CH_3C(S)Mn(CO)_4$, **5b** → **5c**, was 136 kJ mol^{-1}, both substantially larger than the dihapto stabilizations for the formyl and acyl complexes calculated as 68 and 79 kJ mol^{-1}, respectively, and significant enough to compete with solvent molecules for the vacant site. The dihapto formations should thus, for the thio systems where the enthalpies ΔH_{6a} and ΔH_{6b} are small, shift the equilibrium from the parent hydride **6a** and alkyl **5a** complexes to the thioacyl **5c** and thioformyl **6c** systems.

We would like, in closing this section, to note that the C–H bond of $HC(X)Mn(CO)_4$ is weak (Table I) compared to the C–H bond in $H-C(X)H$ (Table II) for X = O as well as X = S. The interaction between $1s_H$ and the acceptor orbital **7a** in the C–H bond of $HC(X)Mn(CO)_4$ is somewhat offset by four-electron repulsive interactions[19] between $1s_H$, **7b**, and the fully occupied orbitals **7c** and **7d** of $C(X)Mn(CO)_4$ (see Figure 3) where **7c** largely is composed of the σ_{CX}-orbital and **7d** primarily of the π-orbital on CX. That is, the bonding combination between $1s_H$ and π^*_{CX} (Figure 3) can interact with σ_{CX} and π_{CX}. The result is that σ_{CX} and π_{CX} as 1a and 2a, respectively, are slightly stabilized in $HC(X)Mn(CO)_4$ (see Figure 3), whereas the bonding combination between $1s_H$ and π^*_{CX} as 3a' is destabilized. The destabilization, however, outweighs, according to general considerations[19] based on perturbational molecular orbital theory (four-electron repulsive interactions),[19] the stabilizations, with the result that the C–H bond is weakened. The destabilization of the C–H bond will be large[19] for large overlaps between $1s_H$ and σ_{CX}

(20) Exploratory calculations along the paths of the two reactions revealed only modest activation barriers.

(21) Clark, G. B.; Collins, T. J.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1978**, *C23*, 157.

Figure 4. Structures and energies of $CH_3C(S)Mn(CO)_4$ and $HC(S)-Mn(CO)_4$. The energies (kJ mol^{-1}) are relative to the parent $CH_3Mn(CO)_4CS$ and $HMn(CO)_4CS$ molecules, respectively. Optimized bond distances in Å. Assumed bond distances are indicated by parenthesis. The $Mn(CO)_4$ framework for all four structures was the same as for $HMn(CO)_5$, and the HCS and CH_3–CS angles are all 120°: (A) monohapto structure of $CH_3C(S)Mn(CO)_4$; (B) monohapto structure of $HC(S)Mn(CO)_4$; (C) dihapto structure for $CH_3C(S)Mn(CO)_4$; (D) dihapto structure of $HC(S)Mn(CO)_4$ with all geometrical parameters except R(C–H) taken from the optimized structure of $CH_3C(S)Mn(C-O)_4$.

Table II. Calculated C–H Bond Dissociation Energies[a] (kJ mol^{-1}) for H_2CO, H_2CS, and CH_4

	H–C(O)H	H–C(S)H	H–CH₃
D(C–H)	354[c] (362)[b]	387[c]	429[d] (435)[b]

[a] Corresponding to dissociation of first hydrogen atom. [b] Standard experimental values. [c] Energy difference between HC(X)H (X = O, S) and the two fragments H and HCX. The calculations on H and HCX were spin-unrestricted. [d] Energy difference between CH_4 and the two fragments H and CH_3 with CH_3 planar. The calculations on H and CH_3 were spin-unrestricted.

and $1s_H$ and π_{CX} and for small energy gaps between $1s_H$ and σ_{CX} and $1s_H$ and π_{CX}. The orbitals **7a**, **7c**, and **7d** of $C(X)Mn(CO)_4$ find their match among the HCX-fragment orbitals in **7f**, **7h**, and **7i**, respectively, but **7h** is compared to **7c** of lower energy (2 eV) as it is strongly bonding in the HCX fragment. The **7h** orbital is further polarized by admixtures of π^*_{CX} so as to have a smaller overlap (0.10) with $1s_H$, **7g**, than **7c** (0.45). The four-electron repulsive interaction between $1s_H$ and **7h** is as a consequence less severe than the four-electron repulsive interaction between $1s_H$ and **7c**, with the result that the C–H bond is stronger in H–C(X)H than in $HC(X)Mn(CO)_4$, Tables I and II. Similar considerations apply to the strengths of the CH_3–C bonds in $CH_3C(X)Mn(CO)_4$ and $CH_3C(X)H$.

