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The Structures and Energies of Main Group Metal Formyl Complexes. The Mechanism of the Reaction of LiH with CO. An ab Initio Study

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Abstract: Formyl complexes, MCHO, of first- and second-row metals and metal hydrides (M = Li, BeH, BH_2, Na, MgH, AlH_2) have been investigated by means of ab initio calculations (MP2/6-31+G*//6-31G* and lower levels). Both η^2 (i.e., bridged) and η^1 coordination of the metals are found: the former is favored by larger electronegativity differences between the metal and the formyl carbon. Such η^2 coordination is characterized by rather long CO bonds, significant alkoxy–carbene character in the formyl group, and a bridging energy of about 5–8 kcal/mol for M = BeH and AlH_2. The formyl carbon–metal interactions are predominantly ionic. The insertion reaction of CO into the LiH bond, a model for similar processes in transition-metal compounds, proceeds via an initially formed linear coordination complex, HLi–CO, and a three-membered ring transition structure. The latter lies energetically about 19 kcal/mol above the complex. The overall activation and reaction energies from LiH + CO to the formyllithium product, LiCHO, are +13 and −3 kcal/mol, respectively. The energies of the reaction of the other metal hydrides with CO to form the corresponding formyl compounds are all endothermic by about 1–7 kcal/mol. Thus, with the exception of M = Li, all the formyl complexes, MCHO, are *thermodynamically* unstable, but they may be observable at lower temperatures if the activation energies for the loss of CO are comparable to that of LiCHO (about 16 kcal/mol). These conclusions are expected to apply to all metal carbonyl compounds with high ionic character such as early transition metals, actinides, and lanthanides.

There has been a continuing interest in the Fischer-Tropsch and related processes as synthetic routes to petroleum products.[1] Initially developed in the 1920s, the Fischer-Tropsch method involves the reaction of CO with H_2 over a metal catalyst to form a mixture of hydrocarbons and related oxygenated compounds. Proposed mechanisms for the Fischer-Tropsch reaction involve CO insertion into a metal hydride on the surface of the catalyst resulting in a formyl–metal intermediate.[1,2] In order to understand this initial step further, many groups have synthesized and characterized model formyl–metal complexes.[3-10] The subject has been reviewed by Gladysz.[11]

Many η^1 formyl–transition metal complexes have now been synthesized by employing Mo, Mn, Re, Ru, Rh, Os, and Ir as the metals, that is, middle-to-late transition metals. Nevertheless, the direct reaction of CO with the corresponding metal hydrides has rarely resulted in the desired formyl complex. Indeed, many such formyl–metal compounds decompose via a decarbonylation mechanism. A rare example of a successful CO insertion comes from Wayland, who has treated CO with rhodium octaethylporphyrin hydride to form the corresponding formyl complex.[5] In general, formyl–transition-metal complexes have been generated not by insertion of CO but by the reaction of cationic metal carbonyls with borohydrides.[11]

These neutral η^1 formyl–metal complexes exhibit some unusual properties. Most notably, they have relatively low C=O stretching frequencies that range from about 1530–1630 cm^{-1}. For example, $Re(\eta^5\text{-}C_5H_5)(PPh_3)(NO)(CHO)$ and $Os(CHO)(H)(CO)_2(PPh_3)_2$ have C=O stretches of 1558–1566 and 1601 cm^{-1}, respectively.[8,9] Crystal structures of several η^1 formyl–transition-metal complexes are known, and they exhibit varying C=O bond lengths (1.19–1.22

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Å;[12,13] the C=O bond length in formaldehyde is 1.21 Å). These results strongly suggest an important contribution from an alkoxy–carbene resonance form in the formyl moiety, **1**, with significant carbon-metal covalency that probably includes backbonding from filled metal d-orbitals.

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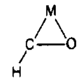
In contrast, direct CO insertions are now common for early transition metals and cyclopentadienyl actinide compounds. Bercaw has suggested an initial CO insertion in the reaction of $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ with CO to form a transient formyl–zirconium intermediate.[14,15] Marks[16] has demonstrated even faster reversible addition of CO to alkoxybis(pentamethylcyclopentadienyl)thorium hydrides to generate formyl–thorium complexes. Moreover, η^2 coordination to the formyl group appears implicated in these compounds. Bercaw has suggested that his intermediate is possibly stabilized by η^2 coordination of the formyl ligand to the metal. In Marks' thorium compounds, spectrometric data, such as the low C=O frequencies of about 1477 cm^{-1}, imply η^2 coordination of the formyl ligand to the metal. Since this represents one of the very few examples of CO directly inserting into a metal hydride to form a formyl–metal complex, it appears that the η^2 coordination may provide a driving force for such insertions.

