Carboxylic Acids as Lewis Bases: Structures and Properties of Strongly Acidic Carboxylic Acid Adducts of $B(C_6F_5)_3$

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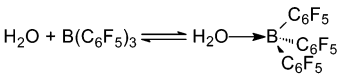
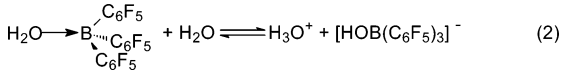
Carboxylic acids react with $B(C_6F_5)_3$ in CH_2Cl_2 to form 1:1 adducts, which have been characterized by room-temperature IR and low-temperature (−30 °C) ^{1}H, ^{19}F, ^{13}C, and ^{11}B NMR spectroscopy. Coordination appears to occur via the carbonyl oxygen atom, and exchange between an adduct and its components is generally sufficiently slow that ^{1}H, ^{19}F, ^{13}C, and ^{11}B resonances of the adduct are readily distinguished from the ^{1}H and ^{13}C resonances of the corresponding free acid and the ^{19}F and ^{11}B resonances of free $B(C_6F_5)_3$. The electron-withdrawing power of the highly electrophilic $B(C_6F_5)_3$ increases the Brønsted acidity of the coordinated carboxylic acids sufficiently that they are able to protonate isobutene and thus initiate its carbocationic polymerization. The enhanced acidity also results in slow, partial cleavage of $B-C_6F_5$ bonds, and with benzoic acid the compound $[(\mu\text{-}C_6H_5CO_2)(\mu\text{-}OH)\{B(C_6F_5)_2\}_2]$ has been isolated and characterized crystallographically. Because of slow $B-C_6F_5$ cleavage, crystallographically useful crystals of a 1:1 adduct of a carboxylic acid have not been obtained, but $C_2H_5CO_2Me{\cdot}B(C_6F_5)_3$, the 1:1 adduct of methyl propionate, has for purposes of comparison been prepared and characterized spectroscopically and crystallographically. In this case coordination occurs unequivocally via the carbonyl oxygen atom.

A very important commercial application of isobutene (IB) polymerization is the manufacture of IB homopolymers and IB−isoprene copolymers via a carbocationic process employing an $AlCl_3$/water mixture as a protic carbocationic initiator system in methyl chloride.[1] Although the mechanisms of the propagation and chain transfer steps of IB polymerization are complex,[1] it has been found that cryogenic temperatures are normally necessary if the effects of chain transfer processes are to be minimized.[1] On the other hand, rates of chain transfer are strongly affected by the nature of the counteranion, and polyisobutene (PIB) of unusually high molecular weight can be obtained at relatively high temperatures by utilizing weakly coordinating anions such as $[B(C_6F_5)_4]^-$.[2] Since commercial manufacture of high molecular weight PIB is of necessity carried out at cryogenic temperatures (−100 °C),[1] high-temperature polymerization processes mediated by weakly coordinating counteranions would be very desirable and, indeed, are of scientific interest in their own right for the insight that they may give to the chemical properties of weakly coordinating anions.[3]

In addition to the $AlCl_3$−water adduct mentioned above, other Brønsted−Lewis acid combinations are also effective initiators for carbocationic polymerization, an example being the adduct formed on reacting water with the very electrophilic borane $B(C_6F_5)_3$ (eqs 1, 2).



(1)



(2)

The Brønsted acidity of the 1:1 adduct has been studied, and its pK_a has been estimated to be 8.6 in acetonitrile, comparable to that of HCl in this solvent.[4] In accord with this finding, the adduct has been shown to be capable of inducing initiation of IB polymerization.[5]

Seeking other potential acidic initiators of IB polymerization, we have recently presented evidence that this same borane, $B(C_6F_5)_3$, reacts with a variety of carboxylic acids RCO_2H (R = alkyl, aryl) to form 1:1 and/or 2:1 adducts of the types $RCO_2H{\cdot}B(C_6F_5)_3$ and $RCO_2H{\cdot}2B(C_6F_5)_3$ (R = alkyl) as in Scheme 1.[6]

Of great interest, adducts of $B(C_6F_5)_3$ with the series of carboxylic acids $CH_3(CH_2)_nCO_2H$ (n = 6, 8, 10, 12, 14, 16, 18, 20) have been shown to behave in CH_3Cl/CH_2Cl_2 mixtures as extremely good carbocationic initiators of isobutene polymerization at −50 °C, inducing the formation of polyisobutene in high conversions and with ultrahigh molecular weights (M_w ∼2 × 10^6, M_w/M_n ∼1.5), although adducts with n = 2, 4 were not as effective.[6f] Thus this series of adducts behave as strong acids, with very weakly coordinating counteranions.

