7 Hz, 1 Hz, H_{3s}), 2.2 (dd, J = 11, 1 Hz, H_{3a}), 1.4 (s, CH_3), 1.0 (s, CH_3).

Thermolysis of (η^3-C_5H_9)Co(CO)$_3$, 22, in a Sealed Tube. **22** was taken up in 0.5 mL of toluene-d_8 and sealed in vacuo (0.001 mm). ^{1}H NMR showed the sample remains unchanged for days at room temperature. The tube was heated to 80 °C for 10 min. ^{1}H NMR indicated **23** had grown in clearly at the expense of **22** (residual solvent signal used as a standard) in a 1:1 ratio. Prolonged heating established K_{eq} = 1.3 at 60 °C. **23**: ^{1}H NMR (toluene-d_8) δ 3.9 (qd, J = 7, 2 Hz, H_1), 3.05 (d, J = 2 Hz, H_{3s}), 2.6 (m, H_{3a}), 1.4 (s, CH_3), 0.9 (d, J = 7 Hz, CH_3).

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Carbonyl Insertion Reactions. 1. Structure and Formation of $(HFe(CO)_4)^-$, $((CO)_3FeCHO)^-$, and $((CO)_4FeCHO)^-$

G. Blyholder,* Kui-Ming Zhao, and M. Lawless

Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701

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Calculations within a MINDO framework have been made for $(HFe(CO)_4)^-$, $((CO)_3FeCHO)^-$, $((CO)_4FeCHO)^-$, and intermediate structures for hydride migration and CO addition. In contrast to previous speculation the bending of the equatorial CO ligands in $(HFe(CO)_4)^-$ toward the hydride ligand is found to be due to increased Fe–C bond strength in the axial CO ligand as the bending occurs. The effect of the hydride ligand on the bonding of the CO ligand and the effect of the CO ligands on the Fe–H bond are discussed. The instability of the formyl group in $((CO)_4FeCHO)^-$ is traced to the highest occupied molecular orbital being high in energy relative to other molecular orbitals, putting a large negative charge on the H atom, and being antibonding for the C–H bond. The calculated potential energy curve for the hydride migration from the Fe atom to a carbon atom indicates that the formyl complex $((CO)_3FeCHO)^-$ is 24–44 kcal/mol less stable than the metal hydride and has no stable potential well. This is in accord with the fact that this hydride migration has never been observed. Oxidation of the complex is calculated to promote the migration. Calculations for CO addition to $(HFe(CO)_4)^-$ to produce a formyl for the case of a concerted addition as the hydride migration occurs and for the case where the CO addition is a second step after the hydride has migrated to give a tetrahedral $((CO)_3FeCHO)^-$ have been made. The activation energies calculated vary from 27 to 31 kcal/mol. The activated complex occurs in all cases when the hydride ligand moved most of its way. The major factor in the activation energy is the hydride migration.

Introduction

There exists a substantial body of organometallic literature dealing with alkyl migration reactions to form acyls.[1] These reactions are important in heterogeneous and homogeneous catalysis as well as in stoichiometric organometallic synthesis. The smallest unit which might be considered to migrate is a hydrogen atom. Although many transition-metal alkyls readily migrate to an adjacent carbonyl to form an acyl, the rearrangement of a transition-metal hydride to a formyl has not been observed.[2-4] The first synthesis of a formyl complex was the synthesis of $((CO)_4FeCHO)^-$ from $Na_2Fe(CO)_4$ by Collman and Winter.[5] Subsequently, many transition-metal formyls have been reported but most have a half-life near room temperature in the range from seconds to a few days.[2] The reluctance of transition-metal hydrides to shift the hydrogen atom to a CO to give a metal formyl has not kept formyl complexes from being suggested as intermediates in the catalytic reduction of CO with H_2.[6-8] The considerable difficulty of a formyl formation step may be greatly reduced by the presence of Lewis acid electrophiles. The promotion of the alkyl migration reaction in $(RFe(CO)_4)^-$ by Na^+ is well-known.[9] Lewis acids have been shown to promote alkyl migration from metals to CO both in solution and on surfaces.[10,11] Oxidation of the metal has been found to induce alkyl migration to form an acyl.[12]

Relatively little theoretical attention has been given to transition-metal alkyl migration reactions to form acyls. Orbital usage has been looked at for some cases.[13] The stability of nickel formyl radicals (NiCHO) relative to NiH, NiCO, and other Ni species has been calculated.[14] In this paper the geometric and electronic structure of $(HFe(CO)_4)^-$ and $((CO)_4FeCHO)^-$ are examined. Calculations are

