methylene hydrogens of the neohexene were integrated by NMR. The procedure was repeated in C_6H_6 and the deuterium incorporation also determined by ^2H NMR.

Competitive Trapping Tebbe's Reagent with Trimethylphosphine and 3-hexyne. Tebbe's reagent (10 mg) was loaded in a NMR tube. A solution of 0.2 mL of C_6D_6, 100 μL of 3-hexyne, and 70 μL of trimethylphosphine was made up in a 2-mL volumetric flask. The NMR spectrometer was stabilized at 25 °C. C_6D_6 (0.2 mL) was syringed onto the Tebbe's reagent. The NMR tube was shaken to dissolve the Tebbe's reagent. Then 0.2 mL of the trap solution was syringed into the NMR tube at the same time that a stop watch was started. The reaction was then followed by an automated kinetic routine. At the time of addition of the traps, the Tebbe's reagent is completely converted to **8** and metallacyclobutene. **8** then reacts with 3-hexyne to form more of the metallacyclobutene. The pseudo-first-order rate constant is 1.24×10^{-3} s^{-1}. At the time that $t = 0$, the logarithm intercept was 0.1215. With use of this intercept and the first-order logarithm expression, it can be calculated that the ratio of products from trimethylphosphine and 3-hexyne is 10.9. When the kinetic expression for mechanism 7 is factored as shown below, then the terms that cause the expression to saturate are in parentheses.

$$\text{rate} = k[R]\left(\frac{k_2[T]}{k_{-1}[O] + k_2[T]}\right)$$

If now [O] is taken to be 1 and the [T] to be 27.9 (as in the case of a 27.9-fold excess of 3-hexyne) and the [O] rate constants to be 1 compared to the 10.9 (as found above) for the [T] rate constants, then the following expression results.

$$\text{rate} = k_1[R]\left(\frac{1 \times 27.9}{10.9 \times 1 + 1 \times 27.9}\right) \Rightarrow \text{rate} = 0.719k_1[R]$$

Therefore 71.9% of the rate-determining k_1 should have been reached when the 3-hexyne is in a 27.9-fold excess.

Competition Trapping Experiments. Three 10-mg samples of compounds **2**, **3**, **7**, **8**, and **9** and Tebbe's reagent were measured into individual NMR tubes. In a 10-mL round bottom was measured out 364 μL (10 equiv) of neohexene, 50 mg of diphenylacetylene (10 equiv), and 3 mL of toluene. In another 10-mL round-bottom 252 μL of cyclopentene (10 equiv), 500 mg of diphenylacetylene (10 equiv), and 3 mL of toluene were measured out. In a third 10-mL round-bottom 399-μL of 4-octyne (10 equiv), 500 mg of diphenylacetylene (10 equiv), and 3 mL of toluene were measured out. Each solution (0.4 mL) was syringed onto each of compounds **2**, **3**, **7**, **8**, and **9** and Tebbe's reagent (along with 10 μL of pyridine) in individual NMR tubes at 25 °C. The reactions were then shaken vigorously and allowed to stand for 1 h. The solvent is then removed in vacuo and each NMR sample taken into the drybox where 0.4 mL of C_6D_6 is added. The product ratios are determined by integrating the cyclopentadienyl resonances.

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Ion Pairing in Transition-Metal Carbonylates Modeled by ab Initio Calculations on BH_2COM_a (M_a = Li, Na)

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Abstract: Ab initio calculations carried out on the title molecules provide an excellent model for the type of ion pairs that have been observed spectroscopically, and by X-ray crystal determination, for various transition-metal carbonylate salts. Three stable ion pair structures have been identified: one involves the alkali metal bonded to the terminal O atom of the CO group with a linear COM_a linkage; the second has a direct alkali-metal-boron bond with essentially tetrahedral geometry around boron; and the third is a π-complex in which the alkali metal is bonded to the CO π-system orthogonal to the plane of the BH_2 group, i.e., stabilization requires an extended π-system involving the nonbonding electrons on B. A study on ion pairing with an (acyl)$BHCOM_a$ system reveals a chelate complex, as has been identified experimentally in related acyl transition-metal carbonylates. Calculated infrared stretching frequencies for the CO group in the various minimum energy structures change from one structural form to the other in a manner exactly paralleling those obtained experimentally for the metal carbonylate ion pairs, e.g., $[BH_2CO]^-$, 2030 cm^{-1}, $[BH_2COLi]$, 1944 cm^{-1}, and $[LiBH_2CO]$, 2103 cm^{-1}. Addition of a water molecule to the alkali-metal ion also causes changes in the CO stretching frequencies that are consistent with experimental data for solvent effects.