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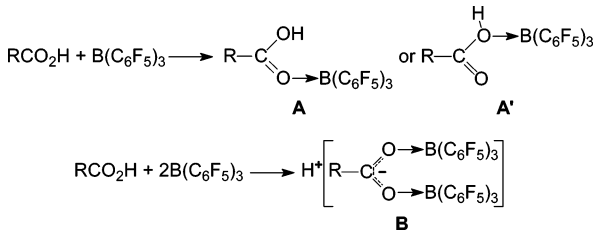
Scheme 1



While the structures and properties of the adducts have to this point been inferred only from their solution chemistry,[6a−d,f] the 1:1 and 2:1 adduct salts $[Me_4N][MeCO_2\{B(C_6F_5)_3\}]$ and $[Me_4N][MeCO_2\{B(C_6F_5)_3\}_2]$ have been prepared and characterized spectroscopically and crystallographically.[6e] The 1:1 adduct contains a monodentate acetate ion coordinated to the $B(C_6F_5)_3$ via the C−O rather than the C═O oxygen, as in (deprotonated) **A′**, while the 2:1 adduct contains a bridging acetate ion bonded to two molecules of $B(C_6F_5)_3$, much as in **B** although the two C−O bond lengths are marginally different.[6e] Thus the structures of the anions in the crystalline solids are similar to the structures proposed in Scheme 1 for the neutral adducts, and both 1:1 and 2:1 adducts appeared to be feasible solution species.

With a view to identifying and better characterizing the solution species which initiate carbocationic polymerization, we have now carried out a spectroscopic investigation (IR, ^1H, ^{19}F, ^{13}C, and ^{11}B NMR spectroscopy) of the species formed in solution on combining $B(C_6F_5)_3$ and several carboxylic acids in various ratios and at various temperatures. In addition to the novelty of simple carboxylic acids behaving as Lewis bases *and* being rendered sufficiently acidic that they can protonate alkenes, this work may be of more general interest because the strongly *Lewis* acidic properties of $B(C_6F_5)_3$ have been used in a wide variety of synthetic organic transformations.[7]

Experimental Section

NMR spectra were recorded on Bruker Avance 400, 500, and 600 NMR spectrometers; IR spectra, on a Perkin-Elmer Spectrum One IR spectrometer. All syntheses and initiator manipulations were carried out under dry nitrogen or argon atmospheres using standard Schlenk line techniques or an MBraun Labmaster glovebox. Toluene and methylene chloride were dried by passing through Innovative Technology solvent purification columns, CD_2Cl_2 by refluxing over CaH_2. Nitrogen and argon were purified by passage through a heated column of BASF catalyst followed by a column of dry, activated 3 Å or 4 Å molecular sieves (Linde). The various carboxylic acids used, propionic ($CH_3CH_2CO_2H$), *n*-butanoic ($CH_3(CH_2)_2CO_2H$), *n*-decanoic ($CH_3(CH_2)_8CO_2H$), and *n*-octadecanoic ($CH_3(CH_2)_{16}CO_2H$) acids, were purchased from Aldrich and distilled or recrystallized from hexanes before use. Propionic acid, ^{13}C-enriched propionic acid ($CH_3CH_2{}^{13}CO_2H$), and *n*-butanoic acid were also dried by passage through a column of activated alumina and were stored over molecular sieves. The compound $B(C_6F_5)_3$ was synthesized as in the literature.[8]