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Table I. Atomic Parameters for Iron

(a) Orbital Exponents[22]

s	p	d
1.3585	1.2[a]	3.7266

(b) Core Parameters (eV)[23]

W_{ss}	W_{pp}	W_{dd}
−102.13	−74.57	−133.28[a]

(c) Slater–Condon Parameters (eV)[23]

	(3d,3d)	(3d,4s)	(3d,4p)	(4s,4s)	(4s,4p)	(4p,4p)
F^0	17.727 86[a]	13.749 49	10.076 14	12.484 22	9.583 63	8.280 28
F^2	8.414 23		0.676 93		2.452 89	
F^4	5.106 33					
G^1			0.250 98		2.201 64	
G^2		1.384 66				
G^3			0.165 81			

[a] Value different from reference value.

Table II. Bond Parameters

bond	Fe–C	Fe–O	Fe–H
β	0.553	1.417	0.624
α	0.976	2.297	1.963

presented for points along the path of the hydrogen migration from the metal to the carbonyl in $(HFe(CO)_4)^-$ transforming to the formyl $((CO)_3FeCHO)^-$. Calculations are also presented for points along the path of CO addition to $(HFe(CO)_4)^-$ and $((CO)_3FeCHO)^-$.

Calculational Procedure

The calculations were done with a semiempirical SCF method which is a modification of MINDO referred to as MINDO/SR. The details of the method as well as its ability to handle a wide variety of compounds including large metal clusters have been reported previously.[15–18] The MINDO/SR procecure explicitly includes electron–electron repulsions and is parameterized to give bond energies and lengths for selected reference compounds in agreement with experimental values.

The computer program used is based on QCPE Program 290 by Rinaldi as modified by Schmidling[19] to incorporate MINDO/3. The Rinaldi program has automatic geometry optimization using analytically calculated gradients. The Schmidling version was modified to incorporate transition metals, symmetry,[20] and selective molecular orbital filling.

Atomic parameters for Fe are given in Table I. These parameters are the same as the ones used in $Fe(CO)_5$ calculations.[21] These parameters include small adjustments in the Fe 4p orbital exponent from the Clementi and Raimondi[22] value and in the d orbital energy and a Slater–Condon parameter by de Brouckere.[23] These adjustments were made to obtain better correlation between properties for diatomic molecules and clusters containing 12 iron atoms.

The bond parameters are given in Table II. In these calculations the β parameters for s, p, and d orbitals are the same. The variation of the p orbital exponent has the effect of taking care of differences in bonding between s and p orbitals. The bond parameters for Fe–H give the diatomic molecule FeH a binding energy of 68 kcal/mol and a bond length of 1.52 Å. The experimental values are not available, but our values are similar to those of other diatomic transition-metal hydrides and to ab initio calculations[24,25] for FeH.

Results and Discussion

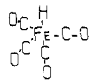
The central interest in this paper is the reaction

$$\underset{\text{I}}{(HFe(CO)_4)^-} \rightarrow \underset{\text{II}}{((CO)_3FeCHO)^-} \quad (1)$$

Although this reaction has never been definitely observed to occur, it has often been suggested to occur in both heterogeneous and homogeneous catalysis. The reaction that has been observed is

$$(RFe(CO)_4)^- + L \rightarrow (RC(O)Fe(CO)_3L)^- \quad (2)$$

where R is an alkyl group but not hydrogen. Whether the ligand, L, adds after the alkyl migration or during it in a concerted process has not been established for iron complexes. Also the hydride reaction might proceed through a different mechanism than the alkyl migration. Before getting into calculations for reaction 1 and its unstable intermediates, the calculated electronic structure and bonding in the observed compounds $(HFe(CO)_4)^-$ and $((CO)_4FeCHO)^-$ are presented and discussed.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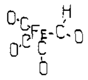
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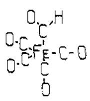
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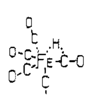
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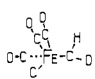
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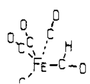
VI

Electronic Structure of $(HFe(CO)_4)^-$. The equilibrium bond lengths, bond orders, and atomic populations for $Fe(CO)_5$ and $(HFe(CO)_4)^-$ with two different sets of bond angles are given in Table III. The electronic structure of $Fe(CO)_5$ in this approximation has been discussed in detail previously[21] and is given here for comparison purposes. An X-ray diffraction study of $(HFe(CO)_4)^-$ shows the H atom in an axial position of an approximately C_{3v} symmetry molecule.[26] The equatorial Fe–C bond lengths in the calculation show a shortening from those in $Fe(CO)_5$ like those in the X-ray structure and other features are in reasonable agreement.