The great interest that has been generated by the study of organometallic transition-metal chemistry has in part been stimulated by the hope of creating new synthetic pathways for organic molecules based upon catalytic and stoichiometric use of transition-metal complexes containing direct metal-carbon σ bonds. Excellent recent textbooks attest to this activity.[1,2] A major route to the formation of transition-metal complexes containing a direct metal-carbon σ bond is the reaction of various transition-metal carbonylate salts with organic halides, as illustrated below for two common salt systems.[3,4]

$$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-Na^+ + CH_3I \rightarrow [(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3] + NaI$$

$$[Mn(CO)_5]^-Na^+ + CH_3I \rightarrow [Mn(CO)_5CH_3] + NaI$$

Due to the central position of this type of salt elimination reaction, a considerable amount of study into the physical and chemical properties of the metalate salts has been published.[5,6] It has become clear that the solution structures of these salts are dependent upon many variables such as temperature, solvent composition, and countercation. An excellent review of this ion pairing aspect has been published.[7] Furthermore, it is abundantly clear that the chemical reactivity of the salts is directly related to the various structural modifications exhibited in solution, e.g.,

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(1) Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole: Monterey, CA, 1985.

(2) Collman, J. P.; Hegedus, L. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980.

(3) Piper, T. S.; Wilkinson, G. *J. Inorg. nucl. Chem.* **1956**, *3*, 104.

(4) Clossen, R. D.; Kozikowski, J.; Coffield, T. H. *J. Org. Chem.* **1957**, *22*, 598.

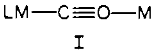
(5) King, R. B. *Acc. Chem. Res.* **1970**, *3*, 417.

(6) Jonas, K. *Adv. Organomet. Chem.* **1981**, *19*, 97.

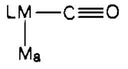
(7) Darensbourg, M. Y. *Adv. Inorg. Chem.* **1985**, *33*, 221.

various ion pair structures are more kinetically reactive and even lead to completely different reaction products.

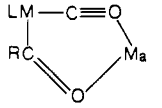
Infrared spectroscopic studies on the transition-metal carbonylates[8-12] and nitrosylates[13] have established two major tight ion pair structures that involve the alkali-metal cation interacting with the carbonylate via the terminal O atom of a carbonyl (or nitrosyl) ligand, I, or interacting directly with the transition-metal atom, II, as illustrated below. A third important tight ion pair structure observed for acyl carbonylates has been established which involves the alkali-metal ion chelating between the acyl carbonyl and a terminal carbonyl group, III.



I



II



III

Type I structures have been established for such carbonylates as $[Co(CO)_4]^-$,[8] $[Mn(CO)_5]^-$,[9] and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$,[11] type II structures for $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$,[11,14] and the type III chelating ion pairs for $[Fe(CO)_3(COPh)(PPh_3)]^-$.[15] In all the infrared spectroscopic studies it has been established that coordination of the alkali-metal ion to the oxygen atom of the carbonyl group results in a significant lowering of the stretching frequency of this CO ligand, with, in general, a corresponding rise for the remaining CO ligands. Furthermore, coordination of the alkali metal to the metal center, or any other ligand, will cause an increase in the CO stretching frequencies observed for the carbonylate salts. It is argued that coordination of the alkali metal on the CO group will increase the amount of metal $d\pi$ – ligand π^* retrodative bonding (metal to ligand electron pair donation), thereby decreasing the C–O bond order and its stretching frequency. Conversely, attachment of the alkali metal ion to some other site will decrease the amount of this retrodative π-bonding and hence increase CO stretching frequencies. It is from such arguments, coupled with the use of alkali-metal ion complexing agents, e.g., crown ethers and superior solvating solvents such as Me_2SO, that the site of ion pairing has been established spectroscopically.

Confirmation of such types of interaction between transition-metal carbonylates and their countercations has also been forthcoming from several important X-ray crystallographic studies. For example, the interaction between Mg^{2+} and a terminal CO group in $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-$ has been established,[16] while penetration of the Na^+ to the metal center has been demonstrated by a structural determination of $[Na_2Fe(CO)_4]\cdot 1.5C_4H_8O_2$ ($C_4H_8O_2$ = dioxane).[17] At the other extreme of interactions, if the countercation is a large species, e.g., $(PPh_3)_2N^+$, or a crown ether complexed alkali-metal ion, the lower electrostatic potential of the cation, coupled with its size, preclude the observation of any interactions between the carbonylate and the cation that effect the observed vibrations of the CO groups. Several structural determinations of this latter type of salt show no evidence for significant cation/anion interactions.[18-20]

The significance of the various ion pairing modes lies not only in their intellectual intrique but also in their often distinctive chemical reactivity patterns. In general, tight ion paired species are less kinetically labile with normal alkyl halides, e.g., $[Fe(CO)_3(NO)]^- + CH_3I$,[13] but an inverse effect has been reported for several salts with more active halides, e.g., $[Mn(CO)_5]^- + PhCH_2Cl$.[9] Finally, it must be understood that the chemical products from reactions involving different ion pairs are often quite distinct.[13,21]

