containing a little tetrahydrofuran (15 mL) and the solution was heated under reflux for 120 h. The solution was cooled and passed through a short column of Florisil/Celite to remove the small amount of insoluble decomposition product. Volatile materials were removed under vacuum, and the yellow residue was recrystallized from benzene: yield 3.95 g, 97%; mp 148–150 °C (under N_2); IR (Nujol) 1970 (s), 1890 (s), 1260 (sh), 1020 (s), 775 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 0.42 (3 H), 4.26–5.25 (5 H); mass spectrum, selected *m/e* (relative abundance) 816 (M^+, 8.0), 732 ($M^+ - 3CO$, 57.3), 596 ($M^+ - Cr(CO)_6$, 54.8), 460 ($M^+ - Cr_2(CO)_9$, 100). Anal. Calcd for $C_{30}H_{24}O_{12}Si_3Cr_3$: C, 44.12; H, 2.94; Si, 10.29; Cr, 19.12. Found: C, 43.15; H, 2.93; Si, 9.63; Cr, 18.88.

Physical Data for Other New Compounds. $D_3^{PhCr(CO)_3}$ (II): mp 218–220 °C; IR (Nujol) 1970 (s), 1890 (s), 1260 (sh), 1020 (s), 785 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 0.56 (2 H), 0.59 (1 H), 4.12–5.23 (5 H); mass spectrum, selected *m/e* (relative abundance) 816 (M^+, 11.2), 732 ($M^+ - 3CO$, 70), 620 ($M^+ - 7CO$, 81.6), 460 ($M^+ - Cr_2(CO)_9$, 100).

$D_4^{PhCr(CO)_3}$ (III): mp 244–248 °C; IR (Nujol) 1965 (s), 1880 (s), 1265 (sh), 1095 (s), 780 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 0.60 (3 H), 4.37–5.32 (5 H); mass spectrum, selected *m/e* (relative abundance) 1088 (M^+, 8), 732 ($M^+ - Cr_2(CO)_9$, 22.5), 648 ($M^+ - Cr_2(CO)_{12}$, 69), 596 ($M^+ - Cr_3(CO)_{12}$, 100). Anal. Calcd for $C_{40}H_{42}O_{16}Si_4Cr_4$: C, 44.12; H, 2.94; Si, 10.29; Cr, 19.12. Found: C, 43.6; H, 2.99; Si, 10.03; Cr, 18.84.

$(CH_3O)_3SiC_6H_5Cr(CO)_3$: mp 42 °C; IR (Nujol) 1985 (s), 1912 (s), 1090 (s) cm^{-1}; ^1H NMR (C_6D_6) δ 3.42 (9 H), 4.16–5.14 (5 H); mass spectrum, selected *m/e* (relative abundance) 334 (M^+, 30.4), 250 ($M^+ - 3CO$, 100). Anal. Calcd for $C_{12}H_{14}O_6SiCr$: C, 43.11; H, 4.19; Cr, 15.57. Found: C, 43.61; H, 4.38; Cr, 15.53.

Hydrosilation Reactions. Reactions were carried out in batches in thick walled tubes, sealed under vacuum. Each tube was filled with nitrogen and then charged with triethoxysilane (0.46 mL, 2.5 mmol), *trans*-1,3-pentaidene (0.25 mL, 2.5 mmol), and catalyst (0.025 mmol for the monomeric catalysts and 0.008 mmol for the trimer). After being sealed under vacuum, the tubes were heated in a temperature controlled oil bath at 80 °C. Several identical tubes were prepared for each catalyst, and one tube of each catalyst was removed at intervals for analysis. Unconsumed reactants were removed by distillation under vacuum at room temperature, and then the product mixture was stripped off under vacuum at 80 °C and collected for quantitative analysis. Product analysis was effected by GC on a 6% Chrom W column (3 m × 3 mm) at an initial temperature of 90 °C and increasing at 16 °C/min.

The structures of the products were established by 2D ^1H NMR, at 200 MHz on the product mixture dissolved in C_6D_6. Compound **1**: $\mathit{CH_3}CH_2$ (triplet, δ 0.09); $SiCH_2$ (doublet of doublets, δ 1.68); $CH_3\mathit{CH_2}$ (pseudoquintet of doublets, δ 2.05); $CCH_2\mathit{CH}{=}$ (quartet of triplets, δ 5.61); $SiCH_2\mathit{CH}{=}$ (multiplet overlapping with analogous peaks from compound **2**, δ 5.40). Compound **2**: $\mathit{CH_3}CH(Si)$ (doublets, δ 1.30); $\mathit{CH_3}CH{=}$ (doublet of triplets, δ 1.63); $Si\mathit{CH}(CH_3)$ (quintet of quintets, δ 1.85); $Si(CH_3)CH\mathit{CH}{=}$ (see compound **1**, δ 5.40); $CH_3\mathit{CH}{=}$ (doublet of doublets of quartets, δ 5.76).