One interesting and previously discussed feature of $(HFe(CO)_4)^-$ is the bending of the equatorial CO's toward the axial hydride ligand. Line 3 in Table III gives our calculated equilibrium structure showing this bent structure, which is 0.8 kcal/mol more stable than the structure with 90° bond angles. Several previous explanations of this deformation have been offered,[25,26] but there have been no published calculations at a level which explicitly includes electron repulsion integrals as do these calculations. One paper after eliminating solid state and steric effects suggests the deformation of the equatorial CO's toward the axial hydride ligand is due to an attractive bonding interaction between the equatorial C atoms and the hydride ligand.[27] While indeed we see such an interaction in our

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Table III. Properties of $Fe(CO)_5$, $(HFe(CO)_4)^-$, and FeH

compound	∠(H–Fe–C), deg	equilibrium bond lengths, Å: Fe–C(eq)	Fe–C(ax)	C–O(eq)	C–O(ax)	FeH	two highest MO's, au
A. $Fe(CO)_5$[a]		1.83	1.82	1.16	1.16		
B. $(HFe(CO)_4)^-$ (I)	90	1.73	1.95	1.18	1.16	1.61	–0.14, –0.12
C. $(HFe(CO)_4)^-$ (I)	85	1.73	1.83	1.18	1.17	1.63	–0.14, –0.11
D. $(HFe(CO)_4)^-$ (I)[b]	81 ± 3	1.75 ± 4	1.72	1.15 ± 1	1.18	1.57	
E. FeH						1.52	

	bond orders: Fe–C(eq)	Fe–C(ax)	C–O(eq)	C–O(ax)	Fe–H	valence atomic pop.: Fe	C(eq)	C(ax)	O(eq)	O(ax)	H
A.	1.13	1.09	1.84	1.84		9.80	3.13	3.14	6.51	6.51	
B	1.24	0.83	1.70	1.80	1.10	9.85	2.99	3.23	6.70	6.58	1.19
C.	1.23	1.01	1.70	1.76	1.05	9.98	2.99	3.13	6.70	6.62	1.21
D.											
E.					1.26	7.85					1.15

[a] Trigonal bipyramid. [b] Experimental.

calculations, it is only of a very small magnitude. In the 90° structure the H–C(eq) bond order is 0.012 and only increases by 0.005 when the bent structure is formed. Likewise, in the partitioning of the energy into monatomic and diatomic terms the attractive H–C(eq) diatomic energy is only 0.041 au and increases by 0.006 au as the bending occurs. Thus this effect while real is small compared to other effects discussed below.

Another approach to explaining the deformation from 90° bond angles examines the bonding capability of the $Fe(CO)_4$ fragment as the equatorial CO's are bent out of the equatorial plane.[28] This approach has the bond to the special ligand (hydride in this case) as the determining factor in the deformation. It would have the FeH bond strengthened as the deformation occurs, and because the main factor is a lowering of the lowest unoccupied a_1 orbital in the $Fe(CO)_4$ fragment as the bending occurs, the highest occupied a_1 orbital in the final $(HFe(CO)_4)^-$ complex should decrease in energy as the bending occurs. Our calculations does not support either of these conclusions as upon bending the equatorial CO's toward the H atom, the Fe–H bond order decreases and the highest occupied a_1 orbital increases in energy. This difference in predicted behavior is presumed to be due to our inclusion of electron repulsion terms, the lack of which sometimes causes difficulty in otherwise beautiful arguments.

Examination of our results as the equatorial CO's are bent toward the hydride ligand indicates that the only major change is in the axial Fe–C bonding. The axial Fe–C bond distance decreases by 0.12 Å, the bond order increases by 0.18, and the diatomic energy increases by 0.15 au as the bending occurs. Thus the primary effect of the bending is not on the bonding to the nonstandard ligand in the axial position but is rather on the bonding to the axial ligand trans to the nonstandard ligand. As the equatorial CO's bend toward the hydride ligand, the center of charge of the complex shifts toward the hydride ligand and away from the axial CO ligand. This destabilizes the highest filled a_1 orbital by 0.01 au and reduces the electron density on the axial C atom, primarily in its 2s orbital. A major share of this reduction occurs in the highest filled a_1 orbital which is antibonding for the Fe–C(ax) bond. Thus the axial Fe–C bond is strengthened (as reflected in its bond order and bond distance) by reducing an antibonding contribution.