In recent years there has developed a vigorous area of research involving sophisticated molecular orbital calculations to model and predict the geometry and chemical behavior of relatively small organic molecules. In this regard there is a body of work on various aspects of complexes of organic carbonyls, including their complexes with cationic species.[22-32] In such studies, Hartree–Fock calculations with relatively small basis sets were employed to search potential energy surfaces for minimum energy equilibrium structures. In general, such studies involve geometry optimizations at the Hartree–Fock level of theory, followed by calculations of interaction energies with a larger basis set at Hartree–Fock or with electron correlation included. In an early study, DelBene[27] showed that the interaction between Li^+ and formaldehyde is predominantly ion dipole in nature, with the lithium lying along the dipolar axis of the base. In contrast, the interaction with the proton is predominantly covalent with a bent C–O–H angle. Similar conclusions have been reached by Raber and co-workers from a related study on the complexes of formaldehyde with the first- and second-row cations. When the cation is relatively hard, i.e., Li, Na, BeH, MgH, or AlH_2, the C–O–M geometry is linear, but for the softer cations BH_2, SiH_3, and CH_3, this geometry is bent.[32] They have further shown that the potential energy surfaces are rather flat around the minima and the C–O–M angles may be readily deviated from the optimum by a few kilocalories per mole. Similar studies by Jorgenson and co-workers on the interaction of M^+ (M = H, Li, Na) with several second-row bases have shown that the interaction with the proton is also covalent whereas that of the metal ions is predominantly electrostatic.[30]

DelBene et al. have studied the interactions of Li^+ with the dinitrogen bases $NH{=}NH$ and $NH_2{-}NH_2$ and also with $NH_2{-}OH$. In each case two isomers were observed, with the lithium atom occupying a bridging position in the more stable isomer.[31] A tendency for Li^+ to attach at the negative end of the dipole moment vector was noted.

Finally, Moffat performed STO-3G calculations on the complex CH_2CNLi.[33] He found three equilibrium structures, the most stable of which involved the Li occupying a bridging position between the C and N atoms of the cyano group, as a predominantly electrostatic interaction between Li^+ and CH_2CN^-. The other two equilibrium structures were described as ion pair linkages between CH_2Li^+ and CN^- and between CH_2Li^- and CN^+.

The size of transition-metal carbonylate complexes precludes an ab initio study directly. Therefore, in this work we have attempted to use the relatively simple species $[BH_2CO]^-$ as a model for transition-metal carbonylates and performed ab initio calculations such as those described above to probe the geometries, energies, and vibrational frequencies of the CO group, in salts

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[8] Edgell, W. F. In *Ion Pairs in Organic Chemistry*; Szwarc, M., Ed.; Wiley: New York, 1972; Vol. 1, Chapter 4.

[9] Darensbourg, M. Y.; Darensbourg, D. J.; Drew, D. A.; Burns, D. *J. Am. Chem. Soc.* **1976**, *98*, 3127.

[10] Darensbourg, M. Y.; Jimenez, P.; Sackett, J. R.; Hanckel, J. M.; Kump, R. L. *J. Am. Chem. Soc.* **1982**, *104*, 1521.

[11] Pannell, K. H.; Jackson, D. *J. Am. Chem. Soc.* **1976**, *98*, 4443.

[12] Watson, P. L.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 2055.

[13] Pannell, K. H.; Chen, Y.-S.; Belknap, K.; Wu, C. C.; Bernal, I.; Creswick, M.; Huang, H.-N. *Inorg. Chem.* **1983**, *22*, 3378.

[14] Nitay, M.; Rosenblum, M. *J. Organomet. Chem.* **1977**, *136*, C23.

[15] Darensbourg, M. Y.; Burns, D. *Inorg. Chem.* **1974**, *13*, 2970.

[16] Ulmer, S. W.; Skarstad, P. M.; Burlitch, J. M.; Hughes, R. E. *J. Am. Chem. Soc.* **1975**, *95*, 4469.

[17] Fachinetti, G.; Floriani, C.; Zanazzi, P. F.; Zanzari, A. R. *Inorg. Chem.* **1978**, *17*, 3002.

[18] Smith, M. B.; Bau, R. *J. Am. Chem. Soc.* **1973**, *95*, 2388.

[19] Wilson, R. D.; Bau, R. *J. Am. Chem. Soc.* **1974**, *96*, 7601.

[20] Teller, R. G.; Finke, R. G.; Collman, J. P.; Chin, H. B.; Bau, R. *J. Am. Chem. Soc.* **1977**, *99*, 1104.