Ambient-Temperature Experiments. The reaction between 10.3 mg of $B(C_6F_5)_3$ (0.02 mmol) and 1.5 mg of propionic acid (0.02 mmol) in 1.0 mL of CH_2Cl_2 was studied at room temperature by IR spectroscopy. Solutions were prepared quickly and run within 1 min. The results are shown in Figure 1, where the spectrum of the adduct formed (Figure 1c) is compared with those of free propionic acid (Figure 1a) and $B(C_6F_5)_3$ (Figure 1b). The reactions between $B(C_6F_5)_3$ and propionic, *n*-butanoic acid, and *n*-octadecanoic acid were also studied by ^1H, ^{11}B, and ^{19}F NMR spectroscopy at 25 °C in CD_2Cl_2. Solutions were generally prepared as above, using a range of $B(C_6F_5)_3$:carboxylic acid ratios, and were run as quickly as possible (within 10 min).

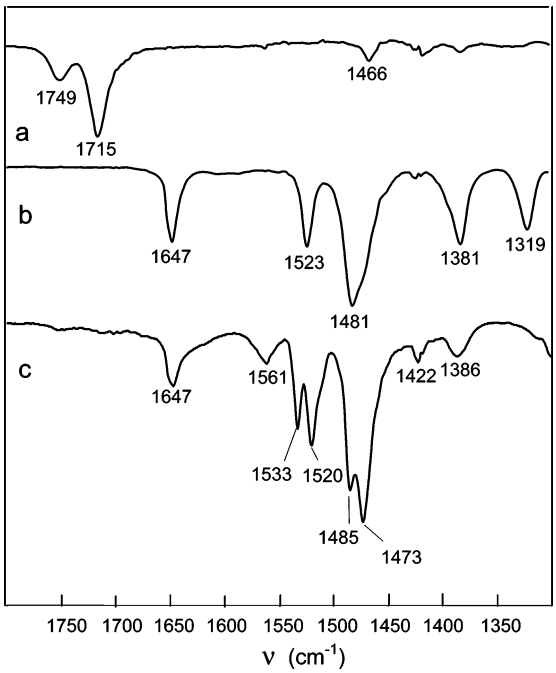


Figure 1. IR spectra (CH_2Cl_2, 21 °C) of (a) propionic acid, (b) $B(C_6F_5)_3$, and (c) propionic acid and $B(C_6F_5)_3$ in a 1:1 molar ratio.

Low-Temperature NMR Experiments Using Propionic Acid. Ten solutions, each containing 3 μL (2.98 mg, 0.0402 mmol) of propionic acid in 0.2 mL of CD_2Cl_2, were made up in NMR tubes and cooled to −30 °C. Aliquots of $B(C_6F_5)_3$ (approximately 0.1, 0.25, 0.5, 0.75, 1, 1.25, 1.5, 1.75, 2.0, 2.5, 2.75 equiv) were dissolved in 0.3 mL of CD_2Cl_2 in separate vials and cooled to −30 °C, and each $B(C_6F_5)_3$ solution was then injected into one of the NMR solutions. The samples were quickly mixed by shaking, and a ^1H NMR spectrum of each was run at −30 °C (100 scans, recycle delay time 10 s). Representative spectra in the range δ 1−14 are shown in Figure 2, and expanded spectra in the range δ 1−3 in Figure 3.

In complementary experiments, several solutions each containing ∼31 mg of $B(C_6F_5)_3$ (∼0.06 mmol) in 0.4 mL of CD_2Cl_2 in an NMR tube were cooled to −40 °C. Solutions containing various amounts of propionic acid or propionic acid enriched in ^{13}C at the carboxylic carbon, also in 0.4 mL of CD_2Cl_2, were then added dropwise to the still cooled $B(C_6F_5)_3$ solutions in NMR tubes such that $B(C_6F_5)_3$:$CH_3CH_2CO_2H$ ratios in the range 0.5:1−2.0:1 were achieved. ^1H, ^{19}F, ^{13}C, and ^{11}B NMR spectra of the solutions were obtained at −30 °C; the ^1H NMR spectra were as obtained previously. The ^{19}F, ^{13}C, and ^{11}B spectra are shown in Figures 4, 5, and 6, respectively.