The effect of substituting a hydride ligand on the bonding of the remaining carbonyl ligands will now be considered. The simplest case is that shown in line 2 of Table III, where the carbonyl ligands all have the same bond angles as in $Fe(CO)_5$. The main effect of the hydride ligand is a trans effect to weaken the remaining axial Fe–C bond. This occurs because the hydride ligand is a stronger σ donor than CO and increases the number of electrons on the Fe atom. In comparing the molecular orbitals for $Fe(CO)_5$ and $(HFe(CO)_4)^-$ the bonding characteristics of the orbitals toward the axial Fe–C bond remain about the same except for the highest filled a_1 orbital. In $Fe(CO)_5$ this a_1' orbital contains a sizable contribution from the axial C s and p_σ orbitals but no contribution from Fe s and p_σ orbitals so it is nonbonding for the axial Fe–C bond. In $(HFe(CO)_4)^-$ due to the increased electron count on Fe caused by the hydride ligand donation, this a_1 orbital also has a contribution from the Fe s and p_σ orbitals which give an antibonding contribution to the axial Fe–C bond. In this manner the hydride ligand destabilizes the trans CO ligand. The bending of the equatorial CO ligands toward the hydride ligand ameliorates this trans effect as noted above.

Another effect of the hydride ligand is to strengthen the equatorial Fe–C bonds. The two highest filled e type levels in $Fe(CO)_5$ and $(HFe(CO)_4)^-$ are bonding to about the same extent so these do not contribute to this difference. The top a_1 type orbitals have little effect on the equatorial bonding but the next lower a_1' orbital in $Fe(CO)_5$ is nonbonding for the equatorial Fe–C bond due to no contribution in this orbital from appropriate Fe orbitals. In contrast the corresponding a_1 orbital in $(HFe(CO)_4)^-$ has a positive contribution to the equatorial Fe–C bonding due to increased Fe orbital contributions resulting from the hydride ligand donation.

The effect of the CO ligands on the Fe–H bond may be seen by comparing Fe–H to $(HFe(CO)_4)^-$ in lines 5 and 3 of Table III. Adding CO ligands puts more negative charge on the Fe and H atoms due to the donor properties of CO ligands. The Fe–H bond order decreases because of different orbital utilizations. In diatomic FeH the Fe s and p_σ orbital contributions all come in molecular orbitals with H s orbital contributions to increase the bonding. By contrast in $(HFe(CO)_4)^-$ some of the Fe s and p_σ contributions come in orbitals that contail little contribution from the H orbital so that these molecular orbitals contribute to Fe–C bonding but not to Fe–H bonding. The result of this changed orbital utilization is a weaker Fe–H bond in $(HFe(CO)_4)^-$ than in FeH.

Electronic Structure of $((CO)_4FeCHO)^-$. A formyl group, CHO^-, is a better σ donor than a CO ligand but not as good a σ donor as a hydride ligand. The negative charge donated by CO, CHO^-, or H^- is 0.35, 0.58, and 0.79 e,

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Table IV. Properties of $((CO)_4FeCHO)^-$, CH_3CHO, $((CO)_3FeCHO)^-$, and $((CO)_3FeCHO)^+$

	equilibrium bond lengths, Å							two highest MO's, au
	Fe–C(eq)	Fe–C(ax)	Fe–CHO	CO(eq)	CO(ax)	HC–O	C–H	
A. $((CO)_4FeCHO)^-$ (III)[d]	1.77	1.85	1.88	1.17	1.17	1.22	1.25	–0.17, –0.07
B. CH_3CHO						1.14		
C. $((CO)_3FeCHO)^-$ (II)[a,b]	1.75	1.89	1.76	1.17	1.17	1.23	1.30	–0.18, –0.06
D. $((CO)_3FeCHO)^-$ (II)[c,b]	1.75	...	1.78	1.17	...	1.23	1.29	–0.18, –0.06
E. $(HFe(CO)_4)^+$ (I)[a]	1.75	1.72	...	1.15	1.15	...	...	–0.60, –0.58
F. $((CO)_3FeCHO)^+$ (II)[a,b]	1.79	1.87	1.89	1.15	1.15	1.15	1.14	–0.54, –0.54

