tributed to larger resonance energy in benzene as opposed to benzene iron tricarbonyl.

Conclusions

The ab initio calculations seem to represent the ground state and transition state of bicyclo[2.2.1]hepta-2,5-dien-7-one reasonably well. The ground-state geometry with C_{2v} symmetry seems reasonable when compared to similar molecules whose geometry is known, and leads to calculated IR spectra of bicyclo[2.2.1]-hepta-2,5-dien-7-one and bicyclo[2.2.1]hepta-2,5-dien-7-one-d_6 which closely match the experimental ones. This geometry appears distorted toward products, which in turn suggests that the transition state is symmetrical. A transition state with C_{2v} symmetry is indeed found. This appears to be a transition state when correlation effects are included at the MP2/4-31G level as well. Furthermore, the activation energy at the MP3/6-31G* level agrees quite closely with the experimental value, and reasonable extrapolation to the MP4/6-31G* level suggests that one should expect even better agreement there. While a nonsynchronous transition state is found at the UHF/STO-3G level, this does not persist at higher levels. The C_{2v} geometry is lower in energy than the nonsynchronous ones with the 4-31G basis set at both RHF and UHF levels, and at the MP2/6-31G* level. The synchronous transition state explains the observed pattern of reactivity of **1** and other norbornenones. Furthermore, it completes a correlation of the exothermicity and reactivity for a series of pericyclic concerted reactions that ab initio calculations suggest all follow synchronous pathways. In the case of bicyclo[2.2.1]hepta-2,5-dien-7-one (**1**), even the ground-state geometry prefigures a symmetrical transition state. Thus while no mechanism can ever be "proven", the synchronous mechanism as reflected by the ab initio calculations provides the best available explanation of the experimental trends of these widely disparate reactions.

Acknowledgment. We thank the NSF for support of this work and for a grant of time on the Cray X-MP/48 at the Pittsburgh Supercomputing Center. We also thank Dr. K. N. Houk and members of his group for helpful discussions.

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Supplementary Material Available: Energies of points in Figure 5, optimized geometries for **1**, synchronous and nonsynchronous transition states, and details of CI calculations (4 pages). Ordering information is given on any current masthead page.

Rotational Barriers in Aldehydes and Ketones Coordinated to Neutral Lewis Acids

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Abstract: Calculations of the energies and geometries of complexes of some aldehydes and ketones with neutral Lewis acids have been performed in order to characterize the conformations and rotational barriers of the Lewis acid–carbonyl complexes and of substituents at the carbonyl. The 6-31G* basis set was used to obtain energies for geometries optimized at 6-31G* or 3-21G, and correction for electron correlation with use of the Møller–Plesset perturbation method was made where practical. Complexes of H_2CO with BH_3, BF_3, AlH_3, and $AlCl_3$ all had bent, C_s symmetry structures as minima, with linear structures 6–10 kcal/mol higher in energy and out-of-plane structures higher still in energy. The effect of BH_3 and BF_3 coordination upon the rotational barriers about the C–C bond adjacent to the carbonyl group of propanal was minimal, while the effect upon the conformational preferences of acetone was pronounced. Rotation about the donor–acceptor bond in the C_s structures of the aldehydes had a barrier of 0.8 to 1.4 kcal/mol with the syn (eclipsed) conformation the minimum for all of the Lewis acids studied, while for acetone the gauche conformations of both the Lewis acid and methyl hydrogens with respect to the carbonyl were lowest in energy.

Lewis acid complexation of carbonyl compounds can have a dramatic effect on the rates and selectivities of reactions at carbonyl centers.[1] There has been much discussion of the mechanisms of Lewis acid catalyzed reactions of carbonyl compounds, and much ambiguity remains. An understanding of the conformations of the Lewis acid–carbonyl complexes and their relative energies and steric requirements is a necessary prerequisite to determining the origin of selectivities and stereochemical preferences in these reactions. In previous papers, we have calculated the conformations and barriers to rotation of some aldehydes, ketones, carboxylic acids, and esters.[2-4] Here we extend these studies to the conformations of aldehydes and ketones coordinated to neutral main group Lewis acids.

Few experimental data are available on the equilibrium geometry of complexes of organic carbonyl compounds with main group Lewis acids. Thus a calculational study should be valuable in elucidating the most stable conformations of the complexes. In addition, calculational methods offer data on conformational energies, rotational barriers, and models for transition states that are difficult or impossible to obtain by experimental measurements. One might hope to get structural and energetic data from molecular mechanics calculations, but parameters for Lewis acid complexes are not well established, so molecular mechanics results would not be reliable. We report here the results of ab initio calculations on conformations and energies of BH_3, BF_3, and AlH_3,

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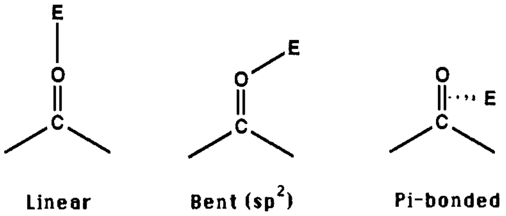

Figure 1. Modes of coordination of Lewis acids to carbonyls.

and $AlCl_3$ complexes of some simple aldehydes and ketones. From these data we can make some generalizations about the conformations of Lewis acid–carbonyl complexes, the energetic cost of unfavorable modes of coordination, and the effect of coordination upon rotational barriers of alkyl groups adjacent to the carbonyl in the organic moiety. These results should shed some light on the mechanisms of boron and aluminum Lewis acid–catalyzed asymmetric reactions of carbonyls.

Modes of Coordination. One might anticipate several different possible modes of coordination of Lewis acids to carbonyl groups (Figure 1). First, purely electrostatic interactions can be considered, where C–O–M = 180°, putting the Lewis acid at the negative end of the C=O dipole. An interaction of this type has been suggested from infrared spectroscopic studies of the related van der Waals complex of hydrogen fluoride with carbon dioxide.[5] Another possibility is covalent attachment of the Lewis acid to a lone pair on the carbonyl oxygen, where the Lewis acid is in the nodal plane of the C=O π bond. This geometry is adopted by the van der Waals complex of formaldehyde with hydrogen fluoride[6] and is the statistically preferred geometry in crystal structures of hydrogen bonds to carbonyl oxygens in ketones.[7] Still another possibility for the interaction is η^2 coordination of the Lewis acid to the C=O π bond. In this case the carbonyl is formally the donor, but back-bonding into the C=O π^* orbital occurs.

