Synthesis and Solution and Solid-State Structures of Tris(pentafluorophenyl)borane Adducts of PhC(O)X (X = H, Me, OEt, NPr^i_2)

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Reaction of the highly electrophilic borane $B(C_6F_5)_3$ with the carbonyl Lewis bases benzaldehyde, acetophenone, ethyl benzoate, and *N*,*N*-diisopropylbenzamide led to isolation of the crystalline adducts **1-H**, **1-Me**, **1-OEt**, and **1-NPr**, respectively, in good to excellent yields (63−89%). Equilibrium measurements and exchange experiments indicated that the order of basicity (from highest to lowest) of these bases toward $B(C_6F_5)_3$ follows the order *N*,*N*-diisopropylbenzamide > benzaldehyde > acetophenone > ethyl benzoate. The solution and solid-state structures were probed to rationalize these observations. In solution, the borane coordinates to the carbonyl lone pair syn to H and Me in the aldehyde and ketone adducts, as indicated by $^1H/^{19}F$ NOE difference experiments. The same coordination geometry was observed in the solid state upon X-ray diffraction analysis of the two adducts. The added front strain associated with the ketone adduct (C−O−B =133.6(3)° vs 126.7(5)° for the benzaldehyde complex) accounts for the observed order of basicity with these two bases. For ethyl benzoate and *N*,*N*-diisopropylbenzamide, the borane coordinates syn to the phenyl group in both solution and the solid state. In addition to the carbonyl oxygen−boron interaction, the two complexes engage in a π-stacking interaction between one of the borane C_6F_5 rings and the syn phenyl group. In addition to the structural proof of this interaction in the solid state, variable-temperature ^{19}F NMR experiments suggest it is important in the solution structures of these adducts as well.

Introduction

Since the recognition in 1960 that $AlCl_3$ dramatically accelerates Diels−Alder cycloadditions,[1] Lewis acids (LA's) have played an important role in the catalysis of organic transformations involving carbonyl functions. While the details of this LA effect can be complicated, it is generally assumed that LA's serve to activate carbonyl-containing substrates through coordination to the carbonyl oxygen atom, further polarizing the C=O double bond and rendering the function more reactive than it is in the absence of the LA.

In addition to this electronic effect, the alteration of the steric environment around the carbonyl function upon coordination to the LA can influence the trajectory of incoming reagents as they approach the coordinated carbonyl compound.[2] This allows for the design of stereo-, regio-, and chemoselective reactions; furthermore, in many instances, the LA need only be present in catalytic quantities, making practical the use of structurally complex chiral LA's for asymmetric transformations.[3] An intimate understanding of the carbonyl−LA interaction from a structural point of view, in both solution and the solid state, is thus essential for the design of catalysts and the understanding of their mode of action.[4]

Boranes constitute a particularly important class of LA's in organic synthesis, BF_3 being the quintessential example. Although several detailed NMR studies exist which probe the solution structure of carbonyl−borane adducts,[5] only two structurally characterized examples

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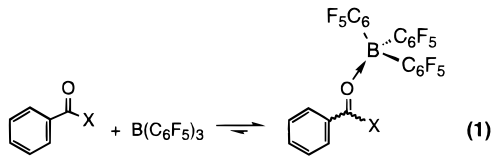
have been reported in the literature, to the best of our knowledge. These are the BF_3 adducts of the aldehydes benzaldehyde[6] and 2-methylacrolein.[7] A growing number of reports have appeared in the literature concerning the application of perfluorinated arylboranes[8] and -boronic acids[9] to synthetic organic problems. In particular, the highly electrophilic tris(pentafluorophenyl)borane, $B(C_6F_5)_3$,[10] is finding utility as an LA catalyst for various reactions. This borane offers several chemical advantages over BF_3,[8f,g] albeit at a higher economic cost; however, it is now commercially available.

During the course of our studies on the use of $B(C_6F_5)_3$ as a carbonyl hydrosilation catalyst,[8b] we found that it forms stable, crystalline adducts with a variety of carbonyl-containing compounds. In this paper, we present the detailed solution and solid-state structures of the adducts formed between $B(C_6F_5)_3$ and benzaldehyde, acetophenone, ethyl benzoate, and *N*,*N*-diisopropylbenzamide.

Results and Discussion

Adduct Synthesis and Relative Basicities. The adducts of $B(C_6F_5)_3$ and benzaldehyde (**1-H**), acetophenone (**1-Me**), ethyl benzoate (**1-OEt**), and *N*,*N*-diisopropylbenzamide (**1-NPr**) were prepared by addition of 1 equiv of the carbonyl compound to a toluene solution of scrupulously dried borane (eq 1).

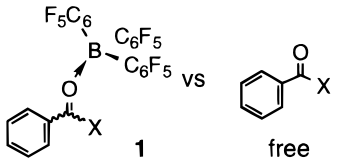


X = H, Me, OEt, NPr^i_2 **1-H**; **1-Me**; **1-OEt**; **1-NPr**

X	K_{eq}
H	$2.1(1)\times10^4$
CH_3	$1.1(1)\times10^3$
OEt	$1.9(1)\times10^2$

Adduct formation is rapid and, upon workup, the adducts **1** are isolated in 63−89% yield as white crystalline solids. NMR and IR spectral data for the products of eq 1, a selection of which is presented in Table 1, are consistent with adduct formation. The ^{11}B NMR chemical shifts are in the region associated with neutral, four-coordinate boron nuclei.[11] Upon coordination, the ^{13}C resonance for the carbonyl carbon shifts downfield by 3.2−15.8 ppm in comparison to the same shift in the free ligand. This reflects the deshielding of this carbon as the LA exacerbates the inherent polarization of the C═O bond. This shift is strongest for **1-Me** and is dampened somewhat if X is more electron donating as in **1-NPr**. Furthermore, the carbonyl stretching frequency in the IR spectra of adducts **1** are red-shifted in comparison to the free substrates by 49−83 cm^{-1}, as would be expected for the lowered bond order of the C═O bond upon activation by the LA.

Table 1. Comparative Spectral Data for Adducts 1 and the Free Ligands



	X			
data[a]	H	CH_3	OEt	NPr^i_2
$\delta(^{11}B)$	5.0	2.3	19.2	−0.05
$\delta(^{13}CO,\mathbf{1})$	199.4	212.8	175.3	174.0
$\delta(^{13}CO,free)$	192.1	197.0	166.2	170.8
Δ	7.3	15.8	9.1	3.2
$\nu_{CO}(\mathbf{1})$	1620	1603	1669	1570
$\nu_{CO}(free)$	1702	1686	1718	1628
Δ	−82	−83	−49	−58

[a] δ in ppm; ν in cm^{-1}. Δ is the difference between δ or ν for adducts **1** and free carbonyl substrate.