[21] Semmelhack, M. F.; Tamura, R. *J. Am. Chem. Soc.* **1983**, *105*, 4099.

[22] Staemmler, V. *Chem. Phys.* **1976**, *17*, 187.

[23] Hinton, J. F.; Beeler, A.; Harpool, D.; Briggs, R. W.; Pullman, A. *Chem. Phys. Lett.* **1977**, *47*, 411.

[24] Kollman, P. A. *Acc. Chem. Res.* **1977**, *10*, 365.

[25] Rode, B. M.; Gstein, K. H. *J. Chem. Soc., Faraday Trans.* **1978**, *74*, 889.

[26] Kollman, P. A.; Rothenberg, S. *J. Am. Chem. Soc.* **1979**, *99*, 1333.

[27] DelBene, J. E. *Chem. Phys.* **1979**, *40*, 329.

[28] Berthod, H.; Pullman, A. *Isr. J. Chem.* **1980**, *19*, 299.

[29] Corongiu, G.; Clementi, E.; Pretsch, E.; Simon, W. *J. Chem. Phys.* **1980**, *72*, 3096.

[30] Smith, S. F.; Chandrasekhar, J.; Jorgensen, W. L. *J. Phys. Chem.* **1982**, *86*, 3308.

[31] DelBene, J. E.; Frisch, M. J.; Raghavacheri, K.; Pople, J. A.; Schleyer, P. v. R. *J. Phys. Chem.* **1983**, *87*, 73.

[32] Raber, D. J.; Raber, N. K.; Chandrasekhar, J.; Schleyer, P. v. R. *Inorg. Chem.* **1984**, *23*, 4076.

[33] Moffat, J. B. *J. Chem. Soc., Chem. Commun.* **1980**, 1108.

Table I. Pertinent Bond Lengths (Å) at HF/3-21G Geometries[a]

	species	B–C	C–O	O–M_a	B–M_a
3	$BH_3{\cdot}CO$	1.651	1.123		
4	$[BH_2CO]^-$	1.420	1.202		
5	$BH_2CO–Li$	1.404	1.244	1.618	
6	$BH_2CO–Na$	1.407	1.235	1.954	
7	$LiBH_2CO$	1.454	1.166		2.243
8	$NaBH_2CO$	1.452	1.168		2.468
9	$BH_2(COLi)$	1.422	1.237	1.778	
10	$BH_2(CONa)$	1.424	1.223	2.154	
11	$BH_2CO–LiH_2O$	1.405	1.230	1.647	
12	$BH_2CO–NaH_2O$	1.408	1.232	1.975	
13	$(H_2OLi)BH_2CO$	1.445	1.175		2.278
14	$(H_2ONa)BH_2CO$	1.442	1.174		2.479
15	$BH_2(COLiH_2O)$	1.419	1.237	1.804	
16	$BH_2(CONaH_2O)$	1.419	1.224	2.158	
17	$[HB(CHO)CO]^-$[b]	1.433	1.183		
	$[HB(CHO)CO]^-$[c]	1.554	1.237		
18	HBCHO(CO)Li[b]	1.426	1.200	1.891	
	HBCHO(CO)Li[c]	1.555	1.277	1.760	
19	HBCHO(CO)Na[b]	1.426	1.197	2.223	
	HBCHO(CO)Na[c]	1.556	1.265	2.095	

[a] Structures **9**, **10**, **15**, and **16** are π-complexes; **18** and **19** are chelate complexes. [b] Terminal carbonyl group. [c] Ketonic carbonyl group.

of the general form $[BH_2COM_a]$ (M_a = Li and Na). Our choice of the $[BH_2CO]^-$ anion as a transition carbonylate model is based on the fact that the central boron atom possesses a filled 2p orbital that has the ability, by virtue of both symmetry and energy, to interact with the π-system of the CO group in a manner that mimics the generally accepted dπ–pπ* retrodative bonding pattern of metal carbonyls. Furthermore, the boron atom in the salt has the ability to expand its coordination number by changing hybridization from sp^2 to sp^3, permitting the direct interaction of the cation with the central boron atom if energetically feasible. By studying the variations of the CO stretching frequencies of the various structures found, we are able to provide a direct comparison between theory and experiment, since many infrared spectral studies have been reported for the various structural variations of the carbonylates, as discussed above.