The identity of the products was further confirmed by GC–MS. Mass spectra, selected *m/e* (relative abundance): compound **1**, 232 (M^+, 2.98), 217 ($M^+ - CH_3$, 5); compound **2**, 232 (1.46), 217 (0.40).

Acknowledgment. Support of this work by grants from the Natural Sciences and Engineering Research Council of Canada and of the Fonds FCAC de Québec is gratefully acknowledged.

Registry No. **1**, 40962-01-4; **2**, 40962-06-9; D_3^{Ph} (I), 3424-57-5; D_3^{Ph} (II), 6138-53-0; D_4^{Ph} (I), 4885-37-4; D_4^{Ph} (II), 5131-04-4; D_4^{Ph} (III), 15331-54-1; D_4^{Ph} (IV), 4885-39-6; $D_3^{PhCr(CO)_3}$ (I), 98679-12-0; $D_3^{PhCr(CO)_3}$ (II), 98719-22-3; $D_4^{PhCr(CO)_3}$ (I), 98679-13-1; $D_4^{PhCr(CO)_3}$ (II), 98719-23-4; $D_4^{PhCr(CO)_3}$ (III), 98719-24-5; $D_4^{PhCr(CO)_3}$ (IV), 98719-25-6; $Cr(CO)_6$, 13007-92-6; $(C_6H_6)Cr(CO)_3$, 12082-08-5; $(CH_3)_3SiC_6H_5Cr(CO)_3$, 33248-13-4; $(CH_3O)_3SiC_6H_5Cr(CO)_3$, 98679-14-2; $PhSi(CH_3O)_3$, 2996-92-1; $(EtO)_3Si$, 998-30-1; *trans*-1,3-pentadiene, 2004-70-8.

Carbonyl Insertion Reactions. 2. Alkali Ion Effect on Hydride Migration in $(HFe(CO)_4)^-$

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Molecular orbital calculations indicate that alkali ion coordination to a carbonyl ligand of $(HFe(CO)_4)^-$ will promote hydride migration to that carbonyl ligand to form a formyl. Coordination of the alkali removes charge from the parent complex and alters the nature of the highest occupied molecular orbital in the formyl so as to lower its energy relative to other molecular orbitals and to remove its C–H antibonding character. The properties of the highest occupied molecular orbital are primarily responsible for the great instability of the formyl structure $((CO)_3FeCHO)^-$. In order to be effective the alkali must be coordinated to the formyl oxygen. Li^+ coordinates more strongly with an equatorial oxygen than with an axial oxygen.

Introduction

The rearrangement of a transition-metal hydride to a formyl has not been observed although alkyls readily migrate to an adjacent carbonyl to form an acyl.[1-4] This is often referred to as a carbonyl insertion reaction. Carbonyl insertion reactions are important in heterogeneous and homogeneous catalysis as well as in stoichiometric organometallic synthesis. Transition-metal formyls have been prepared by other routes,[5] but they are generally of only marginal stability with room-temperature half-lives of seconds to a few days.[2] None-the-less the catalytic reduction of CO by H_2 has been proposed to proceed via formyl intermediates.[6-8]

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Table I. Lithium Bond Parameters

bond	Li–H	Li–O	Li–C[a]	Li–Fe
β	0.352	1.094	0.568	0.663
α	5.021	5.926	4.649	2.445
binding energy, kcal/mol	56.1	83.0	16.9	51.0
exptl D_0	56[b]	83[b]		
calcd R_e, Å	1.60	1.70	2.10	2.20
exptl R_e, Å	1.5953[b]			
Li electron count	0.61	0.43	0.64	1.09

[a] In Li–CH_3. [b] Rosen, B., Ed. "Selected Constants, Spectroscopic Data Relative to Diatomic Molecules"; Pergamon Press: New York, 1970.