In solution, the equilibria depicted in eq 1 lie far toward adducts **1**. As the measured equilibrium constants K_{eq} indicate, the order of basicity of these ligands toward $B(C_6F_5)_3$, from most to least basic, is *N*,*N*-diisopropylbenzamide > benzaldehyde > acetophenone > ethyl benzoate. Although we were unable to measure K_{eq} quantitatively for the amide ligand,[12] exchange experiments indicate that it is the most basic toward $B(C_6F_5)_3$ of the four carbonyl compounds. For example, the benzamide rapidly displaces benzaldehyde to form **1-NPr** and free PhC(O)H. This order of basicity is further supported by observed exchange rates between free and bound carbonyl bases and in the results of other competition experiments. Homo exchange rates and the equilibrium constants for hetero exchange experiments are given in Table 2. For **1-H**, **1-Me**, and **1-OEt**, homo exchange is kinetically rapid; the most rapid homo exchange rate was observed for PhC(O)OEt, the least basic, most weakly bound substrate. However, when excess benzamide is added to a solution of **1-NPr**, no exchange between free and bound ligand is observed on the NMR time scale at room temperature. Hetero exchange experiments show that ethyl benzoate is readily displaced by benzaldehyde or acetophenone when **1-OEt** is treated with 1 equiv of either of the more basic substrates. In the hetero exchange experiments, equilibrium is reached essentially upon mixing of the reagents, qualitatively attesting to the lability of these systems.

The order of basicity observed here does not follow the order of proton basicities for these compounds[13] but

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(12) Proton NMR techniques were used to measure all equilibrium constants and exchange rates; because of the more complex, temperature-dependent ^1H NMR spectra of free *N*,*N*-diisopropylbenzamide, K_{eq} for this substrate could not be determined accurately using this methodology.
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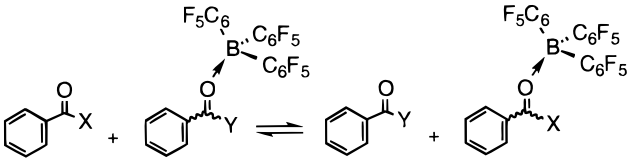
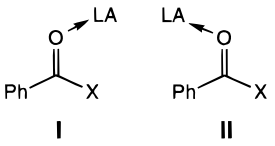
Table 2. Exchange Rates and Equilibrium Constants for Homo- and Heteroexchange Experiments



X	Y	T (K)	k_{ex} (s^{-1})	K_{eq} ($\times 10^{-2}$)
H	H	290	390	
CH_3	CH_3	265	119	
OEt	OEt	203	811	
OEt	Me	295		18(2)
Me	H	295		5.4(5)
OEt	H	295		0.95(7)
H	NPr^i_2	295		<1

rather parallels their observed BF_3 affinities[14] and is in keeping with the notion that the order of carbonyl basicity is determined mainly by steric effects for these neutral borane Lewis acids.[15] In the case of the benzamide ligand, however, the superior π-donating abilities of the NR_2 group render the C═O group more electron rich, and despite being the most sterically demanding ligand, the benzamide is the strongest base toward $B(C_6F_5)_3$.

Solution and Solid-State Structures of 1-H and 1-Me. Since borane LA's are not strong π acceptors, adducts with carbonyl groups tend to assume a bent geometry, utilizing the carbonyl HOMO, which is essentially an unhybridized oxygen 2p orbital.[16] Thus, for unsymmetrically substituted carbonyl functions such as those employed here, there are two possible coordination sites for $B(C_6F_5)_3$ to occupy, i.e. **I** or **II**. For aldehyde



and especially ketone bases, the site of coordination tends to be dictated by the relative steric attributes of the two carbonyl substituents. Consequently, in borane adducts formed from aldehydes, the LA coordinates syn to the aldehyde proton almost exclusively. In the case of acetophenone, it is predicted *a priori* that the borane will coordinate syn to the methyl group on steric grounds.

Spectroscopic studies on **1-H** and **1-Me** strongly suggest that these adducts adopt such structures in solution. For **1-Me** the ^{13}C chemical shift for the methyl carbon is shifted 3.0 ppm upfield in comparison to that found for free benzophenone. This upfield shift is characteristic for the α-carbon of the group syn to the borane in complexed ketones.[5d] Perhaps more convincingly, in $^1H/^{19}F$ NOE experiments in which the resonance for the *ortho* fluorine atoms was selectively irradiated, a strong enhancement of the resonances for the aldehyde and methyl protons was observed in the

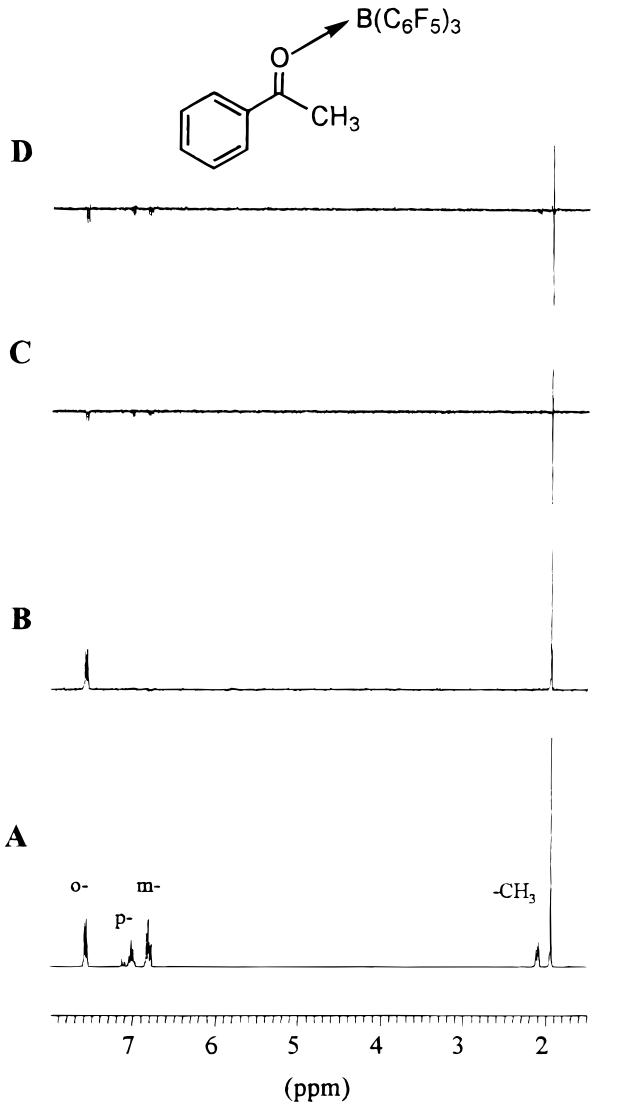


Figure 1. $^1H/^{19}F$ NOE difference spectra for **1-Me** (^1H observe, ^{19}F irradiate): (A) proton NMR spectrum of **1-Me**; (B) NOE difference spectrum with irradiation of ortho fluorines (−136.0 ppm); (C) NOE difference spectrum with irradiation of para fluorines (−157.0 ppm); (D) NOE difference spectrum with irradiation of meta fluorines (−164.6 ppm).

^1H NMR spectra of **1-H** and **1-Me**, respectively. Figure 1 shows the spectra for **1-Me**. A weaker enhancement for the *ortho* protons of the phenyl ring was also observed in both cases. Although this could be interpreted as being indicative of a syn:anti isomerization process, molecular models of these two adducts suggest that the *ortho* protons and *ortho* fluorines can acheive nonbonded contacts of between 2 and 3 Å even when $B(C_6F_5)_3$ is syn to X, well within the range of distances at which NOE effects may be expected.[17] Furthermore, no evidence for an isomer with $B(C_6F_5)_3$ anti to X was found in the low-temperature ^1H or ^{19}F NMR spectra of either **1-H** or **1-Me**.