	bond orders							valence atomic pop.							
	Fe–C(eq)	Fe–C(ax)	Fe–CHO	CO(eq)	CO(ax)	HC–O	C–H	Fe	C(eq)	C(ax)	C(HO)	O(eq)	O(ax)	O(CH)	H
A.	1.19	1.00	1.09	1.76	1.79	1.54	0.78	9.88	3.03	3.15	3.23	6.62	6.58	6.73	1.46
B.						1.69	1.14				3.39			6.47	1.14
C.	1.22	1.00	1.30	1.75	1.79	1.51	0.68	9.62	3.02	3.18	3.14	6.63	6.57	6.78	1.41
D.	1.25	...	1.29	1.75	...	1.52	0.69	9.74	3.00	...	3.14	6.64	...	6.76	1.44
E.	1.27	1.22	...	1.90	1.91	...	0.94	9.76	2.98	2.97	...	6.39	6.37	...	0.77
F.	1.24	1.06	0.85	1.90	1.92	1.93	1.03	9.44	3.12	3.23	2.87	6.41	6.37	6.25	0.77

[a] $\angle(C_{eq}\text{–Fe–}C_{ax}) = 90°$. [b] x coordinate of H atom is 2.0 Å. [c] Approximately tetrahedral angles about Fe. [d] $\angle(\text{Fe–C–H}) = 111°$; $\angle(\text{Fe–C–O}) = 142°$.

respectively. The changes produced by substituting a formyl ligand for an axial CO ligand are similar to but not as great as those produced by a hydride ligand. These changes in bond lengths, bond orders, and atomic charges may be seen by comparing values in Tables III and IV. In view of the direct relations to changes produced by a hydride ligand, they need not be discussed in detail.

The formyl group in $((CO)_4FeCHO)^-$ has some noticeable differences from the formyl group in acetaldehyde as may be seen in Table IV. Much more negative charge is transferred onto the H atom in the metal complex where the H atom charge is –0.46 e than in acetaldehyde where the aldehyde hydrogen has a charge of –0.14 e. The highest filled molecular orbital in the metal complex makes a large contribution to the hydrogen charge and is strongly antibonding for the C–H bond. This is reflected in the low C–H bond order of 0.78 in the metal complex compared to 1.14 in acetaldehyde. The nature of this highest filled molecular orbital explains the strong hydride donor properties of the metal formyl complex in chemical reactions.[2]

Hydride Migration. First the hydride migration will be considered for the case where the angular relations of all of the carbon atoms with respect to each other are kept fixed and next the case where the angles are allowed to relax. In this latter case the end results is $((CO)_3FeCHO)^-$ with approximately tetrahedral angles about the Fe atom. The case with fixed C–Fe–C angles is representative of the situation where the addition of another ligand to give $(L(CO)_3FeCHO)^-$ is a concerted process. In this case the new ligand occupies the position vacated by the hydride ligand as it migrates so that the CO ligands remain approximately in the trigonal-bipyramid positions about the Fe atom. When all the ligands relax as the migration occurs without a new ligand, the situation is representative of the overall reaction occurring as a two-step process. In the first step, for which calculations are done here, the hydride ligand migrates to give an approximately tetrahedral $((CO)_3FeCHO)^-$ complex. The second step is the addition of a new ligand. While a two-step process has been suggested for alkyl migrations, there is no data for Fe complexes that suggests they react by a two-step mechanism. The hydride migrates much less readily than an alkyl so its mechanism may well be different. The fact that the acyl group formed is always cis to the new ligand suggests that a concerted process must be seriously considered as random attack on a tetrahedral complex would produce the trans as well as the cis product. Another reason for considering the fixed C–Fe–C angle case is that future comparisons to surface chemistry are desired and in that case the CO ligands are replaced by relatively immobile surface metal atoms. As will be seen below, the qualitative conclusions about the nature of the reaction are not changed by relaxing the C–Fe–C angles.