Calculations in the preceding paper of this series indicate that a coordinatively unsaturated iron formyl complex is highly unstable.[9] An activation energy around 30 kcal/mol was calculated for the reaction

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

The instability of the formyl is traced to the highest occupied molecular orbital placing a large negative charge on the H atom and being antibonding for the C–H bond.

It has been found that alkali-metal ions form ion pairs with alkyl carbonyl complexes and that such ion pairing greatly increases the rate of alkyl migration to form acyls. The promotion of the alkyl migration reaction in $(RFe(CO)_4)^-$ by Na^+ is well-known.[10] Lewis acids such as $AlBr_3$ have been shown to promote alkyl migration in transition-metal complexes to form acyls and alumina surfaces also promote this reaction.[11,12] Surface reactions similar to the alkali promotion of the formation of formyl groups on metal surfaces from CO and hydrogen have been proposed.[13,14] The question of whether alkali ion interaction would increase the rate of hydride migration to give formyls is addressed in this paper by doing calculations for $Li^+((CO)_4FeH)^-$ as it rearranges to $Li^+((CO)_3FeCHO)^-$ under various assumptions about the Li^+ interaction with the iron complex. This reaction without Li^+ present has been treated in detail in the preceding paper.[9]

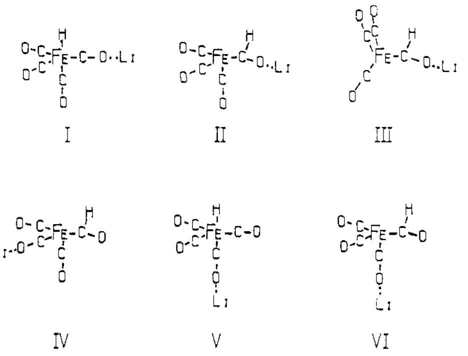
Calculational Procedure

The calculations were done with a semiempirical SCF method which is a modification of MINDO. 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 procedure explicity includes electron–electron repulsion terms and is parameterized to give bond energies and lengths for selected reference compounds in ageement with experimental values and includes automatic geometry optimization using analytically calculated gradients.

The atomic and bonding parameters for Fe, C, O, and H are given in the preceding paper.[9] The parameters involving Li are given in Table I along with calculated results for the diatomic molecules Li–H, Li–O, and Li–Fe and for Li–CH_3.

Results and Discussion

To begin the examination of the effect of alkali ion coordination on the hydride migration, calculations were done for Li^+ coordinated to an equatorial oxygen of the metal hydride complex in structure I. The bond lenghts, bond orders, and atomic charges are given in Table II. In this structure the H–Fe–C(eq) bond angles are 90°. In the calculations for structure I, all bond angles were kept fixed while all bond lengths were optimized. In some calculations the C–O–Li angle was varied but 180° proved to be the optimum value. The effect of Li^+ coordination may be seen by comparing the properties of structure I in Table II to those of $(HFe(CO)_4)^-$ in the preceding paper.[9] The bonding in and to the CO ligands not directly bonded to the Li^+ ion are changed relatively little. For the CO ligand to which the Li^+ is coordinated, the C–O bond is lengthened and weakened while the Fe–C bond is shortened and strengthened. The charge on the H atom is reduced, and the overall electronic charge on the parent complex is reduced by the 0.46e charge on the Li atom. The largest effect of the Li^+ occurs at the CO ligand to which it is coordinated.



STRUCTURES

The atomic coefficients in the molecular orbitals for structure I were examined to see how the Li^+ coordination led to the observed bonding changes from the parent complex $(HFe(CO)_4)^-$. Li orbitals contribute with coefficients greater than 0.10 to 6 of the lowest 14 molecular orbitals among the 25 occupied molecular orbitals. In no case is the coefficient for a Li atomic orbital greater than 0.16. Smaller coefficients than 0.10 for Li atomic orbitals occur in a number of the other molecular orbitals. The inclusion of the Li contribution in this spread-out manner shifts the amount of atomic orbital contribution from all of the other atomic orbitals to give a large number of modest bonding changes which add up to the observed changes. Coordination of Li^+ removes charge from the parent complex and from the carbon of the complexed CO ligand as shown in Table II and reduces the C–O bond order of the CO ligand to which it is complexed.