Insertion reactions of CO are also known for some main group elements. Trialkylboranes react readily with CO to give either alcohols, aldehydes, or ketones depending on the reaction conditions.[17] Hillman has proposed an insertion mechanism that is similar to mechanisms proposed for transition-metal complexes.[18] After CO coordinates with the electron-deficient boron, one of the alkyl groups migrates to give an acyl–borane intermediate, $R_2B\text{–}C(O)R$. A second migration is assisted by coordination of the carbonyl oxygen to boron. Finally, a third migration may occur to give a boronic anhydride, $OB\text{–}CR_3$. Therefore, although their reactivities may differ, acyl–boranes and acyl–transition-metal complexes may be formed by similar paths. Furthermore, oxygen assistance and possible η^2 coordination may play an important role with acyl–borane complexes.

Several aspects of formyl–metal chemistry are of theoretical interest. Bonding to early transition metals and to actinides tends to be more ionic and η^2 coordination to the formyl group may be typical of more ionic bonding. Such bonding characteristics can readily be given by an ab initio study with small model systems and reasonably large basis sets. Moreover, a study of formyl–metal compounds may have direct application to more common acyl–metal analogues where η^2 coordination is well documented.[19] Crystal structures of acyl–titanium, zirconium, and ruthenium complexes show coordination of both the oxygen and the carbon of the acyl ligand to the metal. Such η^2 acyl–metal complexes exhibit low C=O stretching frequencies (1530–1600 cm^{-1}). Inherent in these structures are extremely small O–C–M angles of approximately 70°.[20]

In an important related field, there has been much interest in the synthetic utility of acyllithium complexes. Seyferth and coworkers, extending earlier investigations of other groups,[21-23] have developed the method of direct nucleophilic acylations[24] (aroylations seem to be less satisfactory[25]). The products, in most cases, are consistent with the generation of a formal "acyl anion" intermediate which then reacts with electrophiles, e.g., aldehydes, ketones, and esters. Acyllithiums, however, were not observed directly, presumably due to their high reactivity.[26] Instead, these species are generated and used in situ. Thus, acyl anions are important synthons, and direct utilization of such intermediates shows promise.

There have been previous studies of the formyl anion, but its metal coordination has yet to be fully studied.[27-29] Since formyl and acyl anions have adjacent carbon and oxygen lone pairs available for coordination, either η^2 or η^1 coordination is possible (**2** and **3**, respectively). Moreover, if the formyl or acyl anion's negative charge is transferred to the oxygen by polarization of the π-MO, then considerable alkoxy–carbene character should result. Finally, the η^2 formyl and acyl–metal interactions may be characterized as either a metal d-orbital overlap with the carbon and oxygen lone pairs or an ionic attraction between the cationic metal and the anion.



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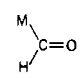

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The present work focuses on formyl complexes of first- and second-row metals and metal hydrides. The first- and second-row metals cover a wide range of electronegativities; therefore, they should provide a useful basis for developing trends in formyl-metal complexation, especially those related to ionic character. These model systems are not expected to show the varied chemistry of transition metals; in particular, these main group metals generally do not employ d-orbitals in bonding, and they will therefore not provide models of transition-metal d-orbital effects. Nevertheless, they should provide a valuable indication of the effects of metal substitution on formaldehyde, and formyl–lithium compounds to be discussed should be excellent models for the synthetically useful acyl–lithium complexes.

For the smallest system, the lithium formyl complex, a more extensive study was undertaken to check the performance of basis sets for geometries and relative energies and correlation energies. In this case two additional structures have been considered: a CO molecule attached to lithium hydride by C and O coordination, respectively (structures **4** and **5**). **4** is a model for a simple metal

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carbonyl, **5** for a hypothetical "isocarbonyl" complex.