Method

The ab initio calculations were performed by using modified versions of the Gaussian 80/82 system of computer programs. Gradient optimization techniques[34,35] were used to determine equilibrium geometries at the Hartree–Fock level with a split valence 3-21G basis set.[36] Unless otherwise specifically noted in the text, no symmetry restraints were placed upon the various molecular species studied by the computation programs. Vibrational frequencies and zero-point vibrational energies for all species were then determined at the 3-21G level. All species were found to correspond to local minima on the appropriate potential energy surface (no imaginary frequencies). For an improvement of the energetics, additional calculations were performed which included electron correlation evaluated at second-order Moller–Plesset theory with the 6-31+G(d,p) basis set, which includes polarization functions on all atoms and an additional set of diffuse functions on non-hydrogen atoms.[37-40]

Results and Discussion

The structural parameters (Figure 1) computed from this study are recorded in Table I and the energies of the stable structures in Table II, while the CO stretching frequencies are reported in Table III.

Table II. Energies (hartrees) for Minimum Energy Structures

	species	HF/3-21G	MP2/ 6-31+G(d,p)	ZPE(3-21G)
	Li^+	−7.18710	−7.23554	
	Na^+	−160.67376	−161.65929	
	$[Li(H_2O)]^+$	−82.86393	−83.52324	0.026294
	$[Na(H_2O)]^+$	−236.32546	−237.93039	0.025311
3	$BH_3{\cdot}CO$	−138.35407	−139.55017	0.03925
4	$[BH_2CO]^-$	−137.74721	−138.95747	0.027863
5	$BH_2CO–Li$	−145.18443	−146.39305	0.030601
6	$BH_2CO–Na$	−300.36958	−300.78261	0.029455
7	$LiBH_2CO$	−145.16861	−146.41941	0.030302
8	$NaBH_2CO$	−300.39394	−300.81696	0.029801
9	$BH_2(COLi)$	−145.18741	−146.41800	0.031251
10	$BH_2(CONa)$	−300.39090	−300.80635	0.030028
11	$BH_2CO-LiH_2O$	−220.83278	−222.66237	0.056231
12	$BH_2CO-NaH_2O$	−374.26121	−377.04043	0.054412
13	$(H_2OLi)BH_2CO$	−220.81783	−222.68475	0.055868
14	$(H_2ONa)BH_2CO$	−374.26203	−377.06854	0.054673
15	$BH_2(COLiH_2O)$	−220.83493	−222.68160	0.056980
16	$BH_2(CONaH_2O)$	−374.26760	−377.06051	0.055158
17	$[HB(CHO)CO]^-$	−249.86550		0.040943
18	HBCHO(CO)Li	−257.33268		0.044811
19	HBCHO(CO)Na	−410.77303		0.043262
	Transition Structures: Linear C–O–M_a to π-Complex			
	Li^+	−145.17774		0.02988[a]
	Na^+	−298.62276		0.02911[a]

Binding Energies (kcal): E(Complex) − {E(Cation) + E($[BH_2CO]^-$)}

	HF/ 3-21G[b]	MP2/ 6-31+G(d,p)		HF/ 3-21G[b]	MP2/ 6-31+G(d,p)
5	156.9	125.5	**11**	141.9	114.0
6	128.5	104.1	**12**	118.3	95.7
7	147.0	142.1	**13**	129.7	128.0
8	108.0	126.6	**14**	118.8	128.0
9	158.8	141.2	**15**	140.4	126.1
10	132.7	119.0	**16**	122.3	108.3

[a] Imaginary frequency ignored in the calculation. [b] Adjustments for ZPE are all in the range of 1.0–2.1 kcal.

Table III. Calculated CO Stretching Frequencies

	species	ν(CO), cm^{-1}		species	ν(CO), cm^{-1}
3	$BH_3{\cdot}CO$	2378	**12**	$BH_2CO–NaH_2O$	1975
4	$[BH_2CO]^-$	2030	**13**	$(H_2OLi)BH_2CO$	2078
5	$BH_2CO–Li$	1944	**14**	$(H_2ONa)BH_2CO$	2073
6	$BH_2CO–Na$	1968	**15**	$BH_2(COLiH_2O)$	1877
7	$LiBH_2CO$	2103	**16**	$BH_2(CONaH_2O)$	1922
8	$NaBH_2CO$	2084	**17**	$[HB(CHO)CO]^-$	2064, 1770
9	$BH_2(COLi)$	1866	**18**	HBCHO(CO)Li	1950, 1571
10	$BH_2(CONa)$	1903	**19**	HBCHO(CO)Na	1977, 1620
11	$BH_2CO–LiH_2O$	1959			

That $[BH_2CO]^-$ is a suitable model for transition-metal carbonylates is reinforced by the calculations performed on this species and the parent neutral borane–carbonyl compound $BH_3{\cdot}CO$. The computed structure of the latter is tetrahedral about B with a C–O bond length of 1.123 Å and a CO stretching frequency of 2378 cm^{-1} while the anion $[BH_2CO]^-$ exhibits trigonal-planar geometry about the boron atom, with a C–O bond length significantly increased to 1.202 Å and a CO stretching frequency reduced appropriately to 2030 cm^{-1}. The HOMO of the anion is an extended π-orbital orthogonal to the molecular plane and encompassing the three atoms B, C, and O. This orbital is bonding with respect to B–C and antibonding with respect to C–O. Hence, polarization of the electron density in this orbital toward the CO group should lead to an increased CO bond length and reduced B–C bond length, as expected for retrodative bonding.