Syn coordination was confirmed via analysis of the solid-state structures of **1-H** and **1-Me**. The molecular structures of these adducts are depicted in Figures 2 and 3, respectively, and selected metrical parameters

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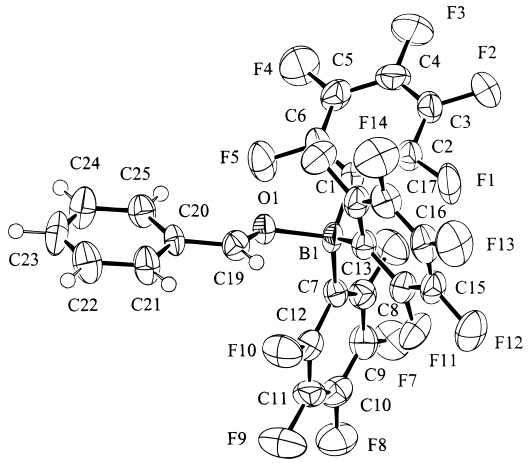


Figure 2. ORTEP diagram of the adduct **1-H**.

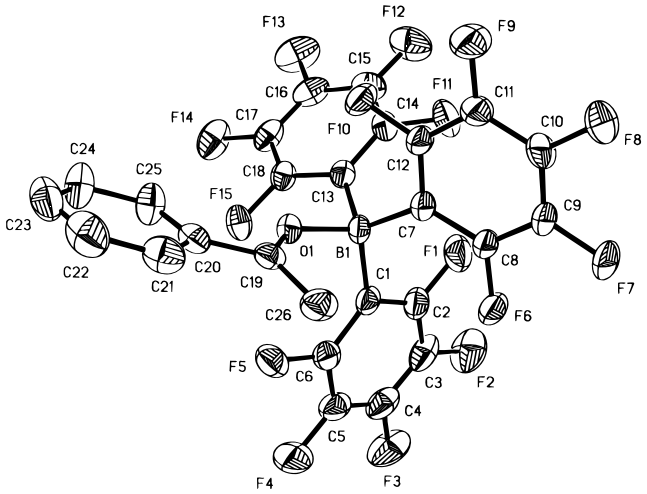
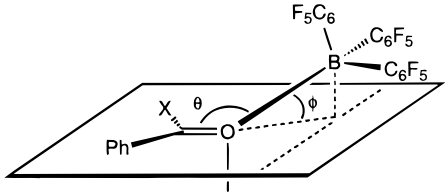


Figure 3. ORTEP diagram of the adduct **1-Me**.

for all of the adducts reported herein are collected for easy comparison in Table 3; the angles θ and ϕ are as defined in **III**.



III

The structures of **1-H** and **1-Me** are quite similar, the slight differences being attributable to the different steric requirements of the X groups. The B−O lengths are not significantly different from those found in the BF_3 adducts of benzaldehyde (1.591(6) Å[6]) and 2-methylacrolein (1.587(8) Å[7]). The carbon−oxygen bond lengths are slightly longer than the distances typical of aldehydes and ketones, ∼1.22 Å.[18] The angle θ for **1-H** is about 6° smaller than the corresponding angle in **1-Me**, while the boron atom is more severely pyramidalized in the latter (Σ[C−B−C] = 337.7° for **1-Me** and 340.2° for **1-H**). These observations are consistent with a higher level of front strain in the more sterically confined ketone complex. The angle ϕ (approximated by the dihedral angle X−C(19)−O(1)-B(1)) is about 4° for each adduct. Although an "in-plane" (ϕ = 0°) geometry might be expected to be energetically the most favorable, it has been shown by computations[19] and in structural studies involving carbonyl adducts of other LA's[4b] that the potential surface for distortions of LA binding out of the carbonyl plane is quite shallow for up to $\phi \approx 15°$.

Table 3. Selected Metrical Parameters for Adducts 1

	X			
	H	CH_3	OEt	NPr^i_2
Bond Distances (Å)				
O(1)−B(1)	1.610(8)	1.576(5)	1.594(6)	1.52(1)
C(19)−O(1)	1.241(7)	1.242(5)	1.253(5)	1.32(1)
C(19)−C(20)	1.427(8)	1.464(6)	1.469(6)	1.49(2)
C(1)−B(1)	1.631(9)	1.626(6)	1.642(6)	1.64(2)
C(7)−B(1)	1.609(9)	1.634(6)	1.626(7)	1.62(2)
C(13)−B(1)	1.634(9)	1.631(7)	1.612(7)	1.65(2)
C(19)−C(26)		1.478(6)		
C(19)−O(2)			1.301(5)	
C(19)−N(1)				1.28(1)
O(2)−C(26)			1.469(5)	
N(1)−C(26)				1.51(1)
N(1)−C(29)				1.51(1)
Bond Angles (deg)				
C(19)−O(1)−B(1), θ	126.7(5)	133.6(3)	138.2(4)	131(1)
O(1)−C(19)−C(20)	123.4(6)	115.8(4)	127.2(4)	121(1)
C(19)−C(20)−C(25)	121.6(6)	119.0(4)	118.8(4)	118(1)
C(19)−C(20)−C(21)	118.3(7)	122.0(4)	120.5(4)	120(1)
O(1)−B(1)−C(1)	103.8(5)	102.3(3)	100.8(3)	104(1)
O(1)−B(1)−C(7)	103.7(5)	105.9(3)	107.2(3)	111(1)
O(1)−B(1)−C(13)	107.9(5)	109.9(3)	107.5(4)	109(1)
C(1)−B(1)−C(7)	113.0(6)	113.3(4)	115.3(4)	103(1)
C(1)−B(1)−C(13)	110.9(6)	107.3(3)	108.3(4)	113(1)
C(7)−B(1)−C(13)	116.3(6)	117.1(4)	116.3(4)	114(1)
O(1)−C(19)−C(26)		122.8(4)		
O(1)−C(19)−O(2)			118.5(4)	
O(2)−C(19)−C(20)			114.3(4)	
O(1)−C(19)−N(1)				118(1)
N(1)−C(19)−C(20)				120(1)
Σ[C−B(1)−C]	340.2	337.7	339.3	330
Torsion Angle, ϕ (deg)				
C(20)−C(19)−O(1)−B(1)	4.6(6)	4.2(4)	15.6(8)	3(1)

The phenyl rings of these two adducts are essentially in conjugation with the C═O double bond, twisting only a few degrees out of the plane defined by O(1), C(19), and C(20). The dihedral angles O(1)−C(19)-C(20)−C(25) are 6(1) and 5(1)° for **1-H** and **1-Me**, respectively. Because the phenyl rings are "in-plane", a close nonbonding contact between one of the ortho fluorine atoms and an ortho phenyl proton occurs, in accord with the solution $^1H/^{19}F$ NOE experiments. The F(5)−HC(25) distance in **1-H** is only 2.85 Å, while the F(15)−HC(25) distance in **1-Me** is ∼2.45 Å; free rotation about the B−C_{ipso} carbons would likely shorten these contacts.