Few crystal structures of organic carbonyl complexes of main group Lewis acids have been obtained.[8] Many more exist of transition-metal complexes with carbonyl compounds, showing a range of coordination geometries.[9-11] The coordination mode of lanthanide shift reagents with carbonyl groups has been the source of some controversy, but the data seem consistent with a linear structure or fast interconversion of bent structures on the NMR time scale.[12] Coordination to the π face of the carbonyl does not seem likely for main group Lewis acids, though it is known for some transition-metal complexes.[11] Finally, a crystal structure of a $TiCl_4$–unsaturated ketoester complex has been published which appears to be an example of a fourth, bent-nonplanar mode of binding,[9] although another structure of a $TiCl_4$–ester complex has a bent planar geometry.[10a]

Free energies of activation for the interconversion of bent complexes of BF_3 with ketones of 8–10 kcal/mol have been estimated by NMR spectroscopy from the coalescence temperature as observed in $CDCl_3$–$CHFCl_2$ solution.[13] No other experimental data for the dynamics of conformational change appear to be available for Lewis acid–carbonyl complexes.

Previous ab initio and semiempirical calculations have examined the coordination of cationic species with carbonyls.[14-17] These calculations indicate that open-shell gas-phase cations such as H^+, CH_3^+, and BeH^+ have a covalent bent mode of attachment with a high barrier to inversion via the linear structure, while closed-shell cations, Li^+ and Na^+, prefer the linear structure by a small amount (1–3 kcal). The latter calculated results are not in agreement with crystal structures of acetone and of an unsaturated ester complexed to lithium cation, in which bent structures were observed.[18] Calculations of charged complexes may not be relevant to the structures and energies of complexes in solution and crystalline solids, since the binding energies for ion–neutral complexes in the gas phase are much higher than in condensed phases. In the most extreme case, protonation, the coordination energies (experimental and calculated) are about 200 kcal/mol in the gas phase.[16] The MNDO semiempirical method has been used to calculate the difference between bent and linear coordination energies of some neutral Lewis acids coordinated to dimethylcyclopropanone.[17] In that study, the differences in energy in some cases of interest were the following: BF_3, 5.2 kcal/mol and $AlMe_3$, 2.8 kcal/mol, with the bent geometry preferred in both cases. The value for BF_3 is smaller than the 8–10 kcal inversion barrier reported experimentally for several ketones.[13]

From the studies discussed above, it is obvious that different Lewis acids can have different modes of binding. It is not clear the extent to which gas-phase calculations for ionic Lewis acids will be relevant to solution chemistry. In addition, the ab initio calculation of transition-metal organometallic complexes with a full complement of ligands is not practical. Therefore we restricted our study to the simple but synthetically relevant cases of neutral main group Lewis acids. Solvent effects are expected to be small for neutral complexes compared to charged complexes.

Little progress appears to have been made toward understanding the effects of Lewis acid coordination on the conformational profiles of aldehydes and ketones. Lewis acid coordination is thought to change the preferred conformation of acrylic acid esters from s-cis to s-trans.[1b,19] When the organic ligand is bidentate, Lewis acid coordination should have a large influence on substrate conformation, not only within the chelate ring but on pendant groups.[20] The effect of simple monocoordination on the conformational equilibria of carbonyl compounds has apparently not been investigated.

Methods

Calculations were carried out with the GAUSSIAN82 package[21] and standard basis sets. Vibrational analysis was performed at the 3-21G level on optimized structures of H_2CO–BH_3 and H_2CO–AlH_3 to verify that optimized structures were minima. Geometries were optimized with the following constraints: the maximum symmetry of the conformation (C_1 or C_s) was used and planar configuration at the carbonyl center was enforced in calculations of propanal complexes. Correction for electron

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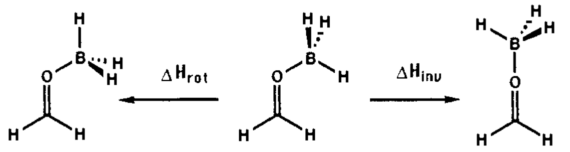
Table I. Energies of H_2CO–BH_3 at Different Basis Levels



Basis		coord. energy, kcal/mol	ΔH_{inv}, kcal/mol	ΔH_{rot}, kcal/mol
energy	geometry			
3-21G	3-21G	17.1	7.66	1.25
6-31G*	3-21G	7.18	7.79	0.96
6-31G*	6-31G*	7.33	4.60	0.84
6-31G**	6-31G*	7.28	4.55	1.05
MP2(FC)/6-31G*	6-31G*	15.8	11.4	1.37
MP2(FC)/6-31G**	6-31G*	16.0	11.6	1.38
MP3(FC)/6-31G*	6-31G*	16.4	11.2	1.37
MP2(full)/6-31G*	MP(2(full)/ 6-31G*	14.4	10.4	1.39

correlation with the Møller–Plesset perturbation method (MP) was carried out with use of only the valence electrons for single-point calculations, but all-electron perturbation was used for the post-Hartree–Fock geometry optimizations. The basis sets used are represented basis-1//basis-2: basis 1 was used to obtain the energy at the basis 2 optimized geometry.

Results and Discussion

Basis Set Considerations. In donor–acceptor complexes, the changes in energy between different conformations often are small and the geometric distortions are "soft", so it is desirable to optimize geometries with bases that include polarization functions and with correction for electron correlation, although the latter is often not feasible. Explicit correction of basis set superposition error of complexation energies at the polarization level is not necessarily reliable,[22] so it was not attempted. This error will in any case have a smaller effect on the relative energies of different coordination geometries than on absolute coordination energies.

No experimental gas-phase complexation energies are available for Lewis acid complexes of carbonyls with which to compare our calculations. As a result, we initially have studied complexes with formaldehyde since its small size permitted a fairly extensive study. The formaldehyde–borane coordination energy and rotational barriers were studied at a number of levels of theory (Table I). The coordination energy was found to double on going from 6-31G* to MP2/6-31G*, but on going to MP3/6-31G*, there was a small change in the coordination energy for H_2CO–BH_3. Geometry optimization at the MP2/6-31G* level for H_2CO–BH_3, while giving a significantly different geometry, did not produce much change in relative energy. Coordination energies of the H_2CO–BH_3 system were not significantly changed by the addition of polarization function (p-type orbitals) at the hydrogens. Thus the MP2/6-31G*//6-31G* level seems desirable for obtaining coordination energies, but this is not practical for some of the larger systems.