The properties of the Li^+–formyl complex, structure II, is given in line two of Table II. Comparison to the properties of the corresponding structure without the Li in the preceding paper shows some major changes. Removal of charge by the Li^+ coordination results in less charge on the H atom and an increase in the C–H bond order. The highest filled molecular orbital with its large contribution from the H 1s orbital is not antibonding for the C–H bond in the Li complex as it is without Li and does not rise in energy with Li as it does without Li. This highest filled molecular orbital is centered on the formyl group where

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Table II. Properties of $Li(HFe(CO)_4)$ and $Li((CO)_3FeCHO)$

Bond Lengths (Å)

molecule	comments	Fe–C(eq)	Fe–C(ax)	C–O(eq)	C–O(ax)	Fe–(CHO)	Fe–H	C–H	HC–O	O–Li	two highest MO's, au
I	*a, e*	1.74	1.91	1.17	1.16	1.58	1.58		1.25	2.17	−0.30, −0.27
II	*b–e*	1.78	1.93	1.17	1.16	1.79		1.22	1.28	2.07	−0.34, −0.27
I′	*a, f*	1.74	1.91	1.17	1.16	1.62	1.59		1.22	2.50	−0.28, −0.25
II′	*b, c, d, f*	1.77	1.91	1.17	1.16	1.81		1.24	1.25	2.50	−0.33, −0.23
III	*d, e, g, c*	1.77		1.16		1.77		1.22	1.28	2.08	−0.34, −0.27
III′	*d, c, g, f*	1.78		1.17		1.80		1.24	1.25	2.50	−0.32, −0.24
IV	*b–e*	1.75 (1.64)[h]	1.87	1.17 (1.23)[h]	1.16	1.73		1.27	1.22	2.22	−0.31, −0.18
V	*a, e*	1.73	1.69	1.18	1.22		1.57			2.27	−0.28, −0.25
VI	*b–e*	1.76	1.73	1.17	1.22	1.76		1.23	1.23	2.22	−0.32, −0.19
V′	*a, f*	1.73	1.77	1.18	1.20		1.59			2.50	−0.27, −0.24
VI′	*b, c, d, f*	1.76	1.78	1.17	1.20	1.77		1.24	1.23	2.50	−0.31, −0.18

Bond Orders

molecule	Fe–C(eq)	Fe–C(ax)	C–O(eq)	C–O(ax)	Fe–(CHO)	Fe–H	C–H	HC–O	O–Li
I	1.24	0.89	1.76	1.84	1.48	1.08	0.04	1.32	0.49
II	1.21	0.96	1.81	1.85	1.21	0.22	0.85	1.26	0.58
I′	1.22	0.89	1.76	1.82	1.38	1.09	0.03	1.44	0.32
II′	1.21	0.98	1.80	1.83	1.19	0.23	0.81	1.37	0.34
III	1.22		1.81		1.24	0.19	0.85	1.27	0.56
III′	1.21		1.80		1.23	0.11	0.83	1.37	0.34
IV	1.25 (1.36)[h]	1.03	1.80 (1.45)[h]	1.82	1.34	0.23	0.73	1.53	0.43
V	1.22	1.15	1.74	1.49		1.11			0.41
VI	1.22	1.18	1.80	1.49	1.27	0.23	0.82	1.52	0.44
V′	1.22	1.03	1.73	1.59		1.11			0.31
VI′	1.21	1.11	1.79	1.59	1.27	0.23	0.80	1.52	0.30

Valence Electron Count

molecule	Fe	C(eq)	C(ax)	C(HO)	O(eq)	O(ax)	O	H	Li
I	10.04	2.99	3.23	2.76	6.62	6.52	6.66	1.11	0.46
II	9.51	3.07	3.24	3.14	6.55	6.49	6.55	1.26	0.58
I′	10.00	3.01	3.22	2.80	6.63	6.54	6.71	1.14	0.32
II′	9.51	3.06	3.22	3.15	6.56	6.52	6.68	1.30	0.40
III	9.65	3.05		3.09	6.55		6.56	1.30	0.57
III′	9.63	3.06		3.09	6.56		6.65	1.38	0.39
IV	9.73	3.02 (281)[h]	3.18	3.11	6.57 (6.61)[h]	6.52	6.73	1.34	0.39
V	10.09	2.99	2.90		6.64	6.60		1.11	0.38
VI	9.67	3.05	3.00	3.14	6.57	6.56	6.74	1.25	0.41
V′	10.05	3.00	2.97		6.65	6.61		1.13	0.30
VI′	9.63	3.05	3.02	3.16	6.58	6.58	6.74	1.27	0.34