Low-Temperature NMR Experiments Using *n*-Decanoic Acid. Solutions containing $B(C_6F_5)_3$ and *n*-decanoic acid in 0.5:1, 1.5:1, and 2:1 ratios were made up in CD_2Cl_2 at −30 °C as above, and ^1H and ^{19}F NMR spectra were run at −30 °C. The ^1H NMR spectra are shown in Figure 7.

Attempted Syntheses of Compounds of the Type $RCO_2B(C_6F_5)_2$; Crystal Structure of $[(\mu\text{-}C_6H_5CO_2)(\mu\text{-}OH)\{B(C_6F_5)_2\}_2]$. A solution of 59 mg of recrystallized benzoic acid (0.49 mmol) in 2 mL of CH_2Cl_2 was treated dropwise with a solution of 205 mg of $B(C_6F_5)_3$ (0.49 mmol) in 5 mL of CH_2Cl_2. The reaction mixture was stirred for 30 min, and then 20 mL of hexanes was added to induce precipitation of the product. The supernatant was then removed, the solid residue was dried in vacuo, and a small number of crystals of $[(\mu\text{-}C_6H_5CO_2)(\mu\text{-}OH)\{B(C_6F_5)_2\}_2]$ were obtained by

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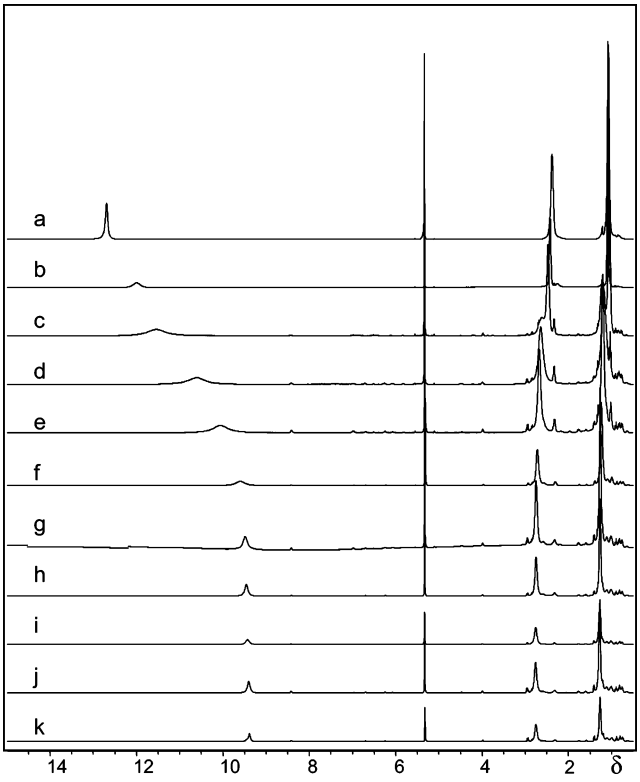


Figure 2. ^{1}H NMR spectra (400 MHz, −30 °C, CD_2Cl_2) of solutions of $B(C_6F_5)_3$ and propionic acid in the ratios (a) 0:1, (b) 0.25:1, (c) 0.5:1, (d) 0.75:1, (e) 1:1, (f) 1.25:1, (g) 1.5:1, (h) 1.75:1, (i) 2:1, (j) 2.5:1, and (k) 2.75:1.

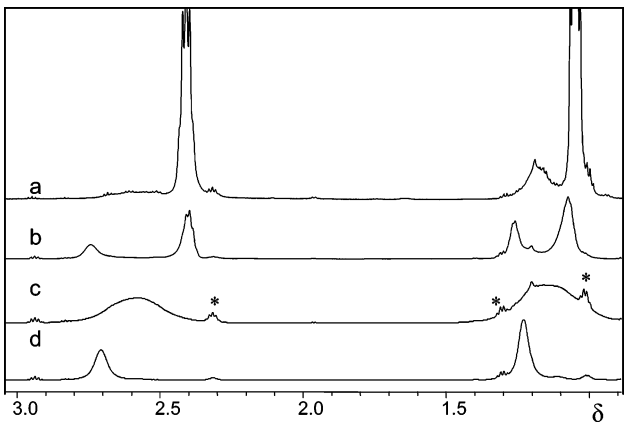


Figure 3. Expanded ^{1}H NMR spectra (600 MHz, −30 °C, CD_2Cl_2) of solutions of $B(C_6F_5)_3$ and $CH_3CH_2CO_2H$ in the ratios (a) 0.25:1 (expanded vertically), (b) 0.5:1, (c) 0.75:1, and (d) 1:1 (* = impurities).