The total energies in hartrees for complexes in their lowest energy conformations are listed in Table II. The coordination energies in kcal/mol are listed in Table III. It was interesting to note that whereas electron correlation had a large effect on the coordination energies for the BH_3 complexes of formaldehyde and of propanal, it had a relatively small effect on the coordination energies for the BF_3 or AlH_3 complexes. The better agreement of 3-21G relative energies than 6-31G* energies with MP2/6-31G* energies is probably due to the compensating effects of ignoring both electron correlation and polarization. The basis set dependence of the rotational barriers follows that of the coordination energy.

For most of the calculations, correlation corrections with Møller–Plesset perturbation to second order (MP2) gave energies close to those obtained with the more time-consuming MP3. Binding energies calculated by the two methods differed by up to 2 kcal/mol (Table III), but relative energies of different structures differed by a few tenths of a kcal/mol or less (Table IV). The structural data are summarized in Table V. Since the difference between single-configuration relative energies and those corrected by MP2 are variable and often a substantial fraction of the total values, MP2 energies are a reasonable choice for calculations of weakly bonded complexes of this type.

For the study of rotational potential functions in the organic moieties (propanal and acetone), the 3-21G optimized structure was found sufficient: little change in relative energies was seen on going from 6-31G*//3-21G to 6-31G*//6-31G*.

There are no gas-phase geometry data with which to compare the calculated coordination geometries. Calculated donor–acceptor bond lengths and angles are not very accurate unless correlation is used,[23] since energy change with geometric distortion in the weak donor–acceptor bonds is very small. Indeed, for the case in which geometry optimization was performed with a correlated basis, H_2CO–BH_3, a significant change in geometry was seen from the single-configuration optimization (Table V). From the limited data available, it appears that the 3-21G optimized geometries may be a better guide to the correlated geometries than the 6-31G* optimized geometries. In any case, the geometric parameters reported for these complexes should be used with caution.

Coordination Energies. The calculated coordination energies of the lowest energy conformations of each of the complexes studied are listed in Table III. Although no experimental gas-phase complexation energy data are available for comparison, agreement of protonation energies of H_2CO and CH_3CH_2CHO at the 6-31G*//3-21G level with the experimental gas-phase values was reasonable. Protonation energies of these compounds is an order of magnitude more exothermic than coordination with neutral Lewis acids. Formaldehyde forms considerably weaker complexes with BH_3 and BF_3 than do propanal or acetone. This was expected due to the greater polarizability and electron-donating ability of methyl groups compared to hydrogens. Propanal and acetone, however, have very similar affinities for BH_3 and BF_3. Stabilization due to the greater Lewis basicity of acetone is apparently offset by steric hindrance of the Lewis acid which must now coordinate syn to a methyl group: coordination of BH_3 syn to the methyl group of acetaldehyde is 2.1 kcal/mol less favored than anti coordination (6-31G*//3-21G).

The value for the inversion energy (bent to linear geometry) of BF_3–H_2CO (4.0 kcal/mol at MP2/6-31G*) is low compared to the reported inversion barriers in ketones from NMR studies (8–10 kcal/mol). On the basis of the trends seen with lower basis sets, the inversion energy at this level of theory of BF_3 complexes with acetone and propanal should be higher by 2 kcal/mol. The calculated coordination energy of BF_3 with dimethyl ether, on the other hand, is considerably higher than an experimental value determined by manometry.[24] From these discrepancies it is clear that the quantitative accuracy of the coordination energies and relative conformational energies is not high. Nevertheless, the computational results should provide a useful semiquantitative guide to what may be expected and will provide the basis for further experimental work.

An interesting finding from the coordination energy data is the relative affinities of ether versus carbonyl oxygens for BF_3.[24] Our data suggest that the equilibrium (in the gas phase) may lie substantially in favor of the BF_3–ether complex and free aldehyde or ketone: the difference is 0.9 and 1.5 kcal/mol (6-31G*//3-21G) for acetone and formaldehyde. This is relevant to synthetic applications since the BF_3–diethyl ether complex is used as a catalyst for reactions of carbonyls.

Geometry and Rotational Barriers in the Complexes. The lowest energy geometry of coordination and the rotational profile about Lewis acid–carbonyl bonds were first investigated for the simplest

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Table II. Energies of Lewis Acid Complexes with Carbonyl Compounds

	energy (hartrees)				
	calculated			MP2/ 6-31G*	MP3/ 6-31G*
	3-21 G^a	6-31 G*	6-31 G*		
complex	3-21G	3-21G	3-31G*	6-31G*	6-31G*
$H_2CO–H^+$			−114.156 46	−144.442 83	−114.453 84
$H_2CO–BH_3$	−139.486 41	−140.266 73	−140.268 02	−140.654 63	−140.673 61
$H_2CO–BF_3$	−436.508 93^b	−437.066 12^b	−437.073 26	−437.957 92	−437.958 56
$H_2CO–AlH_3$	−355.552 01	−357.510 22	−357.512 31	−357.867 96	−357.886 85
$H_2CO–AlCl_3$	−1725.998 03	−1734.479 53			
acetone–H^+	−191.215 12		−192.287 55		
acetone–BH_3	−217.156 25		−218.366 95		
propanal–H^+	−191.193 20	−192.263 66	−192.265 79		
propanal–BH_3	−217.145 67	−218.355 84	−218.357 17	−219.004 62	
propanal–BF_3	−512.391 18	512.159 50			
MeOMe–BF_3	−474.743 43	−477.273 09	−477.278 45	−478.309 15	−478.328 05

[a] The top symbol indicates the basis set used for energy calculation; the geometry was optimized at the level indicated by the lower symbol. [b] 4-31G was used here instead of 3-21G.

Table III. Coordination Energies of Lewis Acids with Carbonyl Compounds

	energy (kcal/mol)					
	calculated			MP2/ 6-31G*	MP3/ 6-31G*	
	3-21G	6-31G*	6-31G*			
complex	3-21G	3-21G	6-31G*	6-31G*	6-31G*	exptl
$H_2CO–H^+$			−187	−174	−177	−177^b
$H_2CO–BH_3$	−17.1	−7.18	−7.33	−15.8	−14.36	
$H_2CO–BF_3$	−18.8^a	−6.37^a	−7.18	−7.04	−9.02	
$H_2CO–AlH_3$	−28.9	−18.1	−18.7	−21.0	−20.3	
$H_2CO–AlCl_3$	−50.3	−28.3				
acetone–H^+	−206		−204			−195^b
acetone–BH_3	−19.9	−9.76	−9.23			
propanal–H^+	−198	−196	−197			−188^b
propanal–BH_3	−19.2		−9.34	−18.2		
propanal–BF_3	−29.9	−9.55				
MeOMe–BF_3	−40.37	−11.1	−11.4	−18.8	−18.4	−13.6^c

[a] 4-31G was used here instead of 3-21G. [b] Aue, D. H.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Wiley: New York, 1979; Vol. 2, p 1. [c] Reference 24.

aldehyde, formaldehyde. All the Lewis acids studied were placed in the nodal plane of the CO π bond or perpendicular to the plane at varying angles, with all other parameters allowed to minimize at each angle. The relative energy values for the different geometries at several basis levels are listed in Table IV.