Addition of Li and Na (M_a) to the anion above resulted in computation of a series of complexes which are described, and discussed, individually below and compared to the appropriate transition-metal carbonylate salts. As noted in the method section, no prior symmetry, bond length, or bond angle constraints were

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(34) Pulay, M. *Mol. Phys.* **1969**, *17*, 197.

(35) Schlegel, H. B. Ph.D. Thesis, Queens University, 1975.

(36) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(37) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quant. Chem. Symp.* **1976**, *10*, 1.

(38) Krishnan, R.; Pople, J. A. *Int. J. Quant. Chem.* **1976**, *14*, 91.

(39) Spitznagel, G. W.; Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comp. Chem.* **1982**, *3*, 363.

(40) Clark, T.; Chandrasekhar, H.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comp. Chem.* **1983**, *4*, 294.

placed upon the molecules prior to geometry optimization. Starting geometries were simply the structure of the anion mentioned above with suitable guesses of M_a–O, B, etc. bond lengths.

BH_2COM_a. Interaction of both cations Na^+, and Li^+ with $[BH_2CO]^-$ produces linear equilibrium structures with the metal bonded to the oxygen atom of the CO group. This interaction increases the retrodative bonding between B and the CO group as evidenced by a decrease in the B–C bond length for both complexes, from 1.420 Å in the free anion to 1.404 (Li) and 1.407 Å (Na) for the alkali-metal complexes. Correspondingly the C–O bond lengths increase as more retrodative bonding is apparent, from 1.202 Å for the anion to 1.244 (Li) and 1.235 Å (Na) for the complexes. The CO stretching frequencies reflect this bond length change, decreasing from 2030 cm^{-1} for the anion to 1944 (Li) and 1968 cm^{-1} (Na) for the alkali-metal ion complexes. Such variations are completely in accord with the experimental results obtained from studies on the transition-metal carbonylate complexes in which ion pairing via the terminal CO oxygen produces significant CO stretching frequency decreases for the bridging CO group. For example, for the carbonylate $[(\eta^5\text{-}C_5H_5)Fe(CO_2]^-$, the solvent-separated anion (e.g., a crown ether complexed Na salt or a tetraalkylammonium salt) exhibits two stretching frequencies at 1866 and 1788 cm^{-1}, whereas the Li and Na tight ion paired structures involving a direct Fe–CO–M_a interaction exhibit the bridging stretching frequency at 1745 and 1770 cm^{-1}, respectively.[11,14] Not only is the general decrease in stretching frequency of the bridging CO group paralleled in the calculation and experiment, but also the more subtle aspect of this interaction distinguishing Li and Na is clearly noted. Thus Li, which forms a stronger complex, polarizes the π-electron density of the HOMO away from B toward the CO group to a greater extent, with resulting greater elongation of the CO bond length and decrease of the CO stretching frequency. This mimics the experimental result of electron flow from the dπ orbitals of Fe to the coordinated CO group.

Further experimental evidence for such cation-dependent stretching frequency variations comes from infrared studies on the salts $[Fe(CO)_3(NO)]M_a^+$, (M_a = K, Na).[13] In these salts the tight ion pairing observed in thf solution involves a direct nitrosyl-oxygen cation interaction, i.e., Fe–N–O–M_a. For the separated ion pair, the ν(NO) stretching frequency is at 1646 cm^{-1}, whereas for the Na and K tight ion pairs it is at 1613 and 1615 cm^{-1}, respectively. Thus again, not only the distinction between tight ion pairs and the corresponding separated ion pairs parallel the reported calculations, but also the more subtle distinctions involving cation variations are reflected in the calculations.

M_aBH_2CO. Structures with direct alkali-metal boron interactions have also been identified via our computations. It is significant that these molecules exhibit a pronounced elongation of the B–C bond in comparison to the free anion $[BH_2CO)]^-$, with a corresponding decrease in the C–O bond length; i.e., the B–C bonds are 1.454 (Li) and 1.452 Å (Na) compared to the free anion at 1.420 Å. The carbonyl stretching frequencies are significantly higher than the free anion: $[BH_2CO]^-$, 2030 cm^{-1}; $LiBH_2CO$, 2103 cm^{-1}; $NaBH_2CO$, 2084 cm^{-1}. This type of variation for a tight ion pair involving a direct alkali-metal–transition-metal interaction is also in accord with published infrared studies. The attachment of the alkali metal to the electron-rich transition-metal drastically reduces the extent of retrodative π-bonding to the carbonyl group, increasing the M–C bond length, decreasing the C–O bond length, and thereby increasing the CO stretching frequency compared to the free anion. For example, for the tight ion pair Li–$Fe(CO)_2(\eta^5\text{-}C_5H_5)$, the stretching frequencies are at 1880 and 1805 cm^{-1}, the stretching frequencies for the sodium salt are at 1877 and 1806 cm^{-1}, and for the much smaller, and hence more tightly bound magnesium salt, the stretching frequencies are much higher at 1918 and 1854 cm^{-1}.[11,14,41] The corresponding values for the separated ion pair are 1866 and 1788 cm^{-1}.