$O{\equiv}C{-}Li{-}H$ **4**

$C{\equiv}O{-}Li{-}H$ **5**

Calculations

Computations were carried out on Vax 11/750, 11/780, CDC 7600, and CYBER 845 computers with Gamess,[30] Gaussian 80,[31] or Gaussian 82[32] quantum mechanical programs. Several basis sets were employed: 3-21+G, 6-31+G*, and 6-311+G* denote the standard 3-21G,[33] 6-31G*,[34] and 6-311G*[35] basis sets with additional diffuse sp orbitals on carbon and oxygen.[36] The 3-21G* basis set is augmented with d-functions on all non-hydrogen atoms.[37]

All structures were optimized with the 3-21+G (or 3-21G), 3-21G*, and 6-31G* basis sets. Single-point calculations on these geometries were carried out with inclusion of correlation corrections at the Møller-Plesset[38] second-order level (MP2/6-31G* and MP2/6-31+G*). Higher level calculations were performed for the lithium systems: Optimizations at 6-31G* and 6-31+G* were followed by single points (MP4/6-31+G*, MP2/6-311G*, and MP2/6-311+G*). For these compounds also zero-point vibrational energies (at 6-31G*, scaled by 0.9)[39] were obtained.

As has been noted before,[36] optimizations with and without diffuse functions (e.g., 3-21G and 3-21+G) give similar results. That the inclusion of diffuse functions has little effect on geometry also is shown by comparing the 6-31G* and 6-31+G* results in Table II. In contrast, d-functions have a larger effect (3-21G or 3-21+G vs. 3-21G*, Tables I and II). There are also significant differences between the 3-21G* and 6-31G* results, and only the parameters obtained at the highest levels employed are discussed (6-31+G* for the lithium systems, Table II).

For the contour maps, wave functions were projected into a planar density grid by the program PROJ.[40] These projected electron density grids were divided into molecular fragments by a program designed to find relative minima in the electron density. These minimum density demarkations of such projected functions are vertical curtains that approximate the virial boundaries of Bader,[41] and the derived integrated fragment populations approximate the true integrations over Bader "basins". Bader has shown that these virial boundaries have important properties and that the integrated populations are uniquely defined and unambiguous atom populations. Our populations are faster to compute and are expected to be qualitatively correct, particularly when electron densities drop to such low levels as between electropositive metals and other atoms. The electron density grids were converted to contour maps and integrated over molecular fragments with use of previously described programs.[42] The integration of the projected density grid over a molecular fragment will be referred to as the fragment population.

Table I. Geometries of Formaldehyde and Formyl–Metal Complexes at Various Levels[a]

		3-21+G	3-21G*	6-31G*
H_2CO		1.207[b]	1.182	1.184
BeH, η^2	CO	1.291[b]	1.254	1.249
	CBe	1.742	1.686	1.673
	OBe	1.592	1.572	1.582
	OCBe	61.2	63.4	63.6
	[BeH][c]		4.18	
	[O][d]		9.26	
BeH, η^1	CO	1.233[b]		1.207
	CBe	1.741		1.738
	OBe	2.526		2.471
	OCBe	115.2		112.9
BH_2 perp, η^1	CO	1.221[b]	1.198	1.197
	CB	1.576	1.587	1.591
	OB	2.446	2.342	2.425
	OCB	121.4	113.7	120.2
	$[BH_2]$[c]		6.42	
	[O][d]		9.26	
BH_2 plan, η^1	CO	1.230		1.197
	CB	1.601		1.611
	OB	2.482		2.457
	OCB	121.9		121.4
Na, η^2	CO	1.288	1.237	1.239
	CNa	2.256	2.180	2.243
	ONa	2.046	2.090	2.165
	OCNa	63.8	69.2	70.3
	[Na][c]		10.10	
	[O][d]		9.33	
MgH, η^2	CO	1.296	1.251	1.247
	CMg	2.140	2.078	2.074
	OMg	1.973	1.957	1.995
	OCMg	64.7	66.8	68.8
	[Mg][c]		12.12	
	[O][d]		9.33	
AlH_2 perp, η^2	CO	1.290	1.249	1.243
	CAl	2.039	1.973	1.956
	OAl	1.930	1.876	1.913
	OCAl	66.5	66.9	69.4
	$[AlH_2]$[c]		14.14	
	[O][d]		9.33	
AlH_2 perp, η^1	CO	1.240		
	CAl	2.044		
	OAl	2.820		
	OCAl	116.2		
AlH_2 plan, η^1	CO	1.236		1.201
	CAl	2.048		2.030
	OAl	2.885		2.825
	OCAl	121.0		119.7

[a] Distances in angstroms, angles in degrees. [b] 3-21G optimization. [c] Electron population on the metal fragment including hydrogens. [d] Electron population on oxygen.

Results

Geometries and Bonding. All structures were found to be planar except formylborane and formylalane which had C_s symmetry and hydrogens on both sides of the mirror plane. The corresponding alternatives with all atoms in the same plane are higher in energy and correspond to transition structures for rotation of the BH_2 and AlH_2 groups, respectively.