The effect of a large distortion of the weak coordination bond from the sp^2 minimum of around 120° to a linear geometry is energetically small (6 and 10 kcal/mol for AlH_3 and BH_3, respectively, at MP3/6-31G*) for these neutral electrophiles, in contrast to the large energy required to distort $^+H—O{=}C$ and $^+CH_3—O{=}C$ bond angles.[14] Thus we may anticipate that the steric demands of these Lewis acids toward substituent groups on the carbonyl will be smaller than would be expected of substituents held more rigidly in an sp^2 geometry. This was found to be the case, as will be discussed for acetone–BH_3 below. Lower barriers calculated for aluminum complexes than for boranes indicate that if the two possible bent isomers of an aldehyde or ketone are in equilibrium, they will probably not be resolvable by low-temperature NMR experiments for complexes containing aluminum, in contrast to the observed BF_3 inversions about ketones.[13]

We have examined the energy difference between bent and linear complexes of propanal to determine whether the results differ significantly from the formaldehyde value. At the 6-31G*//3-21G level, the difference between bent and linear propanal–BH_3 was 10.3 kcal/mol, while for formaldehyde–BH_3 the calculated difference was 7.8 kcal/mol. Interestingly, the difference between the two inversion barriers is about the same as the difference in the coordination energies for these two complexes (Table III).

When the Lewis acids are moved from the nodal plane of the π bond onto its face, the complexes are higher in energy in all cases studied than bent configurations in the nodal plane (Table IV). Structures with the Lewis acid over the carbonyl π bond are less stable than even the high-energy linear configuration at most basis levels. Our observation that the most favorable Lewis acid coordination takes place in the π nodal plane is in agreement with the crystal structure of a benzaldehyde–BF_3 complex[8] and with sp^2 bonding of main group Lewis acids to carbonyl compounds. Planar coordination has also been observed experimentally in complexes of carbonyl compounds with iron, tin, and titanium Lewis acids.[10] Force constants have been estimated of the C–O–B angle in and out of the plane from Table IV and are listed in Table VI. These estimated force constants indicate that while coordination over the π face is energetically unfavorable, a small distortion from planarity (15°) is facile. The rotational profiles

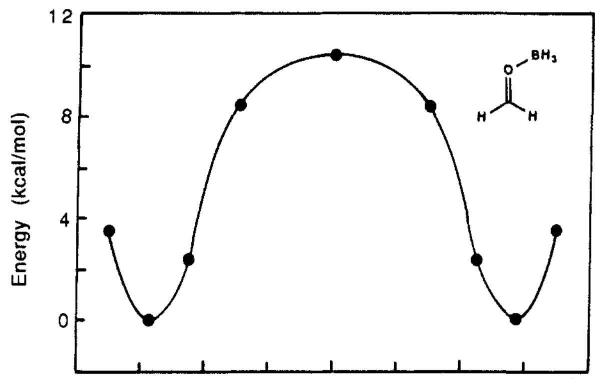


Figure 2. Energy of formaldehyde–BH_3 complex as a function of C–O–M angle (MP3/6-31G*//6-31G*).

Table IV. Relative Energies of Lewis Acid Complexes with Formaldehyde with Various Geometric Constraints

			relative energies (kcal/mol)				
	angles		3-21G	6-31G*	6-31G*	MP2/6-31G*	MP3/6-31G*
COM	τCOMX	τMCOE	3-21G	3-21G	6-31G*	6-31G*	6-31G*
			$H_2CO–H^+$				
opt.					0.00		0.00
180					23.4	24.2	24.2
			$H_2CO–BH_3$				
90	0	0			6.16	–	–
110	0	0			2.39	3.62	3.58
122.5^a	0	0	0.00	0.00	0.00	0.00	0.00
135	0	0			1.52	2.50	2.42
150	0	0			3.65	9.27	8.49
180	0^b	0	7.66	7.79	4.60	10.1	10.4
122.5	0	15	0.71		0.79	1.09	1.11
120	0	45			3.97	9.70	
120	0	90			5.19	12.83	
122.5	180	0	1.25	0.96	0.84	1.37	1.39
120	180	90	10.8	6.26	5.20		
90	180	90	13.8		6.13		
60	180	90	6.8				
			$H_2CO–BF_3$^{c}				
110	0	0			1.00	1.04	
122.1^a	0	0	0.00	0.00	0.00	0.00	
135	0	0			0.68	1.46	
180	0^b	0	7.07	5.76	2.37	4.00.	
122.1	0	15	0.79		0.30	0.53	
122.1	180	0	1.27	0.93	0.48	0.27	
120	180	90	11.2	3.83			
90	180	90	5.4				
			$H_2CO–AlH_3$				
110	0	0			3.13	1.68	1.98
125.1^a	0	0	0.00	0.00	0.00	0.00	0.00
135	0	0			0.61	1.08	1.00
150	0	0			2.58	3.36	3.27
125.1	0	15	0.49		0.52	0.59	0.59
120	0	45			3.81	16.5	
120	0	90			6.7	19.9	
180	0^b	0	2.66	5.22	5.10	6.05	5.95
125.1	180	0	1.25	1.34	0.95	1.10	1.12
120	180	0	11.3	8.64	8.85		
90	180	0	22.0				
			$H_2CO–AlCl_3$				
opt.	0	0	0.00	0.00			
opt.	180	0	0.74	1.15			
180	180	0	1.60	4.63			
120	180	90	13.4				

[a] The optimal bond angle at the geometry studied, 6-31G* value is listed. [b] One M–X bond is in the nodal plane. [c] 4-31G used instead of 3-21G.

of the C–O–M angles in $H_2CO–BH_3$ and $H_2CO–AlH_3$ are illustrated in Figures 2 and 3.