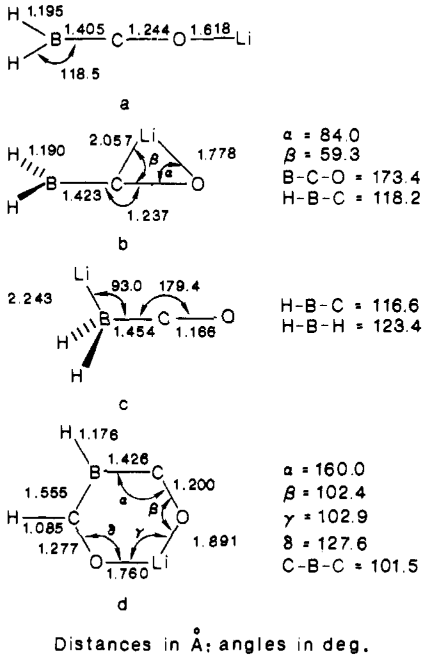

Figure 1. Geometries of minimum energy structures, $[BH_2CO]^-Li^+$ and $[(HCO)BHCO]^-Li^+$.

$BH_2(COM_a)$ π-Complex. For both the lithium and sodium complexes, minimum energy structures containing a stable π-structure involving the direct interaction of the cation with the C–O π-system are obtained from our calculations. The metal interacts with both the C and O atoms of the CO group and significantly increases the C–O bond length and decreases the stretching frequency with respect to the free anion. The C–O bond lengths are now 1.237 (Li) and 1.223 Å (Na), and the stretching frequencies are at 1866 and 1903 cm^{-1}, respectively. It is important to point out that this type of π-complex has only been observed in our calculations when the alkali metal is orthogonal to the molecular plane; i.e., there is a clear need for the extended π-system of the three p orbitals of B, C, and O. No minima were found with the alkali metal in the plane of $[BH_2CO]^-$. In these latter computations we constrained the geometry to force the metal ion to be in the plane of the anion and only the linear structure results from such calculations. It has been previously reported that ab initio calculations on the interaction of free CO with Li^+ gave no evidence for π-interactions, bonding only occurring via the lone pairs on both C and O.[31] Clearly the coordination of CO produces a very different species.

BH(CH=O)COM$_a$ Chelate. The previous example of a π-complex interaction has no experimental counterpart at the present time in terms of transition-metal carbonylates. However, a related example involving an alkali-metal chelate structure between an acyl carbonyl and a terminal carbonyl group has been reported.[15] We therefore decided to study an appropriate model of this system, i.e., $[BH(CHO)CO]^-$. It was very gratifying to find that a minimum energy structure for the corresponding Li and Na complexes, illustrated in Figure 1d, involves a chelate structure. In this structure the cation interacts with a lone pair on the carbonyl oxygen atom and with the π-system of the terminal CO group. Both the CO stretching frequencies are considerably reduced from those exhibited in the parent [*cis*-BH(CHO)CO]$^-$ which are 2064 and 1770 cm^{-1}. For the lithium chelate the frequencies are 1950 and 1571 cm^{-1}, while for the Na complex they are 1977 and 1621 cm^{-1}.

$[BH_2CO]^-[M_a(H_2O)]^+$. In an attempt to assess the effect of solvation upon the spectroscopic properties of the carbonylate ion pairs, a single water molecule was added to the alkali-metal ion and the monohydrated complexes were reoptimized. The presence of a water molecule on the alkali-metal ion allows for electron delocalization, decreasing the positive charge of the cation and reducing it's electrostatic potential. Only in the case of the ion

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(41) McVicker, G. B. *Inorg. Chem.* **1975**, *14*, 2087.