By examining the O–C–M angles and oxygen-metal distances (Tables I and II) it is apparent that LiCHO, HBeCHO, NaCHO,

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Table II. Geometries of LiCHO Isomers at Various Levels^a

			3-21G	3-21G*	6-31G*	6-31+G*	MP2/6-3G*
LiCHO, η^2	**2**	CO	1.280	1.246	1.243	1.244	1.277
		CLi	1.938	1.895	1.902	1.907	1.891
		OLi	1.746	1.762	1.782	1.774	1.835
		OCLi	61.8	64.1	65.1	64.5	67.6
		CH	1.098		1.104	1.104	1.114
		OCH	113.4		112.8	112.6	112.4
		[Li]		2.12^b	2.12^c		
		[O]		9.28^b	8.87^c		
OC–LiH	**4**	CO	1.121		1.107	1.107	
		CLi	2.267		2.339	2.327	
		LiH	1.641		1.643	1.639	
CO–LiH	**5**	CO	1.138		1.119	1.119	
		OLi	1.928		2.042	2.027	
		LiH	1.654		1.641	1.638	
(LiH)(CO)	**6**	CO	1.208		1.191	1.192	
		CLi	1.927		1.947	1.930	
		OCLi	166.5		163.7	167.1	
		CH	1.240		1.209	1.215	
		OCH	113.6		112.4	111.8	
		LiH	2.101		2.180	2.115	

^{a}Distances in angstroms, angles in degrees. ^{b}Integrated electron population on lithium and oxygen at 3-21G*. ^{c}Natural population on lithium and oxygen at 6-31G*.

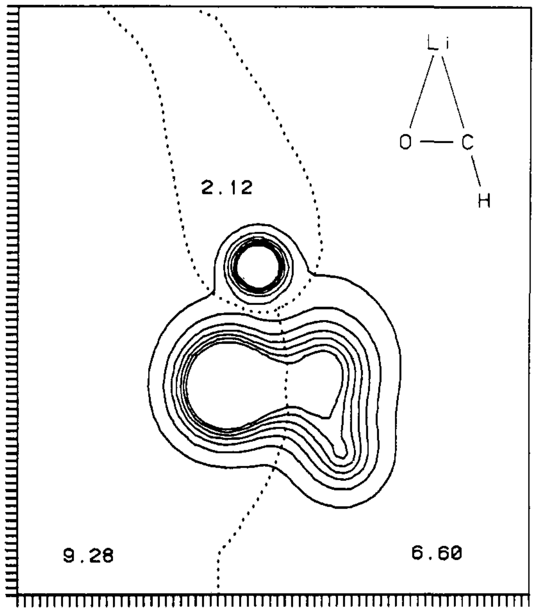

Figure 1. Projected electron density map of formyllithium at 3-21G*. Molecular fragments are demarked by the dotted lines and fragment populations are given. Contour levels are from 0.05 to 0.53 with a gradient of 0.08 e/au.^{2}

HMgCHO, and H_2AlCHO adopt η^2 coordination, **2**. All of these structures are quite similar. The long C=O bonds (1.24–1.25 Å; 1.18 Å in H_2CO at the same levels of theory) indicate a significant perturbation of the carbonyl group. As a test, formyllithium was optimized with correlation corrections at the MP2/6-31G* level.[43] In Table II, it can be seen that correlation has rather minor effects although the C=O bond length is somewhat lengthened compared to the Hartree–Fock structures. All of the η^2 coordinated metals carry large positive charges (ca. +0.85); the interaction with the negatively charged oxygen provides electrostatic stabilization. The charge on the metal is calculated by integrating the projected electron density within a line of demarkation as shown in Figure 1 for formyllithium. The demarkation line represents the gradient minimum of electron density between the metal fragment and the rest of the molecule. In accordance with the ionic radii, the oxygen–metal bonds are shorter than the corresponding carbon–metal bonds. Inherent in the η^2 structures are extremely small O–C–M angles (ca. 65°); this restricts the covalent overlap between the metal and carbon. These calculated structures parallel those in crystal structures of η^2 acyl–metal complexes. Fachinetti et al.[20] have reported O–C–M angles of 78.6° and C=O bond lengths of 1.21 Å with their acyl–zirconium complexes. Zirconium is much larger than any of the metals studied here. In a corresponding ionic model, the greater distance to the metal would result in a larger O–C–M angle and would weaken the perturbation of the carbonyl group.