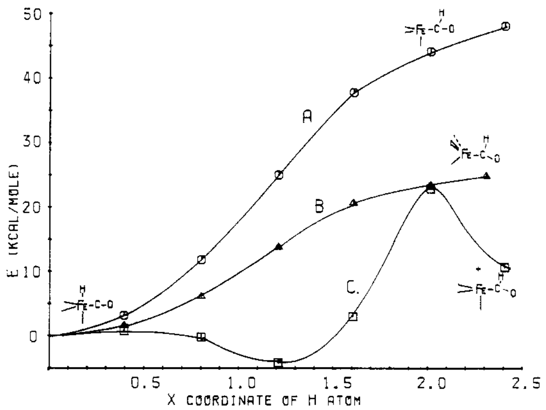

Figure 1. Hydride migration in (A) $(HFe(CO)_4)^-$ with C–Fe–C bond angles fixed, (B) $(HFe(CO)_4)^-$ with bond angles allowed to relax, and (C) $(HFe(CO)_4)^+$ with fixed C–Fe–C bond angles.

The potential energy change as the hydride ligand moves to change structure I into II with fixed C–Fe–C angles is shown in Figure 1. The axial hydride ligand starts on the z axis with the carbon atom to which it migrates being on the $+x$ axis. The abscissa in Figure 1 is the x coordinate of the hydride ligand. The x coordinate of the carbon atom of the final formyl complex is 1.76 Å. For each data point the energy is minimized with respect to all Fe–C and C–O bond lengths, the z coordinate of the H atom, and the Fe–C–H and Fe–C–O bond angles of the formyl group. The most outstanding feature of this curve is that there is no maximum in energy between the metal hydride and the formyl structure. Thus the formyl cannot be a metastable intermediate but to the extent that it exists independently must be at best a saddle point. If the hydride ligand were to migrate all the way to the formyl structure in this model without any additional stabilization from an incoming ligand the activation energy would be about 44 kcal/mol. This process seems unlikely.

If the C–Fe–C bond angles are allowed to relax, the potential curve labeled B in Figure 1 is obtained. Again there is no maximum in the curve so the end product, an approximately tetrahedral formyl $((CO)_3FeCHO)^-$, is not a metastable intermediate. All coordinates were optimized as before with the C–Fe–C bond angles being added to the list of optimized coordinates. The energy to form the unstable tetrahedral formyl structure is about half of that for the modified trigonal-bipyramid structure above, but it is still a formidable 24 kcal/mol. It should be noted that these calculations are for isolated gas-phase ions and solvation effects could change the relative stabilities of the different structures.

Bond lengths, bond orders, and atomic populations with the H atom X coordinte at 2.0 Å for both the cases where the C–Fe–C angles are fixed at trigonal-bipyramid values and where the structure is allowed to relax to form at equilibrium an approximately tetrahedral complex are shown in Table IV. Both have an electronic structure and pattern of bonding about the formyl group very similar to the coordinatively saturated complex $((CO)_4FeCHO)^-$ discussed above. The H atom acquires a large negative charge, and the C–H bond order is low. As the H atom migrates from the Fe atom to the carbon atom, the highest filled molecular orbital raises greatly in energy, acquires a large hydrogen contribution, and becomes antibonding for the C–H bond. The behavior of this orbital is primarily responsible for the instability of the formyl complex either as a saturated complex or as an unsaturated intermediate.

It has been found that the alkyl to acyl migration is induced by oxidation of the metal.[12] In view of the above finding that the highest filled MO is primarily responsible for the instability of the formyl structure, it is reasonable to postulate that oxidation of the metal would also aid in the formation of formyl from the metal hydride by removing charge from this highest filled MO. In order to test this idea calculations were done for points along the path as the hydride ligand migrates for $((CO)_4FeH)^+$. The calculations were just like those above with fixed C–Fe–C bond angles except that two less electrons are placed in the molecular orbitals. The potential energy curve is shown in Figure 1 for comparison with the other potential curves and the properties of the complex when the x coordinate of the H atom is 2.0 Å are given in Table IV. As expected the H atom no longer carries a negative charge, and the C–H bond order is increased. Comparison of the potential curves for $((CO)_4FeH)^+$ and $((CO)_4FeH)^-$, both with fixed C–Fe–C angles, indicates that removal of the two electrons favors the hydride migration. The complex with a positive charge is not regarded as a realistic model, but it does suggest that incorporation of electronegative ligands will aid hydride migration to form formyl complexes.