It has been postulated that aldehyde protons in complexes between aldehydes and borane LA's can engage in C−H···O or C−H···F hydrogen bonds (e.g. **IV**).[20] These interactions may be important in orienting

(18) Sutton, L. E., Ed. *Tables of Interatomic Distances and Configuration in Molecules and Ions*; The Chemical Society: London, 1958.

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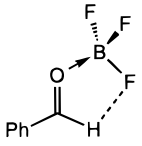
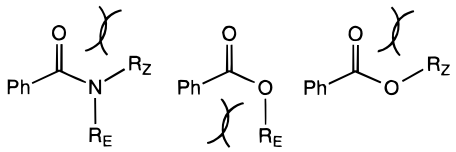
(20) (a) Corey, E. J.; Rohde, J. J.; Fischer, A.; Azimioara, M. D. *Tetrahedron Lett.* **1997**, *38*, 33. An alternative explanation for this conformational preference involves an anomeric effect of n(O) → σ^*-(B−F) character.[20b] Computations suggest that both effects may contribute to the stability of this conformation. (b) Mackey, M. D.; Goodman, J. M. *Chem. Commun.* **1997**, 2383.



IV

aldehyde substrates when they are bound to borane LA's, particularly chiral borane catalysts.[21] The aldehyde proton in **1-H** appears to engage in a similar, albeit weaker, C−H···F contact with one of the $B(C_6F_5)_3$ ortho fluorines. F(10) points up at the aldehyde hydrogen (F(10)−H(1)-C(19) = 91.3°) such that the F(10)−H(1) distance of 2.56 Å[22] is within the sum of the van der Waals radii of H (1.20 Å) and F (1.47 Å)[23] but is longer than the C−H···F separation of 2.35 Å found in the BF_3 2-methylacrolein complex.[7] Given the greater flexibility associated with $B(C_6F_5)_3$, the F(10)−H contact is remarkably close; however, no evidence that this interaction is important in the solution behavior of **1-H** was uncovered.

Solution and Solid-State Structures of 1-OEt and 1-NPr. Syn:anti coordination geometries in borane adducts of esters and amides are also influenced by steric effects. Since OR and NR_2 are both capable of π-donation to the electron-deficient carbonyl carbon, the alkyl groups R are coplanar with the carbonyl function. In amides this places R_Z in steric conflict with any LA coordinating syn to this substituent (**V**). For esters, this

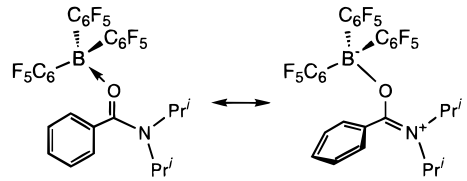


V **VI** **VII**

can be avoided if the alkyl group assumes an *E* geometry as in **VI**; however the *Z* geometry (**VII**) is preferred, because the steric interactions between R_E and Ph are in fact more severe.[24] The presence of a *Z* substituent dictates that the coordination site syn to OR or NR_2 is sterically inaccessible as far as a borane is concerned and coordination of borane anti to the OR or NR_2 group is preferred strongly over the syn isomer. That this coordination geometry obtains for the solution structures of adducts **1-OEt** and **1-NPr** is supported by proton−fluorine NOE experiments, which show strong enhancements in the aryl ortho protons upon irradiation of the *ortho* fluorine resonances in the ^{19}F NMR spectrum. Enhancements are also observed in the signals due to the OCH_2 and the methyl protons of the *Z N*-isopropyl group. As explained above, close contacts between $B(C_6F_5)_3$ and the anti group also occur in these compounds. Inexplicably, similar enhancements are found when the *meta* and *para* fluorines are irradiated; some ambiguity therefore is associated with the proton−fluorine NOE experiments on **1-OEt** and **1-NPr**.

In these two complexes, then, the borane is likely coordinated syn to the (relative to H or Me) bulky phenyl group in solution. This accounts at least partially for the lower observed basicity of ethyl benzoate toward $B(C_6F_5)_3$ in comparison to benzaldehyde or acetophenone. However, since the amide substrate will displace even benzaldehyde in competition for $B(C_6F_5)_3$, the steric properties of the group syn to the borane do not fully account for the observed basicities.

The steric requirements of the phenyl group are attenuated in the adducts **1-OEt** and **1-NPr** since the X groups are able to π-donate to the carbonyl carbon, allowing the phenyl group to rotate out of the plane defined by C_{ipso}−C−O. This phenomenon is expecially evident in **1-NPr** and aids in rationalizing the compound's solution behavior and solid-state structure. The proton NMR spectrum of free *N*,*N*-diisopropylbenzamide is severely broadened due to exchange of the *E* and *Z* isopropyl groups about the C(O)−N bond, which has partial double-bond character. Upon $B(C_6F_5)_3$ coordination, this exchange becomes much slower on the NMR time scale, and two sharp sets of resonances for the *E* and *Z* isopropyl groups are observed in the ^1H NMR spectrum of **1-NPr**. Thus, coordination of the LA significantly raises the barrier associated with this exchange by rendering resonance structure **IX** relatively more important in **1-NPr** vs **1-OEt**.



VIII **IX**

The greater dominance of resonance of **IX** allows the phenyl group in **1-NPr** to be more flexible with regard to rotating out of the plane of the carbonyl function. In addition to allowing for some relief of steric interactions, we have evidence that this also permits a stabilizing interaction between the phenyl group and one of the perfluorophenyl groups of the coordinated $B(C_6F_5)_3$. It has been recently recognized that phenyl−perfluorophenyl stacking interactions are quite favorable and may in fact be used as a tool in crystal engineering.[25] These interactions occur because phenyl and pentafluorophenyl groups have large molecular quadrupole moments which are of similar magnitude but are opposite in sign.[26] The complementarity of charge distribution allows for strong stacking interactions in the solid-state structure of, for example, C_6H_6/C_6F_6.

Variable-temperature ^{19}F NMR experiments on samples of **1-NPr** in CD_2Cl_2 suggest that intramolecular C_6H_5/C_6F_5 stacking may be important in the solution structures of adducts where $B(C_6F_5)_3$ is coordinated syn to a phenyl group.[27] Figure 4 shows a series of partial

(21) (a) Corey, E. J.; Rohde, J. J. *Tetrahedron Lett.* **1997**, *38*, 37. (b) Corey, E. J.; Barnes-Seeman, D.; Lee, T. W. *Tetrahedron Lett.* **1997**, *38*, 1699.

(22) (a) This value is uncorrected for shortening effects,[22b] which in this instance result only in a correction of 0.002 Å. Such effects are more important when C−H···F is near linearity. (b) Churchill, M. R. *Inorg. Chem.* **1973,** 12, 1213.

(23) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(24) (a) George, W. O.; Houston, T. E.; Harris, W. C. *Spectrochim. Acta, Part A* **1974**, *30*, 1035. (b) Knözinger, E. *Ber. Bunsen-Ges.* **1974**, *78*, 1199. (c) Kydd, R. A.; Rauk, A. *J. Mol. Struct.* **1981**, *77*, 227.