The barrier to rotation about the donor–acceptor bond is an important consideration in determining the disposition of substituents of Lewis acids in a complex. This problem arises in the design of chiral Lewis acids as chiral auxiliaries. We found that in all the aldehyde complexes studied, the barrier to rotation about the donor–acceptor bond was 0.8 to 1.4 kcal/mol (Table IV), and the conformations with a bond of the Lewis acid eclipsing the O=C bond were the most stable. This result is consistent with other cases in which substituents adjacent to an sp^2 center prefer to eclipse double bonds,[2-4] although the dipolar nature of the bonds involved and the long donor–acceptor bonds made this result impossible to predict.

The details of all the calculated structures were quite basis-set dependent, but the trends were consistent at all levels studied (Table V). Structural parameters for the lowest energy conformations of formaldehyde, propanal, and acetone complexed to BH_3 and BF_3 are listed in Table V. Two structural parameters that are of primary importance are the M–O–C angle and the O–M bond length. Both can undergo large changes with a small change in energy. The gross feature of the geometry found for the boron complexes is consistent with the structure of a crystalline benzaldehyde–BF_3 adduct,[9] which shows the bent planar structure. Optimized B–O–C angles (6-31G*) vary from a minimum of 123° in formaldehyde to 135° in some of the acetone conformers. The Al–O–C angle is 122° and 141° in the AlH_3 and $AlCl_3$ formaldehyde complexes (3-21G), respectively, and could be larger with little energetic cost, since the linear geometry is only 6 kcal/mol higher in energy (MP3/6-31G* for AlH_3). The donor–acceptor bond lengths were 1.73 (BH_3), 1.71 (BF_3), 1.98 (AlH_3), and 1.87 Å ($AlCl_3$) at the 3-21G level. Electron correlation shortens the donor–acceptor bond by 0.07 Å (BH_3). The bond lengths of the groups attached to the carbonyl change little on complexation, in accord with the small coordination energies we see. The carbonyl bond length is again basis set dependent, but it appears to increase by 0.012 Å upon coordination to BH_3 (MP2/6-31G* and 6-31G*) and by 0.014 Å on AlH_3 complexation (6-31G* and 3-21G). Despite their stronger coordination, the aluminum complexes are more easily distorted from the bent geometry to the linear geometry than borane complexes and O–Al distances remain short in the linear structures. The differences between the coordination and inversion energies of the aluminum complexes versus the boron complexes can be explained by a greater electrostatic contribution to the complexation energy in the former.

Table V. Selected Geometric Parameters of Lewis Acid Complexes with Carbonyl Compounds

carbonyl compound	Lewis acid	basis	bond lengths (Å)				bond angles (deg)			
			CO	OM	MX_a	MX_b	COM	OCR_1	OMX_a	OMX_b
H_2CO		3.21G	1.207							
		6-31G*	1.184							
		MP2/6-31G*	1.220							
CH_3CH_2CHO		3-21G	1.209					114.8		
		6-31G*	1.188					115.0		
CH_3COCH_3		3-21g	1.211					122.5		
		6-31G*	1.192					121.7		
H_2CO	H^+	3-21G	1.232	0.965			117.4	121.7		
CH_3CH_2CHO	H^+	3-21G	1.266	0.979			121.7	119.2		
		6-31G*	1.247	0.961			116.5	118.4		
CH_3COCH_3	H^+	3-21G	1.275	0.977			120.8	122.5		
		6-31G*	1.255	0.960			116.1	121.7		
	BH_3	3-21G		1.188						
		6-31G*		1.188						
H_2CO	BH_3	3-21G	1.219	1.725	1.209	1.197	125.3	121.3	101.6	102.1
		6-31G*	1.196	1.757	1.206	1.197	122.5	121.3	100.9	101.0
		MP2/6-31G*	1.233	1.686	1.209	1.201	120.6	120.8	102.7	101.2
CH_3CH_2CHO	BH_3	3-21G	1.224	1.704	1.212	1.199	125.7	119.3	102.2	102.8
		6-31G*	1.203	1.715	1.208	1.199	123.3	119.0	102.1	101.9
CH_3COCH_3	BH_3	3-21G	1.232	1.685	1.196	1.209	128.2	122.2	103.5	103.7
		6-31G*	1.211	1.696	1.197	1.207	127.0	122.1	101.9	103.4
	BF_3	3-21G			1.329					
		4-31G			1.331					
		6-31G*			1.301					
H_2CO	BF_3	4-31G	1.220	1.705	1.384	1.363	126.7	120.7	100.3	102.8
		6-31G*	1.191	2.210	1.318	1.308	122.1	121.8	93.4	95.4
CH_3CH_2CHO	BF_3	3-21G	1.233	1.648	1.382	1.362	123.7	118.6	100.9	104.3
CH_3COCH_3	BF_3	3-21G	1.242	1.625	1.358	1.379	126.4	121.6	105.0	103.1
	AlH_3	3-21G		1.600						
		6-31G*		1.584						
H_2CO	AlH_3	3-21G	1.221	1.977	1.628	1.609	121.6	121.3	94.3	101.8
		6-31G*	1.199	2.046	1.609	1.594	125.6	121.3	94.6	100.4
	$AlCl_3$	3-21G			2.160					
H_2CO	$AlCl_3$	3-21G	1.230	1.867	2.215	2.187	141.2	120.9	97.3	103.2

Table VI. Estimated Force Constants for Distortion of Oxygen–Electrophile Bond Angles at the MP3/6-31G*//6-31G* Basis Level

complex	coordinate	distortion (deg)	force constant (mdyn/rad)
	C–O–B angle	−12.5	1.04
	H–C–O–B torsion	15.0	0.22
$H_2CO–BF_3$	C–O–B angle	+12.9	0.40
	C–O–B angle	−12.1	0.32
	H–C–O–B torsion	15.0	0.11
$H_2CO–AlH_3$	C–O–Al angle	+9.9	0.47
	C–O–Al angle	−15.1	0.40
	H–C–O–Al torsion	15.0	0.12

Effect of Complexation on Aldehyde and Ketone Conformations. The effect of BX_3 coordination upon the rotational profile of groups α to the carbonyl in acetone and propanal was examined by fixing the OCCC dihedral angle at several values while optimizing the other geometrical parameters (except those constrained by symmetry). First we consider the effect of coordination upon the OCCC dihedral angle potential function of propanal (Table VII). Figure 4 shows the rotational profiles for the 6-31G* optimized geometries (with OCCC dihedral angles fixed as specified).

In previous papers we have reported the calculated rotational profile of propanal and discussed the components of the rotational barriers.[2,3] The eclipsed (τ_{OCCC} = 0°) conformation is favored over the skew conformation (τ_{OCCC} = 127°) by 1.2 kcal/mol. Barriers to rotation at 71° and 180° are 2.2 and 1.8 kcal/mol in height, respectively.