Table III. Stabilization by η^2 Coordination

	OCM^a	energy^b	ΔE^c
HBeCHO, η^2	63.6	−128.83692	8.3
HBeCHO, η^1	112.9	−128.82365	
H_2AlCHO perp, η^2	69.4	−356.69872	6.7
H_2AlCHO plan, η^1	119.7	−356.68808	
H_2AlCHO perp, η^2	66.5	−356.69876^d	4.9
H_2AlCHO perp, η^1	116.2	−356.69096^d	

^{a}Angle in degrees. ^{b}Total energy (au) at MP2/6-31+G*//6-31G*. ^{c}Energy difference between η^2 and η^1 structures in kcal/mol. ^{d}Total energy (au) at MP2/6-31+G*//3-21+G.

For HBeCHO and H_2AlCHO, η^1 coordinated local minima also could be located in C_s symmetry. At 6-31G* only a η^2 isomer survives for H_2AlCHO; the open form found at 3-21+G closes upon further optimization to give the bridged structure.

Optimization of formylborane led to a η^1 coordinated structure, **3**, with the normal carbonyl bond length, 1.20 Å, which characterizes all of the η^1 species. The moderate positive charge on the borane fragment (+0.58) implies a strong covalent contribution to the carbon–boron bond[44] resulting from the small electronegativity difference between these elements. A low metal fragment charge also reduces the driving force for coordination to the oxygen. Therefore, although the oxygen may assist in the alkyl migrations involved in reactions of trialkylboranes with CO, it does not appear that η^2-coordinated acyl-borane intermediates are present.

It is useful to evaluate the energy differences between η^2 and η^1 structures. For HBeCHO this can be done directly, since η^1 and η^2 isomers are both local minima. The MP2/6-31+G*//6-

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(43) A referee has called attention to the flatness of the LiCHO potential energy surface around an Li–C–O angle of 110°, where his CASSCF calculations indicate a very shallow minimum. We thank the referee for his interest. Our SCF calculations indicate that if such a minimum exists, it would lie substantially above the bridged structure.

(44) This modest positive charge is not an artifact of the η^1 structure. With a 3-21+G basis set, HBeCHO and H_2AlCHO have η^1 coordinated local minima. Integration of the density about these η^1 coordinated metal fragments leads to a relatively large positive charge (ca. +0.80).

Table IV. Basis Set Truncation Effects on the Geometry of Formyllithium

basis set	3-21G*	3-21G*(1s)[a]
CO (Å)	1.246	1.249
CLi (Å)	1.895	1.881
OLi (Å)	1.762	1.700
OCLi (deg)	64.1	62.0

[a] Carbon, oxygen, and hydrogen have standard 3-21G* basis sets and lithium has a 3-21G basis set with two valence shells removed.

31G* energy difference is 8.3 kcal/mol. For H_2AlCHO, two comparisons with the η^2 energies can be made. The η^2 form is 6.7 kcal/mol lower in energy at MP2/6-31+G*//6-31G* than the η^1 isomer with the AlH_2 group rotated into the plane. Alternatively, the MP2/6-31+G*//3-21+G single-point energy for the perpendicular η^1 form gives nearly the same η^1–η^2 difference, 4.9 kcal/mol (Table III).

In the η^2 formyl complexes, the carbonyl bonds are rather long (ca. 1.25 Å) and the oxygen carries a large negative charge (ca. −1.3). As a reference, formaldehyde has a C═O bond length of 1.18 Å and an oxygen charge of −1.03 at the 3-21G* level;[45] therefore, there appears to be a contribution from an alkoxy-carbene resonance form, **1**, in the formyl ligand. However, since this resonance form is the result of a π-bond polarization, it is more useful to examine the population effects in the π-MO. The contour representations of the π-MOs of formaldehyde and formylberyllium hydride in Figure 2 show that the π-bond of the formyl–metal complex is more highly polarized than that of formaldehyde. Moreover, integration over the oxygen fragments of the π-MOs yields populations of 1.73 and 1.56 electrons for formylberyllium hydride and formaldehyde, respectively. This shows that much of the increase in the oxygen electron density of the formyl-metal complex is the result of a π-bond polarization; hence the formyl anion in these complexes has significant alkoxy–carbene character.