pair with a direct B–M_a interaction is there a significant geometric change, increasing the B–Li bond length from 2.243–2.278 Å (B–Na from 2.468–2.479 Å) and altering the geometry around B which returns to a more trigonal arrangement. The general reduction in electrostatic potential of the metal ion reduces the interaction of the ion with $[BH_2CO]^-$, and in the case of the BH_2CO-M_a and $BH_2(COM_a)$ π-complexes this is reflected in slightly shorter C–O and longer B–C bond lengths and increased C–O stretching frequencies, e.g., BH_2CO-Li, ν(CO) = 1944 cm^{-1}, and $BH_2CO-LiOH_2$, ν(CO) = 1959 cm^{-1}. These changes may be compared to the results obtained from solvent variation studies on the lowest carbonyl stretching frequency in the sodium salt of the cluster anion $[HFe(CO)_{11}]^-$.[42] The reported values are 1655 (diethyl ether), 1690 (THF), and 1749 cm^{-1} (diglyme), reflecting an increasing ability of the solvent to coordinate the alkali metal, thereby reducing the electrostatic potential of that cation, in turn reducing the strength of its interaction with the carbonyl group. The reduced interaction in the hydrated complexes is also reflected in the MP2/6-31+G(d,p) binding energies that are reduced 11–15 kcal/mol for the Li complexes and 8–12 kcal/mol for the Na complexes.

Structural/Energetic Features of the Complexes. The energies of the various complexes have been computed by using both the HF/3-21G and the larger 6-31+G(d,p) basis sets, the latter including the effects of electron correlation evaluated at second-order Moller–Plesset theory. The results are presented in Table II. The binding energies of the complexes in which the cation interacts with the carbonyl group are significantly reduced at the higher level of theory relative to HF/3-21G, whereas the stability of the complexes with Li coordinated to B is reduced only slightly, and the corresponding Na complex is stabilized to a significant extent. As a result, the relative stabilities of the various complexes are different at MP2/6-31+G(d,p) compared to HF/3-21G; however, it is important to remember that the MP2/6-31+G(d,p) energies are computed with HF/3-21G optimized geometries, vide infra.

At MP2/6-31+G(d,p), the most stable complex has Li bonded to B with a binding energy of 142.1 kcal/mol, which is reduced to 140.5 kcal/mol when the zero-point vibrational energy (ZPE) is added. This complex is only slightly more stable than the π-complex, which has a binding energy of 141.2 kcal/mol (139.1 kcal/mol with ZPE). The Na complexes exhibit a parallel stability pattern. The least stable of the complexes have the alkali-metal ion bonded to the carbonyl oxygen, with binding energies (kcal/mol) of 125.5 (123.8 with ZPE), Li, and 104.1 (103.1 with ZPE), Na. In all cases the lithium complexes are computed to be more stable than their sodium analogues as a natural result of the greater electrostatic potential of the smaller ion.

We have examined the potential energy surfaces for bonding of both Li and Na at the carbonyl oxygen atom as a function of the C–O–M_a angle maintaining the geometry of the remainder of the molecule. Although both equilibrium structures are at 180°, the shape of the surfaces is very flat when the angular dependence is restricted in the plane perpendicular to the BH_2 plane, and we have been able to locate the HF/3-21G transition states for the interconversion of the C–O–M_a complex to the π-complex. The activation energies are very low, 4.8 kcal/mol for Li and 2.1 kcal/mol for the Na system at this level of computation. For the Li system, we have computed this activation energy at the MP2/6-31+G(d,p) level, using geometries optimized at this level, and find that it is further reduced to 2.43 kcal/mol (1.99 kcal/mol with added ZPE).[43] It is clear that the low activation energies of our model computations suggest that both types of structure can coexist in solution where external solvation factors not considered in this study could overwhelm any intrinsic energy differences. Furthermore, it is noteworthy that the various structures published for transition-metal carbonylate ion pairs in which sodium binds to a terminal carbonyl group have a nonlinear C–O–Na angle, of approximately 150°. The shape of the potential energy surfaces for movement of the cation around the C–O group restricted to the BH_2 plane in which no π-complex exists indicate a steeper increase for the Li system than that for Na, again reflecting the weaker interaction of Na to the carbonyl group.

Finally, it is significant that for all the complexes discussed in this article, our calcualtions indicate that the alkali metal strongly polarizes the electron density of the anion and results in electron transfer to the metal. Electron transfer is highest in the complexes with the alkali metal bonded to B and least when bonded to the carbonyl oxygen. This order parallels the stability order of the complexes computed at MP2/6-31+G(d,p). Although the complexes are stabilized predominantly via electrostatic interactions, i.e., ion pair type interactions, it appears that the degree of covalent bonding within the individual structures may play a role in determining the relative stabilities.

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(42) Chen, C. K.; Chang, C.-H. *Inorg. Chem.* **1983**, *23*, 3378.

(43) These calculations were performed on a Cray X/MP-24 at the University of Texas System Center for High Performance Computing. The energy values (hartrees) are the following: BH_2CO-Li, −146.41523 (ZPE = 0.028635); transition structure −146.41137 (ZPE = 0.027947).