Migratory Aptitude of Hydride and Methyl toward Carbene in $RMn(CO)_4CH_2$

The 1,2 shift of a hydride[22] or alkyl[23] group

$$L_nRM{=}CH_2 \rightarrow L_nMCH_2R \tag{11}$$

as well as the reverse α-elimination reaction have been implied[24]

(22) (a) Cooper, N. J.; Green, M. L. J. *J. Chem. Soc., Dalton Trans.* **1979**, 1121. (b) Canestrani, M.; Green, M. L. J. *J. Chem. Soc., Dalton Trans.* **1982**, 1789.

(23) (a) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984. (b) van Leeuween, P. W. N. M.; Roobeek, C. F.; Huis, R. *J. Organomet. Chem.* **1977**, *142*, 243. (c) Trelkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650. (d) Lisko, J. R.; Jones, W. H. *Organometallics* **1985**, *4*, 944.

in several catalytic processes, such as the Ziegler–Natta polymerization and the olefin metathesis, as a key step. The migration step (11) is further observed to be more facile than the corresponding step toward carbon monoxide with the migratory aptitude of hydride and methyl given[23c] by H > CH$_3$.

We have calculated the enthalpy for the two migratory steps CH$_3$Mn(CO)$_4$CH$_2$ → CH$_3$CH$_2$Mn(O)$_4$ (**8a** → **8b**) and HMn(CO)$_4$CH$_2$ → CH$_3$Mn(CO)$_4$ (**9a** → **9b**). For the methyl mi-

8a   **8b**   **9a**   **9b**
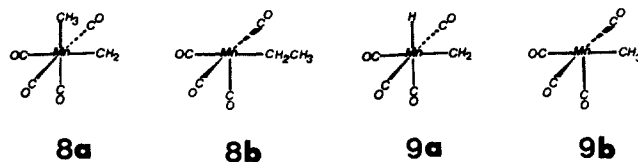
gration we find an enthalpy of ΔH_{7a} = –71 kJ mol^{-1} with the enthalpy for the hydride migration, **9a** → **9b**, given by ΔH_{7b} = –113 kJ mol^{-1}. The energetics are thus very favorable for both hydride and methyl migration toward carbene, and we find in contrast to the analogous reactions involving CO and CS that the kinetic products **8b** and **9b** are more stable than the parent hydride and methyl complexes **8a** and **9a**.

The favorable energetics are primarily the result of a stronger C–R bond in RCH$_2$Mn(CO)$_4$ than in RC(X)Mn(CO)$_4$; see Table I. The C–R bond in RCH$_2$Mn(CO)$_4$ is formed in a way similar to the C–R bond in RC(X)Mn(CO)$_4$ (see Figure 3) from the interaction between σ_R and the vacant p$_z$-carbene acceptor orbital **7e**, but the carbene orbital **7e** is capable of a stronger bonding interaction with σ_R than either π^*_{CO} or π^*_{CS}, **7a**, in the first case because it is of lower energy (1.4 eV) than π^*_{CO} and in the second case because it, although of the same energy as π^*_{CS}, is concentrated on the carbon terminus and thus able to overlap better with

σ_R than π^*_{CS} is. Of still further importance for the strong C–R bond in RCH$_2$Mn(CO)$_4$ is the fact that carbene lacks an occupied orbital analogous to π_{CX}, **7d**. The C–R bond in RCH$_2$Mn(CO)$_4$ is thus not destabilized by a repulsive interaction similar to that between σ_R and π_{CX}, **7d**; see Figure 3.

The trend in the enthalpies for the methyl and hydride migration calculated here parallels the observed[23c] order of migratory aptitute H > CH$_3$. The reverse reaction, α-elimination, is calculated to be endothermic, and such a reaction is in fact for methyl only observed[23d] to take place under forcing conditions. Hydride can, however, although for metal centers and coligands different from the one studied here, undergo migration to carbene and α-elimination reversibly.[22a] This point is currently under investigation.

Concluding Remarks

We find in contrast to a previous theoretical study,[2a] that the 1,2-hydride shift reaction 4 is considerably more endothermic than the corresponding 1,2-methyl shift reaction and explain the apparent inability of hydride to migrate toward CO on account of the reaction being too endothermic; see also ref 2h. We have further, from quantitative calculations and a qualitative analysis based on simple perturbational molecular orbital arguments,[19] tried to explain why the hydride migrations to CS (6) and CH$_2$ (7) in contrast to (4) are viable reactions.

Attempts experimentally[1c,d] to infer the structure of the coordinatively unsaturated intermediate CH$_3$C(O)Mn(CO)$_4$ of (8) have lead to conflicting conclusions. We find in contrast to a previous theoretical study[2a] that CH$_3$C(O)Mn(CO)$_4$ as its ground-state geometry has a dihapto structure **4d** and that CH$_3$C(O)Mn(CO)$_4$ after it is formed with the square pyramidal structure **4a** readily can rearrange to **4d**. We have finally reconciled those findings with the known stereochemistry[1b,d] of (8).

(24) (a) Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449. (b) Pettit, R.; Brady, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 6182. (c) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.