If the interaction between the lithium cation and the formyl anion were completely ionic, then the 2s (and 2p) shell on lithium would be empty. By limiting lithium to a basis set that contains only a 1s shell (3-21G with valence shells removed), the lithium can be forced to interact completely ionically. The structure of formyllithium, optimized with a 3-21G* basis set with only a 1s shell on lithium, is compared in Table IV along with the 3-21G* results. This drastic change in basis sets results in only small changes in geometry. Thus, the η^2 geometry is indeed given by a totally ionic model. Previous work[40,41,46] indicates that the carbon–lithium bond in general is largely ionic. Since the other η^2 formyl-metal complexes have structures and electron distributions similar to formyllithium, their carbon–metal bonds are also expected to be dominated by ionic interactions.

Finally, the atomic populations in the formyl-metal systems can also be considered by use of Reed, Weinstock, and Weinhold's Natural Populations.[46] Natural Populations are atomic orbital-like basis populations that are relatively basis set independent. As a test, these atomic populations were calculated for formyllithium, **2**, at the 6-31G* level. The lithium population is calculated as 2.12 electrons with both our integrated populations and Reed et al.'s Natural Populations (Table II). This result points out the utility of the Natural Populations in organolithium compounds.[46] However, there is a difference in the oxygen populations. Such differences between real space (integrated populations) and the Hilbert space (Natural Populations) partitions appear to be general for covalent bonds between atoms of different electronegativities.[45]

The Mechanism of LiH/CO Reactions.[47] The course of the reaction of RLi with CO was investigated theoretically by exploring the potential energy surface of the smallest system, HLi/CO, at rather high levels. Our earlier calculations on related mechanisms show that HLi is a good model for CH_3Li and larger $(RLi)_n$ systems.[48]

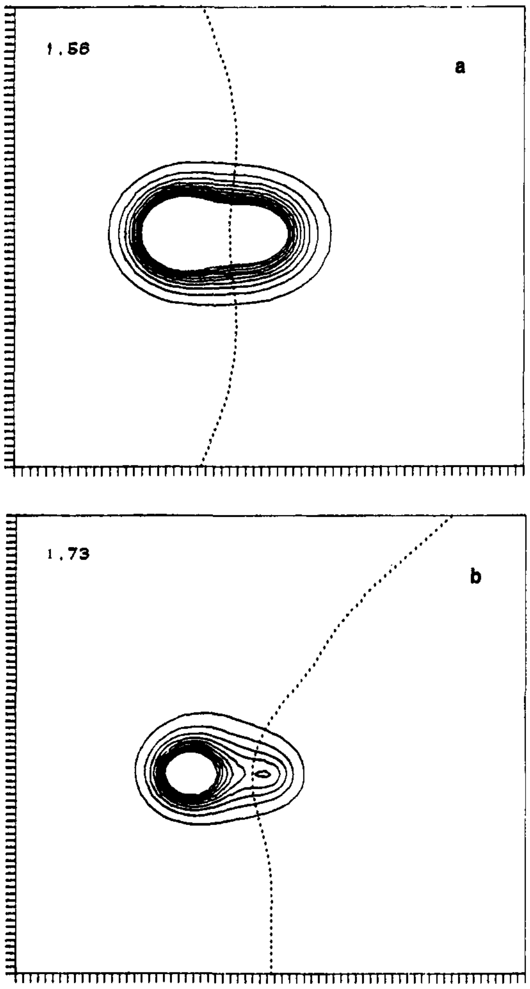

Figure 2. Projected electron density maps of the π-MOs of formaldehyde (a) and formylberyllium hydride (b) at 3-21G*. The contour levels are from 0.03 to 0.30 with a gradient of 0.03 e/au.^{2} In each case the oxygen is on the left.

Lithium hydride and carbon monoxide first form a complex. There are two possibilities: lithium attached to oxygen or to carbon in linear geometries. Both complexes as well as the addition product, LiCHO, are true minima on the 6-31G* potential hypersurface (no imaginary frequencies). The relative energies depend on the level of theory employed (Table V). HLi–OC is slightly more stable than HLi–CO with larger basis sets, and also is the global minimum at the Hartree–Fock level. Inclusion of electron correlation corrections, however, reverses the relative stability of the two linear complexes. This is undoubtedly due to the known change in the CO dipole moment direction at correlated levels.[49] At MP2/6-311+G*//6-31+G*, HLi–CO is more stable than HLi–OC by 3.4 kcal/mol, but the addition product, LiCHO, is 2.8 kcal/mol lower in energy. These relative energies, however, refer to the hypothetical motionless states. Correction for zero-point vibrational energies (at 6-31G*, scaled by 0.9)[39] disfavors the addition product by about 4.4 kcal/mol relative to the linear complexes. Our final estimate (referring to 0 K) predicts the linear complex HLi–CO to be the global minimum. HLi–OC and formyllithium, LiCHO, are less stable by 2.1 and 3.1 kcal/mol, respectively. Nevertheless, all of these

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(45) Bachrach, S. M.; Streitwieser, A., Jr., results to be published.