layering a CH_2Cl_2 solution with hexanes. ^{1}H NMR (CD_2Cl_2): δ 8.93 (s, br, 1H, OH), 8.32 (d, J = 8.1 Hz, 2H, *ortho*-H), 7.90 (t, J = 7.6 Hz, 1H, *meta*-H), 7.66 (t, J = 7.8 Hz, 2H, *para*-H). ^{19}F NMR (CD_2Cl_2): δ −138.1 (d, J = 15.7 Hz, 8F, *ortho*-F), −154.2 (t, J = 20.3 Hz, 4F, *para*-F), −163.2 (t, J = 18.8 Hz, 8F, *meta*-F). A similar procedure was also carried out with $CH_3CH_2CO_2H$, ultimately giving only a small amount of $[(\mu\text{-}C_6H_5CO_2)(\mu\text{-OH})\{B(C_6F_5)_2\}_2]$, which could not be obtained pure but which was identified by NMR spectroscopy. ^{1}H NMR (CD_2Cl_2): δ 8.19 (s, br, 1H, OH), 2.94 (q, J = 7.4 Hz, 2H, CH_2), 1.35 (t, J = 7.4 Hz, 3H, CH_3). ^{19}F NMR (CD_2Cl_2): δ −138.2 (d, J = 14.5 Hz, 8F, *ortho*-F), −154.4 (t, J = 21.0 Hz, 4F, *para*-F), −163.4 (t, J = 17.1 Hz, 8F, *meta*-F).

A crystal of $[(\mu\text{-}C_6H_5CO_2)(\mu\text{-OH})\{B(C_6F_5)_2\}_2]$ (colorless, block-shaped, size 0.35 × 0.30 × 0.28 mm) was mounted on a glass fiber with grease and cooled to −93 °C in a stream of nitrogen gas controlled with Cryostream Controller 700. Data collection was performed on a Bruker SMART CCD 1000 X-ray diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), operating at 50 kV and 30 mA over 2θ ranges of 3.56−56.36° at −93 °C controlled with Crysostream Controller 700. No significant decay was observed during the data collection. Data were processed on a Pentium PC using the Bruker AXS Windows NT software package (version 5.10).[9a] Neutral atom scattering factors were taken from Cromer and Waber.[9b] The raw intensity data were converted to structure amplitudes and their esds using the program SAINT-Plus. Empirical absorption corrections were applied using the program SADABS. The structure was solved and refined by using SHELXTL. The crystal is monoclinic, space group *C*2/*c*, based on the systematic absences, *E* statistics, and successful refinement of the structure. The structure was solved by direct methods. Full-matrix least-squares refinements minimizing the function $\sum w(F_o^2 - F_c^2)^2$ were applied to the compound. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were located gradually from the difference Fourier map, and their contributions were included in the structure factor calculations.

Convergence to final R_1 = 0.0551 and wR_2 = 0.0651 for 2509 $I > 2\sigma(I)$ independent reflections and R_1 = 0.1321 and wR_2 = 0.0725 for all 5333 (R(int) = 0.0804) independent reflections by using 528 parameters were achieved, with the largest residual peak and hole being 0. 228 and −0.264 e/Å^3, respectively. Crystallographic data are shown in Table 1, the molecular structure is shown in Figure 8, and important bond lengths and angles are given in Table 2.