Coordination of a bare proton to propanal leads to a pronounced lowering of the rotational barriers and of the local minimum at ~120°. This is consistent with the substantial C=O bond lengthening in the protonated molecule (0.06 Å at 3-21G) and reduction of the C=O bond dipole accompanying protonation, reducing the dipole–induced dipole stabilization of the minimum energy conformation.[2] As discussed earlier, however, protonated gas-phase species are probably not relevant to solution.

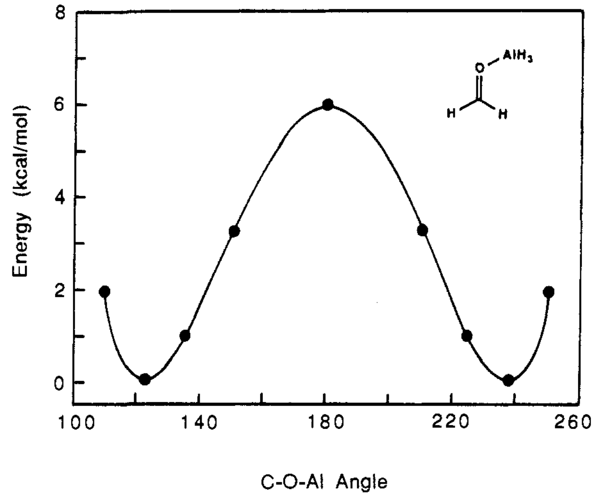


Figure 3. Energy of formaldehyde–AlH_3 complex as a function of C–O–M angle (MP3/6-31G*//6-31G*).

The coordination of BH_3 and BF_3 also lower the barriers and the local minimum, but only by about 10%. The energy profiles as a function of CCCO dihedral angle are essentially identical with that of propanal alone: the global minimum is at 0°, the maximum is at 180°, and a local minimum is at about 120°. Thus we find that for simple aldehydes, the conformations of groups α to the carbonyl and anti to the Lewis acid are essentially unchanged upon coordination. Of course if steric constraints are severe, or if the Lewis acid coordinates with another site on the ligand as well as the carbonyl oxygen, changes in conformation of the organic moiety will occur upon coordination. Also we may expect that a substantial effect will be exerted on the ligand

Table VII. Energies of Propanal–Lewis Acid Complexes as a Function of OCCC Dihedral Angle

compd (ϕ, deg)	energy, hartrees (kcal/mol) 3-21G//3-21G	6-31G*//3-21G	6-31G*//6-31G*
propanal			
(0)	-190.877 76 (0.00)	-191.951 24 (0.00)	-191.952 27 (0.00)
(71)	-190.873 10 (2.92)	-191.947 71 (2.21)	-191.948 94 (2.09)
(127)	-190.875 00 (1.73)	-191.949 41 (1.15)	-191.950 45 (1.14)
(180)	-190.873 90 (2.42)	-191.948 37 (1.80)	-191.949 42 (1.79)
propanal-H^+			
(0)	-191.193 20 (0.00)	-192.263 66 (0.00)	-192.265 79 (0.00)
(71)	-191.191 67 (0.96)	-192.261 39 (1.42)	-192.263 62 (1.36)
(120)	-191.192 34 (0.54)[a]	-192.262 84 (0.52)[a]	-192.265 07 (0.45)
(180)	-191.190 67 (1.58)	-192.261 56 (1.32)	-192.263 54 (1.41)
propanal-BH_3			
(0)	-217.143 67 (0.00)	-218.354 29 (0.00)	-218.355 82 (0.00)
(71)	-217.139 92 (2.35)	-218.351 28 (1.89)	-218.352 80 (1.90)
(121)	-217.141 26 (1.51)	-218.352 84 (0.91)	-218.354 30 (0.95)
(180)	-217.140 20 (2.18)	-218.351 76 (1.59)	-218.353 14 (1.68)
propanal-BF_3			
(0)	-512.386 64 (0.00)	-515.158 96 (0.00)	-515.161 88 (0.00)
(71)	-512.383 29 (2.10)	-515.155 92 (1.91)	-515.158 89 (1.87)
(121.3)	-512.384 36 (1.42)		-151.160 37 (0.95)
(180)	-512.383 69 (1.85)	-515.156 46 (1.57)	-515.159 28 (1.63)

[a] OCCC = 109.2.

Table VIII. Energies of Acetone–BH_3 Complexes at Various Geometries

conformation	energy, hartrees (kcal/mol) 3-21G//3-21G	6-31G*//3-21G	6-31G*//6-31G*
acetone			
ee		-190.887 22 (0.00)	-191.962 23 (0.00)
es		-190.885 75 (0.92)	-191.960 89 (0.86)
ss		-190.883 02 (2.64)	-191.958 65 (2.25)
acetone·H^+			
ee		-191.215 12 (0.03)	-192.287 55 (0.00)
es		-191.215 16 (0.00)	-192.287 46 (0.05)
se		-191.215 11 (0.03)	-192.287 34 (0.31)
ss		-191.213 82 (1.34)	-192.285 89 (1.04)
acetone[a]·BH_3[a]			
ee e	-217.154 09 (1.36)	-218.364 25 (1.70)	
ee s	-217.154 85 (0.88)	-218.365 85 (0.69)	
es e	-217.153 21 (1.91)	-218.363 46 (2.19)	
se e	-217.153 94 (1.45)	-218.365 03 (1.21)	
es s	-217.156 25 (0.00)	-218.366 95 (0.00)	
se s	-217.154 58 (1.05)	-218.365 25 (1.07)	
ss e	-217.152 41 (2.41)	-218.363 06 (2.44)	
ss s	-217.154 18 (1.30)	-218.364 83 (1.33)	

[a] Acetone geometry refers to the dihedral angles OCCH and OCC'H, syn and anti to boron, respectively. BH_3 geometry is the HBOC angle. e = 0°, s = 60°.

conformation when the lewis acid must reside on the same side of a carbonyl group as an alkyl substituent (syn), as for ketones and acylic esters.

The lowest energy anti conformation of propanal–BH_3 (OCCC = 0°) is favored over the lowest syn conformation (OCCC = 180°) by 2.5 kcal/mol at the 6-31G*//6-31G* level. A MNDO calculation showed 1.8 kcal difference between syn and anti forms of benzaldehyde–BF_3[8]. Thus it should generally be safe to ignore syn-complexation in conformational populations of complexed aldehydes, although a few percent of the complexes may exist in syn conformations.