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Table V. Relative and Zero-Point Vibrational Energies (kcal/mol) of LiCHO Isomers

	LiCHO **2**	OC–LiH **4**	CO–LiH **5**	T.S. **6**	CO + LiH
3-21G//3-21G	0.0	+4.7	+0.5	+29.8	+17.5
6-31G*//6-31G*	0.0	-2.3	-2.4	+24.6	+5.7
MP2/6-31G*//6-31G*	0.0	+2.5	+5.0	+23.4	+12.9
6-31+G*//6-31G*	0.0	-1.6	-1.8	+22.4	+5.6
MP2/6-31+G*//6-31G*	0.0	+3.7	+6.3	+20.2	+12.3
6-311G*//6-31G*	0.0	-3.8	-4.1	+23.0	+2.8
MP2/6-311G*//6-31G*	0.0	+1.1	+4.2	+21.7	+9.7
6-31+G*//6-31G*	0.0	-1.6	-1.8	+22.4	+5.6
MP2/6-31+G*//6-31+G*	0.0	+3.6	+6.3	+19.9	+12.3
MP3/6-31+G*//6-31+G*	0.0	+4.7	+5.8	+20.6	+13.0
MP4/6-31+G*//6-31+G*	0.0	+2.0	+3.6	+19.3	+10.5
6-311+G*//6-31+G*	0.0	-2.7	-2.9	+21.3	+3.5
MP2/6-311+G*//6-31+G*	0.0	+2.8	+6.2	+19.3	+10.8
ZPE[a]	10.5	6.2	6.0	8.0	4.9
final est[b] (0 K)	0.0	-3.1	-1.0	+16.2	+3.4

[a] Zero-point vibrational energy at 6-31G*, scaled by 0.9.[39] [b] Final estimate evaluated with MP2/6-311+G*//6-31+G* data plus ZPE corrections, adjusted for the MP2–MP4 differences at 6-31+G*.

Table VI. Reaction Energies (kcal/mol) of Equation 1: MH + CO → MCHO

M	3-21+G// 3-21+G	6-31G*// 6-31G*	MP2/6-31G*// 6-31G*	6-31+G*[a]	MP2/ 6-31+G*[a]
Li, η^2	-18.6	-5.7	-12.9	-5.6	-12.3
BeH, η^2	-5.3[b]	+3.6	-5.6	+4.7	-4.3
BeH, η^1	+5.9[b]	+13.0	+4.8	+12.8	+4.1
BH_2 perp, η^1	+6.1[b]	+10.2	+2.9	+9.7	+1.7
BH_2 plan, η^1	+2.4	+12.3	+5.1	+12.3	+4.5
Na, η^2	-18.4	+3.3	-3.1	+2.3	-4.2
MgH, η^2	-7.4	+5.5	-2.1	+6.4	-1.0
AlH_2 perp, η^2	-1.2	+7.3	-2.5	+8.5	-1.2
AlH_2 perp, η^1	+2.4				+3.7
AlH_2 plan, η^1	+2.4	+15.5	+6.6	+15.0	+5.5

[a] Geometries at various levels (6-31G* or 6-31+G*). [b] 3-21G//3-21G.

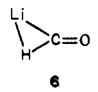
Table VII. Reaction Energies (kcal/mol) of Equation 2: $CH_3M + HCHO \rightarrow MCHO + CH_4$

M	3-21+G// 3-21+G	6-31G* a	MP2/ 6-31G*[a]	6-31+G*[a]	MP2/ 6-31+G*[a]
Li, η^2	-28.9	-25.8	-24.9	-24.5	-21.8
BeH, η^2	-9.6[b]	-6.9	-8.4	-5.0	-5.5
BeH, η^1	+1.6[b]	+2.5	+2.0	+3.1	+2.8
BH_2 perp, η^1	+1.4[b]	+0.6	+0.8	+0.6	+0.6
BH_2 plan, η^1	+1.8	+2.7	+3.1	+3.1	+3.4
Na, η^2	-29.5	-21.5	-18.4	-20.1	-16.0
MgH, η^2	-12.2	-12.0	-11.0	-9.8	-7.7
AlH_2 perp, η^2	-1.3	-5.3	-6.8	-3.4	-4.1
AlH_2 perp, η^1	+2.2				+0.7
AlH_2 plan, η^1	+2.3	+2.9	+2.3	+3.1	+2.5

[a] Geometries at various levels (6-31G* or 6-31+G*). [b] 3-21G//3-21G.

isomers are very close in energy.