(25) Coates, G. W.; Dunn, A. R.; Henling, L. M.; Dougherty, D. A.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 248 and references therein.

(26) Williams, J. H. *Acc. Chem. Res.* **1993**, *26*, 593.

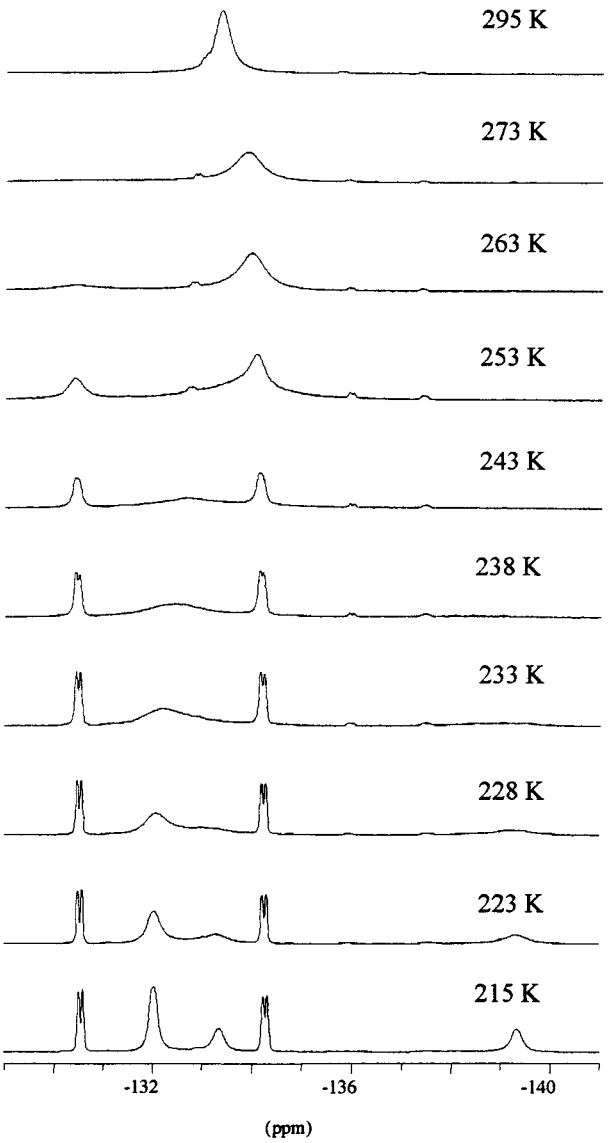
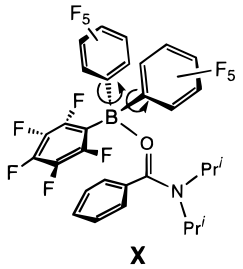


Figure 4. Partial ^{19}F NMR spectra of **1-NPr** taken at various temperatures (−127 to −141 ppm, ortho fluorine region of the spectrum).

^{19}F NMR spectra taken at various temperatures; for clarity, only the ortho fluorine region of the spectrum is shown. At room temperature, all of the ortho fluorine atoms are equivalent. As the temperature is lowered, the resonances broaden and reemerge such that all six ortho fluorines are inequivalent at −80 °C. Careful examination of the spectra allows the conclusion that the six ortho fluorines undergo coalescence in a pairwise fashion and that one of the C_6F_5 rings has its rotation arrested at significantly higher temperature than the other two. Similar behavior is observed in the meta and para resonances. These observations are consistent with an exchange process which involves rapid rotation of each C_6F_5 ring and the $B(C_6F_5)_3$ group as a whole at room temperature. As the temperature drops, one of the C_6F_5 rings is "trapped" by the phenyl group, while the other two are yet free to rotate as in **X**; these



X

undergo restricted rotation at lower temperatures. The spectra could also be interpreted simply in terms of arrested rotation without invoking a π-stacking interaction, although one might expect the rotations of all three rings to freeze out at similar temperatures. It should also be noted that similar behavior was observed when this experiment was carried out in d_8-toluene, a medium in which the π-stacking interaction might be expected to be more effectively solvated. On the other hand, the chelating nature of the interaction is entropically favorable.

Although these NMR spectra studied do not provide definitive support for π-stacking in solution, the solid-state structures of **1-OEt** and **1-NPr** clearly advocate this feature. The molecular structures of **1-OEt** and **1-NPr** are shown in Figures 5 and 6, respectively. In the case of **1-NPr**, a low reflection-to-parameter ratio was obtained, resulting in relatively high esd's for the metrical parameters (Table 3). Nonetheless, the structure is included here because it clearly demonstrates the phenyl−pentafluorophenyl π-stacking architectural motif and the structural features of the adduct which allow such an interaction to be accommodated. Because of the high esd's, however, discussion of specific metrical details for the structure of **1-NPr** will be limited.

As expected on the basis of the solution studies detailed above, the borane is syn to the phenyl group in both compounds. In the case of the ester adduct, the ethyl group is in the *Z* geometry. In both compounds, the phenyl group is rotated out of conjugation with the C═O; the dihedral angles O(1)−C(19)-C(20)−C(21) in **1-OEt** and **1-NPr** are 32.5(7) and −76(1)°, respectively. Interestingly, the two structures differ significantly in the angle ϕ; for **1-OEt** this parameter is 15.6°, while for **1-NPr** the borane is essentially in-plane, similar to **1-H** or **1-Me**. As mentioned above, carbonyl ligation to LA's is quite flexible in this regard. It seems entirely likely, therefore, that in the case of **1-OEt** the borane leaves the carbonyl plane in order that one of the C_6F_5 groups may more effectively π-stack with the phenyl group, which does not abandon completely conjugation with the carbonyl group.

Figure 7 depicts the C_6H_5−C_6F_5 stacking in these complexes in more detail, giving side and top views for both compounds. For **1-OEt**, the two rings are virtually eclipsed but not entirely parallel as illustrated by the steady gradient in distances separating the rings from C_{ipso} to C_{para}. The angle between the planes defined by C(7)−C(12) and C(20)−C(25) is 26.59°. Although it is not immediately apparent from the view in Figure 7A, the plane of the C_6F_5 ring is tilted away from the B−C(7)(ipso) vector by about 10°, such that this ring is leaning toward the C_6H_5 ring. The separation between the two rings is in the same range as that observed in

(27) Although the low-temperature limit was not reached in the case of **1-OEt**, severe spectral broadening was observed under similar conditions, suggesting that π-stacking is a significant solution structural motif in this adduct as well.

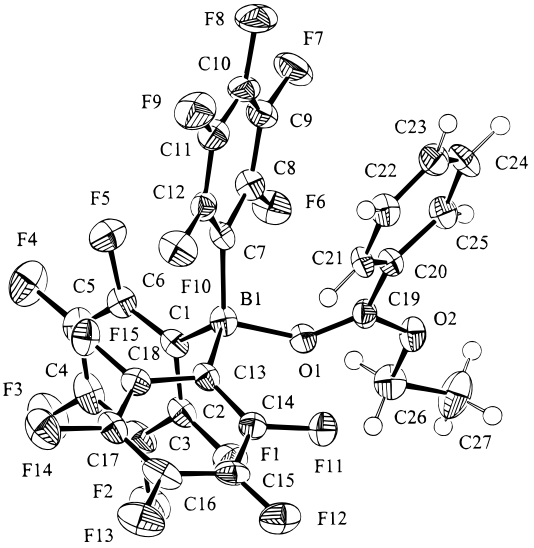


Figure 5. ORTEP diagram of the adduct **1-OEt**.