[a] Trigonal bipyramid (TB). [b] C–Fe–C angles as in TB. [c] L(Fe–C–H) = 100° ± 1, L(Fe–C–O) = 152° ± 7. [d] x coordinate of H is 2.00. [e] Li–O distance optimized. [f] Li–O distance fixed at 2.5 Å. [g] Approximately tetrahedral about Fe. [h] Value for CO ligand coordinated to Li^+.

the C and H atoms make the largest contributions to it. A bonding interaction for the Li–O bond also helps to stabilize this orbital. With Li the formyl complex (II) is still less stable than the metal hydride (I) but the difference is much less with Li than without. Thus the primary effect of the Li is to lessen the antibonding contribution of the highest filled molecular orbital to the C–H bond, which is primarily responsible for the instability of the formyl complex. Lewis acid catalysis has been suggested to contribute to the alkali ion effect on alkyl migrations but no calculations on this effect were made.[19]

The potential energy curve for the hydride migration from structure I to structure II is shown as curve A in Figure 1. For curve A the C(eq)–Fe–C(ax) bond angles were fixed at 90° but all bond lengths were allowed to vary so as to minimize the energy. As in the case without Li (preceding paper[9]) the formyl structure is unstable with respect to hydride migration to the metal and there is no potential energy maximum between structures I and II. Therefore the coordinatively unsaturated formyl cannot be a metastable intermediate. Taking the activation energy for the hydride migration as the energy rise when the x coordinate of the H atom is 2.0 Å indicates that for this case the energy rise for hydride migration with Li is reduced to 13 kcal/mol from 44 kcal/mol without Li.

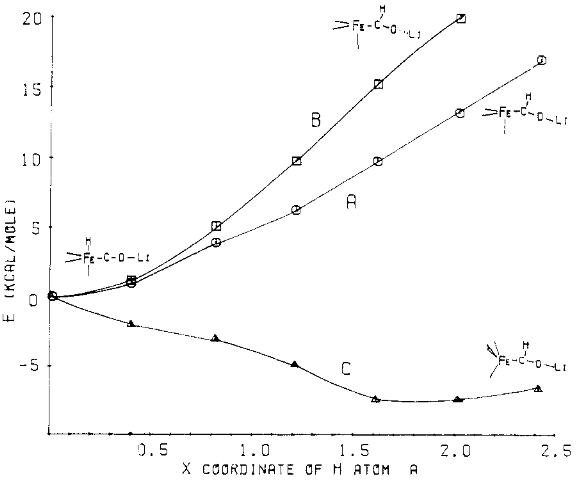

Figure 1. Hydride migration in $Li^+(HFe(CO)_4)^-$; A, fixed C–Fe–C bond angles and Li–O distance optimized; B, fixed C–Fe–C bond angles and Li–O distance fixed at 2.5 Å; C, optimized C–Fe–C bond angles and optimized Li–O distance.

For curve A of Figure 1 the Li–O distance was optimized with the result that a Li–O bond was produced having a length of from 2.1 to 2.2 Å and a bond order of about 0.5. This procedure ignors the interaction of the Li^+ with other

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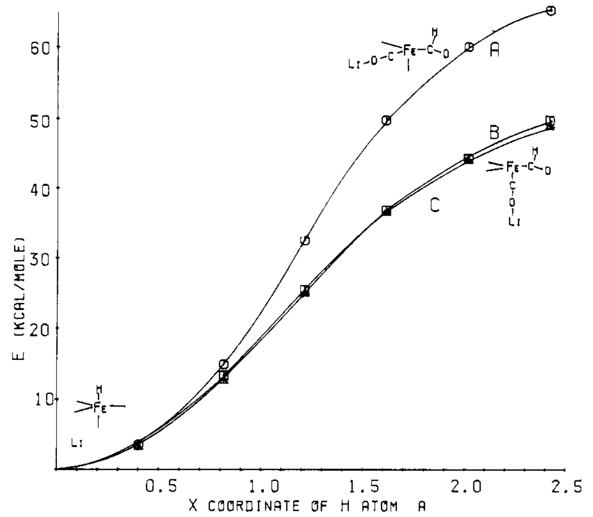

Figure 2. Hydride migration in $Li^+(HFe(CO)_4)^-$ with C–Fe–C bond angles fixed in all cases; A, Li coordinated in equatorial position but not to formyl; B, axial coordination of Li with Li–O distance optimized; C, axial coordination of Li with Li–O distance fixed at 2.5 Å.

solvent molecules. On the assumption that these interactions would lessen the Li–O interaction, calculations were made in which the Li–O distance was fixed at 2.5 Å. The results are shown in curve B of Figure 1 and the properties of the beginning and ending complexes given in Table II as structures I′ and II′. The result is a decrease in the effect of the Li but the qualitative picture is unchanged.