We have located the transition structure **6** (one imaginary frequency) leading from HLi–CO to formyllithium, LiCHO, at 3-21G, 6-31G*, and 6-31+G* levels. Our best theoretical estimate of the activation energy is about 19 kcal/mol (Table V). Similar three-membered ring transition structures for alkyl migration to coordinated carbon monoxide have been proposed in transition-metal chemistry,[50] although it is known that the migration is facilitated by adding CO, donor ligands, or Lewis acids.[51-53] Isotope labeling shows that the CO cis to the incoming CO forms the acyl ligand.[51] Thus the additional CO molecule (or donor ligand) is not directly involved in the alkyl migration. The additional CO only lowers the activation energy somewhat by occupying a further coordination site at the metal, but does not alter the mechanism. Hence, our mechanism for the formation of LiCHO may be a good model for CO insertions in general.



6

Recently, Morokuma[47a] has investigated theoretically the insertion of carbonyl into the methyl-metal bond of a model palladium complex. The transition structure for this process also is a three-membered ring and is similar to that in our lithium system. Both indicate that the methyl (or hydride) migrates as the metal–CO axis remains almost linear during the transformation to the transition state.

Energy Evaluations. The relative energies of the other formyl systems can be assessed by means of eq 1 and 2. Equation 1 gives the energy involved by inserting CO into the MH bond, and eq

$$MH + CO = MCHO \qquad (1)$$

$$CH_3M + HCHO = MCHO + CH_4 \qquad (2)$$

2 evaluates the stabilization energy of the metal ligands bound to the formyl with respect to CH_3M as a standard. Because of its isodesmic character, eq 2 is not as sensitive as eq 1 to the level

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of theory employed; the latter is heavily affected by basis set superposition error (BSSE)[54] which is largely eliminated when diffuse and polarization basis sets are employed (see Table VI).

For M = Li we have evaluated eq 1 at rather high levels (Table V). The calculated energies vary somewhat, but the values at MP4/6-31+G*//6-31+G* and at MP2/6-311+G*//6-31+G* are reasonably close to the results obtained at the highest level used for all other metals (MP2/6-31+G*//6-31G*). This level, therefore, should be a good basis for comparison. Only the formation of the η^2-coordinated species has favorable energies in eq 1, and lithium is by far the best. This may be due to the small radius of the lithium cation, resulting in a very effective electrostatic interaction with the oxygen of the carbonyl group. The reaction energies of eq 1 and 2 parallel one another; both reflect the interaction of the metals with the carbonyl group. There are a few exceptions, but most of the reaction energies for both eq 1 and 2 are within the 0 ± 5 kcal/mol range.

Conclusions

Formyl complexes with η^2 geometries involving first- and second-row metals and metal hydrides have been demonstrated. The η^2 coordination does not require metal d-orbital or even p-orbital involvement and is best described as an ionic interaction between a cationic metal center and the lone pairs on carbon and oxygen. The large charge transfer to oxygen and the C=O bond lengthening in the η^2 complexes confirms the presence of an alkoxy–carbene resonance form in the formyl ligand, **1**. Finally, η^2 coordination can provide a chemically significant amount of stabilization and should be most important in systems where the ionic nature of the interaction is large.

Since the activation energies for the addition of CO to LiH and loss of CO from LiCHO are only 19.3 and 16.2 kcal/mol, respectively, for the monomeric species in the gas phase, LiCHO can clearly serve as a catalyst or intermediate for further reactions. Such catalytic activity is well-known with transition metals.[55] Since the overall reaction is almost thermoneutral, the equilibrium may well be promoted by solvation or aggregation affects. These findings may encourage attempts to isolate derivatives of such lithium–carbonyl species. The other metal–formyl complexes are indicated to be thermodynamically unstable with respect to loss of CO, but also may be stable kinetically if decomposition barriers are sufficiently large.

The present conclusions are expected to apply generally to any metal–carbonyl bonding with high ionic character; that is, η^2 coordination as a characteristic even of wholly ionic bonding is more important than may have been appreciated in the past. Examples of metals with high electropositive character are the early transition metals, actinides, and lanthanides. The η^2 coordination observed for acyl complexes of these metals is a normal consequence of ionic bonding and does not necessarily represent unusual bonding modes.[56] Late transition metal compounds are expected to show more covalent character with d-orbital involvement.

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