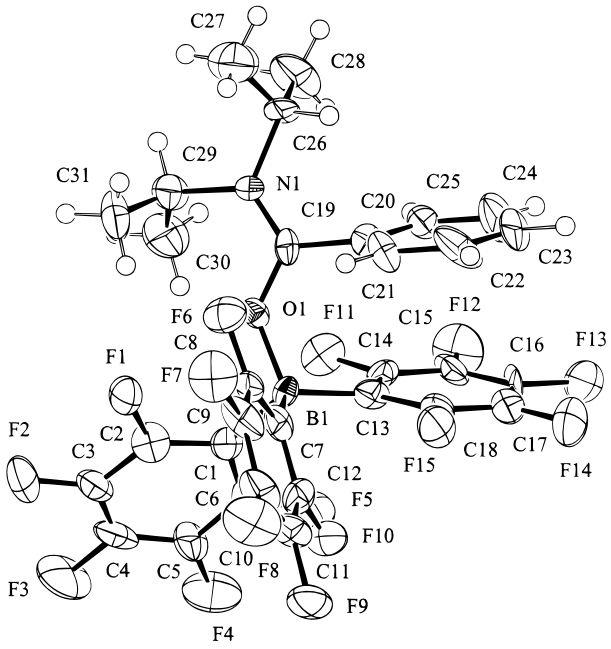


Figure 6. ORTEP diagram of the adduct **1-NPr**.

the diyne structures reported by Coates et al., where interstack distances of about 3.7 Å were observed.[25] In **1-NPr**, the rings are closer to being parallel (angle between planes defined by C(13)−C(18) and C(20)−C(25) is 12.31°; Figure 7C). Because the NR_2 group is a more effective π-donor than OEt, the phenyl ring in this adduct more readily twists out of conjugation with the C=O bond and allows for a stronger π-stacking interaction. The rings have slipped somewhat from the more eclisped situation observed in the ester adduct (Figure 7D), but this may actually enhance the attractive interaction by allowing for better HOMO−LUMO overlap in the stacked rings.

Conclusions

Organic carbonyl functions form strong adducts with the highly electrophilic borane $B(C_6F_5)_3$, and we have fully characterized its benzaldehyde, acetophenone, ethyl benzoate, and *N*,*N*-diisopropylbenzamide com-

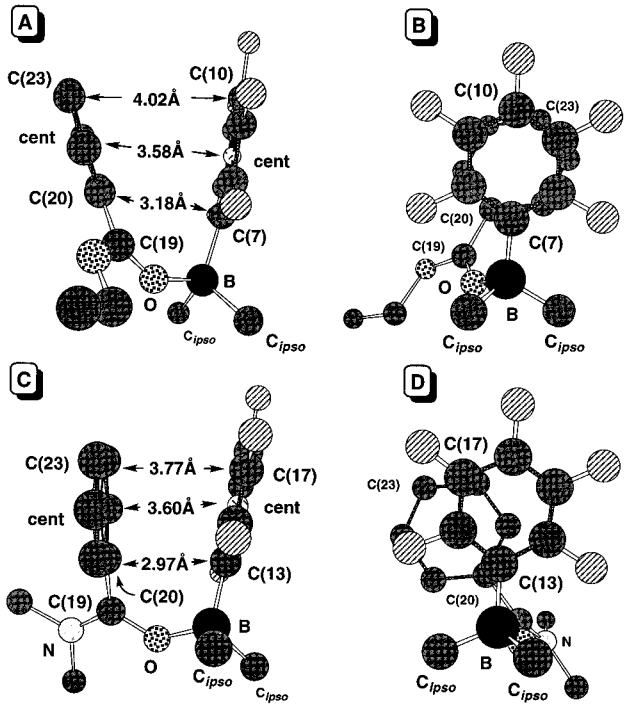


Figure 7. Chem 3D diagrams depicting the details of the metrical parameters associated with C_6F_5/C_6H_5 stacking in the adducts **1-OEt** and **1-NPr**: (A) side view of the stacking interaction in **1-OEt**; (B) top view of the stacking interaction in **1-OEt** (C) side view of the stacking in **1-NPr**; (D) top view of the stacking in **1-NPr**.

plexes. We chose these aromatic ligands to impart crystallinity upon the adducts and allow for solid-state structure determination as well as solution studies. We find that the solution structures of these adducts, on the basis of extensive NMR investigations, are essentially the same as those found in the solid state. The most interesting aspect of this study is the finding that the carbonyl ligation to $B(C_6F_5)_3$ is augmented by two types of nonbonded interactions. In the aldehyde adduct **1-H**, a weak C−H···F hydrogen bond is postulated on the basis of the solid-state structural analysis. A more substantial intramolecular interaction was found in the **1-OEt** and **1-NPr** adducts, namely a phenyl−perfluorophenyl π-stacking interaction which arises because the borane coordinates the carbonyl syn to the phenyl group. This interaction is strong enough in the **1-NPr** complex to observe in solution at low temperature, implying that such interactions are important not only in the solid state but under chemically relevant reaction conditions as well. The role of aromatic π-stacking in determining the tertiary structure of complex biological molecules[28] and in crystal engineering[29] is only beginning to be appreciated. Our results show that these are potentially exploitable tools for use in the design of LA catalysts as well.

Experimental Section

General Considerations. Unless otherwise noted, all manipulations were carried out under argon using an Innovative Technology System One drybox and/or standard Schlenk

(28) Hunter, C. A. *Chem. Soc. Rev.* **1994**, *23*, 101.
(29) Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: Amsterdam, 1989; pp 1−25.

techniques on double-manifold vacuum lines.[30] Toluene, hexanes, and THF were dried and deoxygenated using the Grubbs solvent purification system[31] and were stored in evacuated glass vessels over titanocene[32] or sodium benzophenone. Deuterated NMR solvents d_6-benzene (C_6D_6) and d_8-toluene ($C_6D_5CD_3$) were dried and distilled from sodium/benzophenone ketyl, and d_2-dichloromethane (CD_2Cl_2) was dried and distilled from calcium hydride (CaH_2). NMR spectra were recorded on Bruker AC 200, AM 400, and AMX2 300 MHz spectrometers at room temperature in C_6D_6 unless otherwise specified. Proton and carbon spectra were referenced to solvent signals, boron spectra to external $BF_3{\cdot}Et_2O$ at 0.0 ppm and fluorine spectra to $CFCl_3$ at 0.0 ppm. NMR data are given in ppm; ^{13}C resonances for the C_6F_5 groups were not obtained. $^1H/^{19}F$ variable-temperature NOE experiments were performed on the AMX2 300 MHz spectrometer in either $C_6D_5CD_3$ or CD_2Cl_2 solution. IR spectra were run on a Matteson Instruments 4030 Galaxy Series FT-IR instrument. Elemental analyses were performed in the microanalytical laboratory of the Department of Chemistry at the University of Calgary.