The hydride migation case with the C(eq)–Fe–C(ax) angles fixed at 90° is approximately representative of the case where an incoming ligand adds to the complex in a concerted process as the hydride migrates so that the C–Fe–C bond angles to not change much during the process. This would also be the case for hydride migration on a metal surface where all but one of the CO ligands are replaced by relatively immobile metal atoms. In a two-step process for reaction of the complex, the first step of hydride migration to form the coordinatively unsaturated formyl would be followed by a separate ligand addition step. In the first step the bond angles might relax so that the unsaturated formyl had a tetrahedral structure as illustrated in structure III. The calculated properties of structure III (Li–C distance optimized) and III′ (Li–O distance fixed at 2.5 Å) are given in Table II. The bond lengths, bond orders, and atomic charges for the tetrahedral complex are quite similar to those of the complex with trigonal-bipyramid angles (structure II). The main difference is that the relaxation of angles allows the tetrahedral structure to drop about 20 kcal/mol lower in energy than structure II. The potential energy curve C in Figure 1 is for the hydride migration with the angles allowed to relax so that the formyl has an approximately tetrahedral structure. In curve C the Li–O distance is optimized and the Li formyl complex is about 6 kcal/mol more stable than the metal hydride. As noted above this model ignors Li–solvent interactions. If the Li–O distance is fixed at 2.5 Å, the tetrahedral formyl with Li has approximately the same energy as the metal hydride. Thus the relaxation of bond angles, if it is permitted by the mechanism, lowers the energy required to make the hydride migration.

The experimental data indicates that in the alkali assisted alkyl migration the coordination of the alkali occurs at the formyl oxygen.[9] To examine the effect of coordination of the Li^+ at an equatorial position, different from that to which the hydride migrates, calculations for structure IV were made. The properties of structure IV are reported in Table II, and the potential energy curve along the path from structure I to IV is given in curve A of Figure 2. The calculations for structure IV with the Li not coordinated to the formyl oxygen show that the H atom has acquired a large negative charge, the C–H bond order is low, and the highest occupied molecular orbital has a large contribution from the H 1s orbital and is raised in energy considerably above the next highest orbital. These features are like the formyl complex without Li. The Li–O bond being weaker in the formyl structure IV than in structure I also contributes to the relative instability of the formyl structure with Li. The result shown in curve A of Figure 2 is that coordination of the Li^+ to a non-formyl equitorial oxygen raises the hydride migration energy above its value without Li.

In order to examine the effect of Li^+ coordination at an axial position rather than an equatorial position, calculations were done for structure V and VI. These calculations were done with the C–Fe–C angles fixed for both the case with the Li–O bond length optimized and the case with the Li–O bond length fixed at 2.5 Å. The molecular properties are given in Table II, and the potential energy curves are shown in curves B and C in Figure 2. The axial coordination of the Li primarily affects the bonding of the axial CO ligand. As the hydride migration occurs the highest occupied molecular orbital is raised as before without Li. The curves in Figure 2 indicate that the hydride migration requires about as much energy with Li in the axial position as without any Li.

In summary, alkali ion coordination has been found to promote hydride migration from a metal atom to an adjacent carbonyl ligand to form a formyl by removing charge from the complex and altering the nature of the highest occupied molecular orbital in the formyl so that it no longer becomes antibonding for the C–H bond and no longer goes to an energy much above the next highest orbital. In order to have this effect the Li^+ must be coordinated to the formyl oxygen. Presumably any Lewis acid such as Al^{3+} either in solution or as part of a surface or any metal ion in a positive oxidation state on a catalyst surface could promote migration to a carbonyl by coordinating with the oxygen. The Li^+ coordinates more strongly with the equitorial oxygen in $(HFe(CO)_4)^-$ than with the axial oxygen as indicated by Li–O bond orders because the equitorial oxygen carries a larger negative charge. Coordination of the alkali makes the cabon atom in the coordinated carbonyl more positive which also facilitates migration of a nucleophile to that carbon.

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Registry No. $(HFe(CO)_4)^-$, 18716-80-8; $Li^+(HFe(CO)_4)^-$, 98854-90-1; $Li^+((Co)_4FeCHO)^-$, 66791-64-8.