CO Addition Process. The above work indicates that the hydride does not readily migrate to give a tetracoordinated iron formyl, which is not a stable species in any configuration. To further investigate the process, calculations have been done for the addition of a CO ligand to form the metastable pentacoordinate Fe formyl, $((CO)_4FeCHO)^-$. Two situations are examined. The first is the addition of the CO to the metal hydride in a concerted process. The second is the addition of CO to a preformed tetrahedral formyl. In this latter situation the reaction is considered for addition both cis and trans to the formyl group.

Concerted CO Addition to $(HFe(CO)_4)^-$. Calculations were done for the geometry shown in structure IV at various fixed values for the x coordinate of the H atom. The C–Fe–C angles of the initial hydride complex were kept fixed while the angle of the incoming CO group to the z axis was allowed to vary. All bond lengths were allowed to vary in reaching an energy minimum for each fixed value of the H atom x coordinate. The results of these energy minima calculations as a function of the H atom x coordinate are shown in Figure 2. For the initial point with the H atom on the z axis the incoming CO group reaches an energy minimum when it is close to a line from the Fe atom through the center of the trangular face formed by the H atom and two of the equatorial C atoms. At the saddle point the H atom x coordinate is 1.6 Å, the incoming CO group is only 10.5° from the z axis and the Fe–C distance is 2.1 Å which is only 0.2 Å longer than for the other axial CO group. The energy zero in Figure 2 is taken as separated CO plus $(HFe(CO)_4)^-$ so the activation energy for the reaction

$$CO + (HFe(CO)_4)^- \rightarrow ((CO)_4FeCHO)^- \quad (3)$$

is calculated to be 31 kcal/mol by this mechanism. The reaction path calculated here produces a complex with the formyl group in an equatorial position. Since calculations with this model give the complex with an axial formyl 4 kcal/mol lower than the equatorial, calculations were done with the H atom x coordinate at 1.6 Å in which the all C–Fe–C angles were allowed to relax to see if distortion toward an axial formyl complex would produce a lower energy. No noticeable lowering of the energy was found.

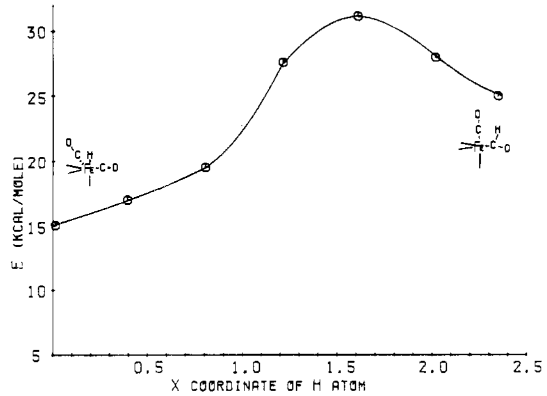

Figure 2. Concerted CO addition and hydride migration in $(HFe(CO)_4)^-$.

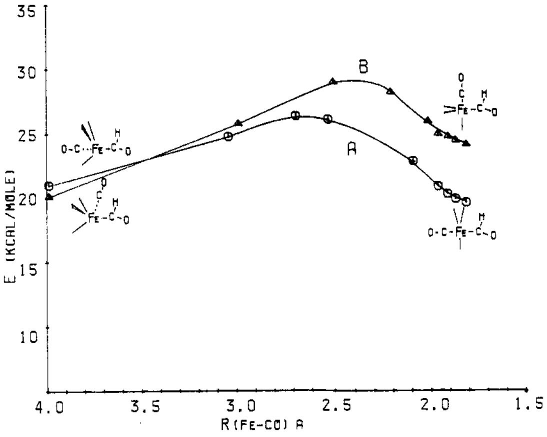

Figure 3. CO addition to tetrahedral $((CO)_3FeCHO)^-$ with (A) CO attack trans the CHO ligand and (B) CO attack cis to the CHO ligand.

Trans Addition of CO to Tetrahedral $((CO)_3FeCHO)^-$. Calculations were done for the geometry shown in structure V as the CO group comes in along the $-x$ axis. The three original CO groups (not bonded to the H atom) are kept in planes which make 120° angles to each other, but the C(H)–Fe–C angles are allowed to vary so that these three CO groups become the equatorial CO groups in the product complex. The energy as a function of R, the distance of the incoming C from the Fe atom, is shown in Figure 3. The energy is minimized with respect to all distances, and the C–Fe–C angles at each point subject to the above restraint. The energy maximum in this curve occurs at $R = 2.7$ Å. At this value for R, the H–C–Fe angle is 108°, the C(H)–Fe–C angles are about 99°, and incoming C–Fe–C angles are about 87°. The saddle point occurs at the relatively long Fe–C distance of 2.7 Å for this case of attack on the tetrahedral complex, whereas in the case of attack on the trigonal-bipyramid complex, the energy maximum occurs at $R = 2.1$ Å where the CO is almost in to its equilibrium position. In this latter case the activated complex is very product like. For the energy curve with attack on the tetrahedral unstable intermediate, the energy zero is taken as the separated CO and the trigonal-bypyramid hydride complex. Thus, right to begin with, this curve incorporates the energy rise of the hydride migration.