Acetophenone, benzaldehyde, and ethyl benzoate were purchased and used after distillation from CaH_2. *N*,*N*-Diisopropylbenzamide was prepared from benzoyl chloride and diisopropylamine by standard methods. Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) was purchased from Boulder Scientific, dried over trimethylchlorosilane, and sublimed under high vacuum.

Synthesis of 1-Me. $B(C_6F_5)_3$ (195 mg, 0.381 mmol) was added to a dry 25 mL round-bottomed flask and attached to a swivel-frit assembly. The frit was evacuated, and toluene (10 mL) was condensed into the flask using a dry ice/acetone bath. The frit assembly was backflushed with argon; then the solution was warmed to room temperature. Dry acetophenone (44 μL, 0.381 mmol) was added to the stirred solution via syringe under an argon purge. The solution was stirred at room temperature for 5 min; then the solvent was removed under reduced pressure, leaving a viscous oil. Hexanes (10 mL) was condensed into the flask at −78 °C, which was then warmed to room temperature. The flask was sonicated for 20 min, during which time the oil turned into a white precipitate which was isolated by filtration and washed twice with hexanes. The solvent was removed under reduced pressure, and the white precipitate was isolated (210 mg, 87% yield). ^1H NMR: 7.52 (m, 2H, H_{ortho}); 6.95 (m, 1H, H_{para}); 6.73 (m, 2H, H_{meta}); 1.82 (s, 3H, CH_3). ^{13}C NMR: 212.8 (*C*═O); 138.6, 133.8, 131.3, 129.5, (C_6H_5); 23.5 (CH_3). ^{19}F NMR: −136.0 (d, J = 20.2 Hz, 2F, *ortho*); −157.0 (t, J = 21.1 Hz, 1F, *para*); −164.6 (m, 2F, *meta*). ^{11}B NMR: 2.3. Anal. Calcd for $C_{26}H_8BOF_{15}$: C, 49.40; H, 1.28. Found: C, 49.40; H, 1.00. IR (KBr pellet, cm^{-1}): 1647 (s), 1603 (m), 1594 (s), 1564 (s), 1473 (vs), 1369 (s), 1325 (s), 1647 (s), 1287 (s), 1103 (vs), 980 (vs), 768 (vs).

Synthesis of 1-H. This compound was prepared using the same procedure as above for **1-Me** with dry benzaldehyde (23.4 μL, 0.23 mmol) and $B(C_6F_5)_3$ (118 mg, 0.23 mmol), giving 89 mg of the adduct (63% yield). ^1H NMR: 8.81 (s, 1H, C*H*═O); 7.30 (m, 2H, H_{ortho}); 6.88 (m, 1H, H_{para}); 6.61 (m, 2H, H_{meta}). ^{13}C NMR: 199.4 (*C*═O); 141.5, 135.1, 130.1, 128.3 (C_6H_5). ^{19}F NMR: −133.9 (d, J = 21.2 Hz, 2F, *ortho*); −154.3 (t, J = 20.5 Hz, 1F, *para*); −162.5 (m, 2F, *meta*). ^{11}B NMR: 5.0. Anal. Calcd for $C_{25}H_6BOF_{15}$: C, 48.57; H, 0.98. Found: C, 50.52; H, 1.04. These data are an average of four analyses; complete removal of the toluene solvate was apparently not possible. IR (KBr pellet, cm^{-1}): 1620 (s), 1597 (s), 1575 (s), 1519 (s), 1461 (vs), 1105 (s), 970 (s).

(30) Burger, B. J.; Bercaw, J. E. *Experimental Organometallic Chemistry;* Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987.

(31) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(32) Marvich, R. H.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1971**, *93*, 2046.

Table 4. Data Used To Obtain Equilibrium Constants for Eq 1[a]

	X		
	H	CH_3	OEt
δ_f[b]	9.658	2.079	1.003
δ_b	8.789	1.815	0.745
δ_{obs}	8.807	1.840	0.798
$[PhC(O)X]_0$	0.0935	0.0943	0.0933
N_f[c]	0.0211	0.0959	0.206
K_{eq}[d]	206	11.1	1.96

[a] $[B(C_6F_5)_3]$ = 0.0938 M, room temperature. [b] In ppm. [c] Mole fraction of free carbonyl compound. [d] $\times 10^{-2}$.

Synthesis of 1-OEt. This compound was prepared using the same procedure as above for **1-Me** with dry ethyl benzoate (112 μL, 0.781 mmol) and $B(C_6F_5)_3$ (400 mg, 0.781 mmol), giving 460 mg of the adduct (89% yield). ^1H NMR: 7.59 (m, 2H, H_{ortho}); 6.75 (m, 3H, $H_{para,meta}$); 4.06 (q, ^3J_H = 7.1 Hz, 2H, OCH_2); 0.82 (t, 3H, OCH_2CH_3). ^{13}C NMR: 175.3 (*C*═O); 135.3, 130.5, 128.8, 127.7 (C_6H_5); 67.6 (OCH_2); 13.9 (OCH_2CH_3). ^{19}F NMR: −132.8 (br s, 2F, *ortho*); −151.7 (br s, 1F, *para*); −162.4 (m, 2F, *meta*). ^{11}B NMR: 19.2. Anal. Calcd for $C_{27}H_{10}BO_2F_{15}$: C, 48.98; H, 1.52. Found: C, 48.35; H, 1.24. IR (KBr pellet, cm^{-1}): 1669 (m), 1649 (m), 1519 (s), 1468 (vs), 1297 (m), 1106 (m), 970 (s), 719 (m).

Synthesis of 1-NPr. This compound was prepared using the same procedure as above for **1-Me** with dry *N*,*N*-diisopropylbenzamide (40 mg, 0.195 mmol) and $B(C_6F_5)_3$ (100 mg, 0.195 mmol), giving 107 mg of the adduct (76% yield). ^1H NMR: 6.71 (m, 3H, $H_{ortho,para}$); 6.58 (m, 2H, H_{meta}); 3.10 (m, 2H, NC*H*); 1.27 (d, ^3J_H = 6.9 Hz, 6H, $NCHCH_3$), 0.29 (d, ^1J_H = 6.7 Hz, 6H, $NCHCH_3$). ^{13}C NMR: 174.0 (*C*═O); 131.2, 131.0, 129.2, 125.6 (C_6H_5); 54.8, 50.2 (N*C*H); 20.0, 19.7 ($NCHCH_3$). ^{19}F NMR: −132.7 (br s, 2F, *ortho*); −157.6 (m, 1F, *para*); −164.6 (br s, 2F, *meta*). ^{19}F NMR (−80 °C, CD_2Cl_2): −130.5, −132.0 (2F), −132.9, −134.2, −139.3 (*ortho*); −158.2, −158.9, −159.5 (*para*); −164.7 (2F), −165.1, −165.5 (2F), −166.0 (*meta*). ^{11}B NMR: −0.05. Anal. Calcd for $C_{31}H_{19}BNOF_{15}$: C, 51.91; H, 2.67; N, 1.95. Found: C, 51.55; H, 2.24; N, 1.94. IR (KBr pellet, cm^{-1}): 1650 (m), 1570 (vs), 1519 (vs), 1469 (vs), 1366 (s), 1286 (m), 1096 (vs), 1015 (vs), 794 (vs), 776 (m).