We have previously reported the calculated rotational profile of acetone.[2] The doubly eclipsed (τ_{OCCH} = 0°) conformation is preferred by 0.9 kcal/mol over the eclipsed-gauche conformation. When hydrogen orientations are explicitly considered, many conformations are available to the acetone–BH_3 complex. These are all within a few kcal/mol in energy, but the results (Table VIII) were surprising. Since the lowest energy conformation of acetone has two hydrogens eclipsing the carbonyl oxygen, we expected that conformer B in Figure 5 would be lowest in energy. Instead, conformer A was found to be the energy minimum. The B–O–C angle in conformer A is 127°, and the distance between the methyl and borane hydrogens is 2.5 Å. The acetone–BF_3 conformational surface was investigated at only a few points—the staggered and eclipsed geometries of Figure 5. In this case the

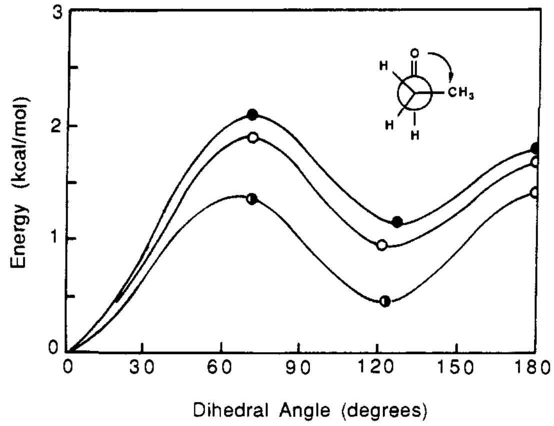


Figure 4. Energy of propanal–Lewis acid complexes as a function of CCCO dihedral angle (6-31G*//6-31G*). Propanal alone (closed circles), propanal–H^+ (half-filled circles), propanal–BH_3 (open circles). Propanal–BF_3 gives essentially the same curve as propanal–BH_3.

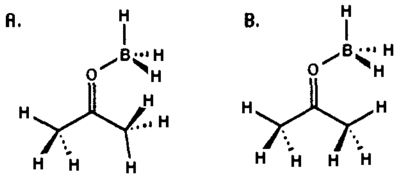
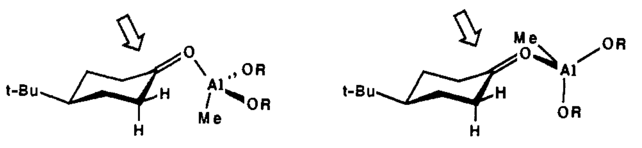


Figure 5. Conformations of the acetone–BH_3 complex. Structure A is the lowest energy conformation (es-s).



Pi Coordination

In-Plane Coordination

Figure 6. Bulky Lewis acid effects upon transition states: (a) aluminum bonded to the π face of ketone; (b) aluminum in the π nodal plane of ketone.

staggered geometry was again energetically preferred (by 0.8 kcal/mol at 6-31G*//3-21G), in contrast to uncomplexed acetone. This finding shows that the steric requirements of BH_3 and BF_3 are not severe, but that these Lewis acids do perturb the ground-state conformation of ketones. Thus while the effects of anti coordination to propanal were minimal, syn coordination to propanal and coordination to acetone caused a 180° change in the dihedral angle at the α carbon in the lowest energy conformation. The rotational preference about the donor acceptor bond was also reversed, with the COBH(F) dihedral angle adopting a gauche arrangement.

Effects of Lewis Acids upon Stereoselectivity of Carbonyl Reactions

In this section we attempt to apply our findings on the structure of Lewis acid complexes with carbonyl groups in a qualitative way to the problem of stereoselection in nucleophilic reactions of carbonyl centers. The coordination energies, inversion barriers, and geometries reported here may be used to prepare empirical parameters for carbonyl–Lewis acid complexes, with the caveats that the single-configuration energies are not accurate for complexes involving BH_3 and that the energies in solution may change. In particular it is expected that the bent forms, having slightly larger dipoles than the linear forms, will be preferentially stabilized in polar solvents.

No experimental or theoretical evidence supports equilibrium π-coordination of the neutral main group Lewis acids studied here. Despite this, a stereoselective equatorial (anti-Cram) alkylation of a substituted cyclohexanone was rationalized to occur by π-complexation of the nucleophile ($MeAl(OR)_2$) preferentially to one π face of the ketone.[25] On the basis of our studies, a more consistent geometry of the ketone–aluminum complex has aluminum in the π nodal plane of the ketone, with the bulky alkoxide ligands asymmetrically oriented, blocking the otherwise less hindered face of the ketone, as shown in Figure 6. This model could apply as well to stereoselective anti-Cram hetero-Diels–Alder reactions catalyzed by $Eu(FOD)_3$,[26] whether the C–O–M geometry in the complex was linear or bent.

The often-invoked Zimmerman–Traxler transition state for aldol-type reactions[27] is generally drawn in a chair-cyclohexane form with the Lewis acid 60° from the plane of the carbonyl and a tetrahedral C–O–M angle, despite the preference for at least the Lewis acids discussed here to reside near the plane of the carbonyl, as well as to have long O–M bonds[28] and large C–O–M angles. Transition-state conformers need not put the Lewis acid in the most stable configuration, but the energetic cost of the distortions must be accounted for in the comparison of different transition states. We are currently investigating model cyclic aldol transition states in order to clarify the geometric requirements of these systems.

The use of Lewis acids as chiral auxiliaries in reactions of organic carbonyl compounds has been investigated by several groups.[29,30] With a few exceptions, the enantioselection seen in reactions utilizing chiral Lewis acids has not been large. Our finding that rotation about the O–M bond is facile and that the coordination modes in general are soft indicates that it may be difficult to achieve a rigid structure favoring reaction at one face of the carbonyl. This problem has been circumvented by making the groups involved very large, and by adding a second point of attachment to the complex. Our results suggest that boron Lewis acids are more promising as chiral auxiliaries than aluminum acids because the O–M bond is shorter and the barrier to assuming the linear geometry is larger. Depending on the reaction conditions, however, aluminum can be hexacoordinate and the structural data herein would not apply. Hexacoordinate octahedral Lewis acids offer a better opportunity for chiral ligands to influence the environment of the reactive center since ligands are forced closer together.