The major factor in the activation energy is the migration of the H atom in all cases. For attack on a tetrahedral complex this has already occurred so the saddle point occurs early in the CO attack, while for a concerted mechanism, the attack on a trigonal-bipyrimid hydride has the saddle point occurring after the CO has almost reached its equilibrium position with respect to the Fe atom when the H atom has almost completed its migration.

Cis CO Addition to Tetrahedral ($(CO)_3FeCHO)^-$. Calculations have been done for structure VI as the CO group approaches in the *xz* plane cis to the formyl group. The energy as a function of R, the incoming C distance to the Fe atom is shown in Figure 3. This calculation was done in the same manner as for the trans attack with the incoming CO having the additional freedom to vary the C(H)–Fe–C angle. Again the energy maximum occurs at the relatively long Fe–C distance of 2.5 Å. At the activated complex the H–C–Fe angle is 106° while the CO groups have moved from 1 to 13° toward the trigonal-bipyramid angles. The incoming C–Fe–C(H) angle is 85°. Thus the cis attack is remarkably like the trans attack.

The three activation energies are close enough that none can be eliminated on the basis of this calculational model. In all cases the major factor in the activation energy is the hydride migration.

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Mechanisms of the Elimination Reactions of $Os(CO)_4(H)R$ and $Os(CO)_4R_2$

W. J. Carter, S. J. Okrasinski, and J. R. Norton*[†]

Departments of Chemistry, Princeton University, Princeton, New Jersey 08544, and Colorado State University, Fort Collins, Colorado 80523

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Kinetic and labeling studies of alkane elimination from *cis*-$Os(CO)_4(H)R$ have shown that the rate-determining step is isomerization of *cis*-$Os(CO)_4(H)R$ to a reactive intermediate (probably an acyl hydride); this intermediate can then react either with unisomerized *cis*-$Os(CO)_4(H)R$ to give intermolecular R–H elimination (and $HOs(CO)_4Os(CO)_4R$) or with another nucleophile L to give intramolecular R–H elimination (and $Os(CO)_4L$). The *cis*-$Os(CO)_4(H)R$ is slightly more reactive toward the intermediate than are phosphines and phosphites, including Et_3P. The formation of methane from *cis*-$Os(CO)_4(CH_3)_2$ proceeds via an intermediate (most likely a methyl radical) which displays high H/D selectivity in attacking alkane solvents. The formation of ethylene and ethane from *cis*-$Os(CO)_4(C_2H_5)_2$ involves a reversible β-hydrogen elimination; thus the ethylene from *cis*-$Os(CO)_4(C_2H_5)_2$ and *cis*-$Os(CO)_4(C_2D_5)_2$ contains all possible H/D isomers. Simple intramolecular reductive elimination has not been observed from any *cis*-$Os(CO)_4RR'$.

As evidence has accumulated[1] that dinuclear elimination is involved in cobalt-catalyzed hydroformylation, the intermolecular formation of C–H bonds from organometallic precursors has received increasing attention. Systems investigated include *cis*-$Os(CO)_4(H)R$,[2] $CpMo(CO)_3R$/$CpMo(CO)_3H$,[3] various alkyl complexes/$CpV(CO)_3H^-$,[3b] and *cis*-$Mn(CO)_4LR$/*cis*-$Mn(CO)_4LH$ (L = CO or tertiary phosphine).[4]

The $Os(CO)_4(H)R$ system originally attracted our attention because these hydrido alkyls were less stable than either *cis*-$Os(CO)_4H_2$ or the corresponding dialkyls. The hydrido methyl and hydrido ethyl complexes nevertheless proved sufficiently stable to permit their preparation[5] and manipulation on a vacuum line at room temperature. We now present a complete account of our kinetic and mech-

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[†] Colorado State University.

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