Measurement of K_{eq} for Adduct Formation. Equilibrium constants for adduct formation as shown in eq 1 were determined by ^1H NMR methods. In 1:1 mixtures of PhC(O)X and $B(C_6F_5)_3$, the position of the proton resonance of X may be used to calculate the mole fraction of free carbonyl substrate, N_f, by using the expression:

$$N_f = (\delta_{obs} - \delta_b)/(\delta_f - \delta_b)$$

where δ_{obs} is the observed chemical shift of X in the sample, δ_b is the chemical shift of X in the adduct, and δ_f is the chemical shift of X in the absence of $B(C_6F_5)_3$.[33] Once N_f is known, K_{eq} may be readily calculated.

The values for δ_f were obtained from samples of pure carbonyl compound of about 0.094 M concentration, while δ_b was obtained by adding 10 equiv of $B(C_6F_5)_3$ to these samples and measuring the chemical shift of X. No change in this value was observed upon further addition of $B(C_6F_5)_3$. Samples for use in obtaining δ_{obs} were prepared from a stock solution of $B(C_6F_5)_3$ in C_6D_6 prepared by dissolving $B(C_6F_5)_3$ (96 mg, 0.188 mmol) in 2.0 mL of dry C_6D_6 in a volumetric flask ($[B(C_6F_5)_3]$ = 0.0938 M). A 0.6 mL aliquot of this solution was placed in a sealable NMR tube, and the carbonyl compound (0.0563 mmol, [carbonyl] ≈ 0.094 M) was added via syringe. The tube was flame-sealed; then the ^1H NMR spectrum was recorded. Data obtained for X = H, CH_3, OEt are given in Table 4, along with calculated values of N_f and K_{eq}.

(33) Drago, R. S. *Physcial Methods for Chemists,* 2nd ed.; Saunders: New York, 1992; p 257.

Table 5. Summary of Data Collection and Structure Refinement Details for 1-H, 1Me, 1-OEt, 1-NPr

	1-H	1-Me	1-OEt	1-NPr
formula	$C_{25}H_6BOF_{15}\cdot 0.5C_7H_8$	$C_{26}H_8BOF_{15}$	$C_{27}H_{10}BO_2F_{15}$	$C_{31}H_{19}BONF_{15}$
fw	664.18	632.13	662.16	717.28
cryst syst	triclinic	monoclinic	monoclinic	orthorhombic
a, Å	12.380(3)	12.3720(18)	36.836(15)	18.111(2)
b, Å	12.476(2)	10.7021(12)	7.686(3)	19.247(4)
c, Å	9.538(2)	18.351(3)	18.867(5)	17.479(2)
α, deg	100.25(1)			
β, deg	96.89(2)	96.40(3)	108.68(3)	
γ, deg	111.34(1)			
V, Å^3	1322.5(5)	2414.7(6)	5060(3)	6092(1)
space group	$P\bar{1}$	$P2_1/n$	*C*2/*c*	*Pbca*
Z	2	4	8	8
F(000)	658	1249.08	2624	2880
d_{calc}, Mg m^{-3}	1.668	1.739	1.738	1.564
μ, mm^{-1}	0.173	0.18	0.183	0.157
R	0.042	0.053	0.045	0.045
R_w	0.042	0.045	0.044	0.038
GOF	2.10	4.32	2.52	1.63

Measurement of K_{eq} for the Heteroexchange Reactions. 1-Me/Benzaldehyde. In a dry NMR tube was added **1-Me** (21 mg, 0.0332 mmol) in a measured volume of C_6D_6. Benzaldehyde (3.4 μL, 0.0332 mmol) was added to the sample via syringe. The ^{1}H NMR of the sample was obtained, and the chemical shifts of the methyl protons of acetophenone (δ_{obs} 2.0019 ppm) and the aldehyde proton of benzaldehyde (δ_{obs} 9.0414 ppm) were recorded. These values were compared to the known chemical shifts for the free and fully bound carbonyl compounds (see Table 4) and the equilibrium constant calculated.

1-OEt/Acetophenone. An identical procedure using **1-OEt** (27 mg, 0.0408 mmol) and acetophenone (4.8 μL, 0.0408 mmol) yielded chemical shifts for the methyl protons of acetophenone (δ_{obs} 1.8589 ppm) and the methyl protons of ethyl benzoate (δ_{obs} 0.9728 ppm). These values were compared to the known chemical shifts for the free and fully bound carbonyl compounds and used to calculate K_{eq}.

1-OEt/Benzaldehyde. An identical procedure using **1-H** (23 mg, 0.0370 mmol) and ethyl benzoate (5.3 μL, 0.0370 mmol) yielded chemical shifts for the aldehyde proton (δ_{obs} 8.8971 ppm) and the methyl protons of ethyl benzoate (δ_{obs} 1.0000 ppm). These values were compared to the known chemical shifts for the free and fully bound carbonyl compounds and used to calculate K_{eq}.

X-ray Structural Determinations. Summaries of data collection and structure refinement details for each adduct are given in Table 5.

1-Me. Single crystals suitable for X-ray crystallography were mounted in thin-walled glass capillaries and optically centered in the X-ray beam of an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.709 30 Å). Unit cell dimensions were determined via least-squares refinement of the setting angles of 24 high-angle reflections, and intensity data were collected using the $\omega-2\theta$ scan mode in the range 38.6−48.2°. Data were corrected for Lorentz, polarization and absorption effects but not for extinction. All structures were solved using direct methods. Aryl hydrogen atoms were placed in calculated positions (D_{C-H} = 1.00 Å). Methyl hydrogen atoms were located via inspection of difference Fourier maps and fixed, temperature factors being based upon the carbon atom to which they are bonded. A weighting scheme based upon counting statistics was used with the weight modifier *k* in kF_o^2 being determined via evaluation of variation in the standard reflections that were collected during the course of data collection. Neutral atom scattering factors were taken from ref 34. Values of *R* and R_w are given by $R = (F_o - F_c)/\sum F_o$ and $R_w = [\sum(w(F_o - F_c))^2/\sum(wF_o^2)]^{1/2}$. All crystallographic calculations were conducted with the PC version of the NRCVAX program package[35] locally implemented on an IBM-compatible 80486 computer.

1-H, 1-OEt, and 1-NPr. Suitable crystals were placed in glass capillaries, sealed and mounted onto a Rigaku AFC6S diffractometer. Measurements were made using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) at 23, −103, and −73 °C for **1-H**, **1-OEt**, and **1-NPr**, respectively. The structures were solved by direct methods and refined by full-matrix least-squares calculations. The non-hydrogen atoms were refined anisotropically; hydrogen atoms were included at geometrically idealized positions with C−H = 0.95 Å and were not refined. The final difference maps were essentially featureless. All calculations were performed using the TEXSAN[36] crystallographic software package of Molecular Structure Corp.

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Supporting Information Available: Listings of positional and thermal parameters, bond distances and angles, torsion angles, and nonbonded contacts for **1-H**, **2-Me**, **1-OEt**, and **1-NPr** (52 pages). Ordering information is given on any current masthead page.

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