One approach to the flexibility problem in designing a chiral Lewis acid auxiliary, taken by Kelly and co-workers, is to use a chelate substrate containing a second oxygen.[29] Another interesting approach that we propose is the use of a bidentate chiral Lewis acid. The second point of contact would restrict the orientations available to the Lewis acid. Bidentate Lewis acids are known,[31] though no chelation of carbonyl groups in solution has been reported. $F_2BCH_2CH_2BF_2$ chelates alkoxides, but not carbonyls[31c] (we find that the coordination enthalpy of a second BH_3 to formaldehyde is less than half of that for the first BH_3 (6-31G*)).

Conclusions

The calculated structures and energies of the complexes are basis dependent, but the orientational preferences were consistent at all levels of theory. The Lewis acid complexes of BH_3, BF_3, AlH_3, and $AlCl_3$ with formaldehyde were found to prefer bent, C_s geometries. C–O–M angles in these complexes varied from 123° to 135° in boron complexes and from 122° to 141° in aluminum complexes. Steric effects at α-carbons can be relieved by opening the C–O–M angle at small energetic cost, thus the steric demands of these Lewis acids towards substituent groups on the carbonyl are smaller than expected for substituents of sp^2 geometry. Structures with these Lewis acids coordinated to the π face of the carbonyl group are higher in energy than C_s structures. Rotation about the donor–acceptor bond in the C_s structures of the aldehydes had a barrier of 0.8 to 1.4 kcal/mol with the syn (eclipsed) conformation the minimum for all of the Lewis acids studied, while for acetone the gauche conformations of both the Lewis acid and methyl hydrogens with respect to the carbonyl were lowest in energy.

The electronic effects of BH_3 and BF_3 anti-coordination upon the energy of the OCCC dihedral angle profile of propanal are negligible. Syn coordination accounts for a few percent of the total conformations of propanal and acetaldehyde complexes of BH_3 and BF_3. Syn coordination to propanal and coordination to acetone cause the conformational preference of the α-carbon to invert. Our findings should be taken into account in the study

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of asymmetric reactions of ketones catalyzed by main group Lewis acids.

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Registry No. H_2CO-H^+, 18682-95-6; H_2CO-BH_3, 60048-48-8; H_2C-O-BF_3, 116025-23-1; H_2CO-AlH_3, 116025-24-2; H_2CO-$AlCl_3$, 116025-25-3; MeOMe-BF_3, 353-42-4; acetone-H^+, 43022-03-3; acetone-BH_3, 80394-09-8; propanal-H^+, 18682-97-8; propanal-BH_3, 116025-26-4; propanal-BF_3, 31169-83-2.

The Ni–CO Binding Energy in $Ni(CO)_x$ (x = 1–4). A Theoretical Investigation

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Abstract: The Ni–CO binding energies have been calculated for the sequence $Ni(CO)_x$ (x = 1–4) with high-accuracy quantum chemical methods. The results obtained in these calculations are 30 kcal/mol (exptl = 29 kcal/mol) for the first carbonyl, 29 kcal/mol (54 kcal/mol) for the second, 36 kcal/mol (13 kcal/mol) for the third, and 24 kcal/mol (25 kcal/mol) for the fourth carbonyl. The calculated total binding energy for $Ni(CO)_4$ is thus 120 kcal/mol (exptl = 120 or 140 kcal/mol), which is a major improvement compared to a previously calculated value of 79 kcal/mol. The main reason for the improvement of the theoretical results is that electron correlation effects for the CO ligand electrons are taken into account in the present calculations, which was not the case in the previous study. For the individual carbonyl binding energies large discrepancies still remain between theory and experiment, however. These discrepancies remain even if very large atomic basis sets are used in the calculations and they are therefore most probably due to an error in the experimental value. To test the adequacy of the present calculations the C–O frequency shift in $Ni(CO)_2$ was also calculated. This is a difficult property to calculate, but reasonable agreement with experiment was still obtained. A strong coupling between the two carbonyl ligands is found to give an important contribution to the C–O frequency shift.

I. Introduction

The transition metal–carbonyl bond is of fundamental importance in both organometallic chemistry and surface chemistry. It has therefore been extensively studied, both experimentally and theoretically, and the bonding mechanism is now essentially understood. A puzzling observation, which still needs further investigation, however, is the irregular trend in the experimentally determined carbonyl binding energies for $Ni(CO)_x \rightarrow Ni(CO)_{x-1} + CO$ for x = 1–4. The binding energies are obtained from a combination of photoelectron spectroscopy measurements by Stevens et al.[1] and appearance potential measurements by Compton and Stockdale[2] on the negative ions $Ni(CO)_x^-$ (x = 1–3). These experiments give a total Ni–CO binding energy of 120 kcal/mol for $Ni(CO)_4$, thus yielding an average Ni–CO binding energy of 30 kcal/mol. The first and the fourth carbonyl groups are bound by 29 and 25 kcal/mol, respectively. This is reasonably close to the average. Surprisingly enough, however, the second carbonyl obtains a much larger binding energy of 54 kcal/mol, and the third carbonyl a very small binding energy of 13 kcal/mol. Previous theoretical investigations[3,4] gave roughly the same binding energy for the first and the second carbonyl, 24 and 27 kcal/mol, respectively.[3] These theoretical results, however, cannot be considered definitive since in particular the discrepancy between the calculated total binding energy of $Ni(CO)_4$ of 79 kcal/mol and the relatively well established experimental value of 140 kcal/mol[6] is very large. In a recent paper[5] on NiCO we showed that the previous results suffered from not correlating all ten CO valence electrons. When all valence electrons are correlated, the binding energy of NiCO increases from 24 to 33 kcal/mol. Since it is likely that ligand correlation is responsible for the major part of the discrepancy between theory and experiments for the total binding energy of $Ni(CO)_4$, we have investigated the effects of ligand correlation on the whole series of binding energies up to $Ni(CO)_4$.

Apart from the rather uncertain dissociation energies, the most accurate experimental data that exist for the series $Ni(CO)_x$ (x = 1–4) is the vibrational frequencies of the IR active CO stretching modes, measured by DeKock[7] in an argon matrix experiment. A larger frequency shift (relative to free CO) is obtained for the antisymmetric stretch in $Ni(CO)_2$ than for NiCO, 171 cm^{-1} compared to 142 cm^{-1}. In a simplified interpretation, where the C–O force constant is taken to be proportional to the vibrational frequency, this result seems to support the larger binding energy obtained experimentally for the second carbonyl group. Thus, as a check of our calculations for the NiCO and $Ni(CO)_2$ binding energies, we have also considered the vibrational frequencies. Since our previous study on NiCO has shown that a reliable shift for the CO stretching frequency can be obtained if all valence electrons are correlated, similar calculations have been performed for $Ni(CO)_2$. However, there are some questions about the impor-

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