Synthesis, Characterization, and Crystal Structure of $C_2H_5CO_2Me\cdot B(C_6F_5)_3$. A solution of 103 mg of methyl propionate (1.17 mmol) in 3 mL of CH_2Cl_2 was added dropwise to a solution of 400 mg of $B(C_6F_5)_3$ (0.78 mmol) in 10 mL of CH_2Cl_2 at room temperature. The mixture was stirred for 5 min, the solvent was removed in vacuo, and the resulting yellow oil was washed twice with 10 mL portions of hexanes to give a white, crystalline solid (380 mg, 0.63 mmol, 81%), which was recrystallized from a mixture of 2 mL of CH_2Cl_2 and 10 mL of hexanes. ^{1}H NMR (CD_2Cl_2): δ 4.18 (s, 3H, OC*H*$_3$), 2.37 (q, 2H, C*H*$_2$CH$_3$), 1.07 (t, 3H, CH$_2$C*H*$_3$). ^{19}F NMR (CD_2Cl_2): δ −135.8 (*ortho*-F), −157.7 (*para*-F), −165.0 (*meta*-F). ^{11}B NMR (CD_2Cl_2): δ 6.28 (sharp). ^{13}C NMR (CD_2Cl_2): δ 188.0 (*C*═O), 58.8 (O*C*H$_3$), 28.2 (*C*H$_2$CH$_3$), 8.3 (CH$_2$*C*H$_3$). Anal. Calcd for $C_{22}H_8O_2BF_{15}$: C, 44.00; H, 1.34. Found: C, 44.44; H, 1.54. IR (Fluorolube mull): ν(C═O) = 1601 cm^{-1}.

A crystal of $C_2H_5CO_2Me\cdot B(C_6F_5)_3$ (colorless, prism-shaped, size 0.25 × 0.10 × 0.10 mm) was mounted on a glass fiber with grease and cooled to −93 °C in a stream of nitrogen gas controlled with Cryostream Controller 700. Data collection was performed on a Bruker SMART CCD 1000 X-ray diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), operating at 50 kV and 35 mA over 2θ ranges of 3.92−50.00°. No significant decay was observed during the data collection. Data were processed as above. The crystal is monoclinic, space group $P2_1/c$, based on the systematic absences, *E* statistics, and successful refinement of the structure. Convergence to final R_1 = 0.0328 and wR_2 = 0.0562 for 2594 ($I > 2\sigma(I)$) independent reflections and R_1 = 0.0559 and wR_2 = 0.0596 for all 3874 (R(int) = 0.0322) independent reflections, with 393 parameters, were achieved. The largest residual peak and hole were 0.172 and −0.234 e/Å^3, respectively. Crystallographic data are given in Table 1, the molecular structure is shown in Figure 9, and important bond lengths and angles are given in Table 3. Crystallographic data, atomic coordinates, and equivalent isotropic

(9) (a) *Bruker AXS* Crystal Structure Analysis Package, Version 5.10, *SMART NT* (Version 5.053), *SAINT-Plus* (Version 6.01), *SHELXTL* (Version 5.1); Bruker AXS Inc.: Madison, WI, 1999. (b) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, UK, 1974; Vol. 4, Table 2.2 A.

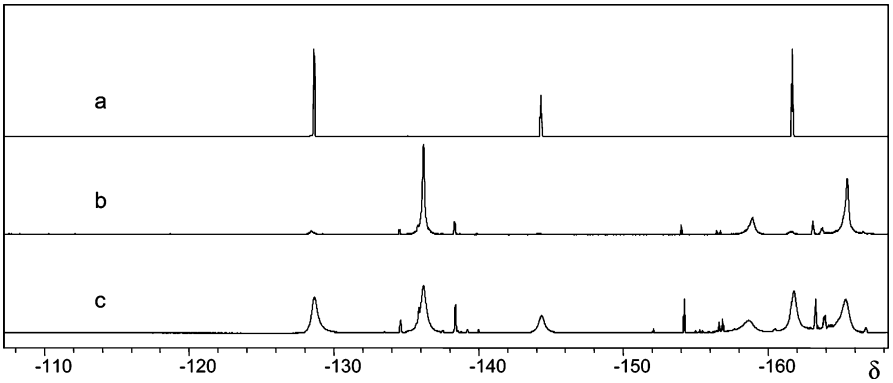


Figure 4. ^{19}F NMR spectra (CD_2Cl_2, −30 °C) of (a) $B(C_6F_5)_3$, (b) a mixture of $B(C_6F_5)_3$ and propionic acid in a 1:1 ratio, and (c) a mixture of $B(C_6F_5)_3$ and propionic acid in a 2:1 ratio.

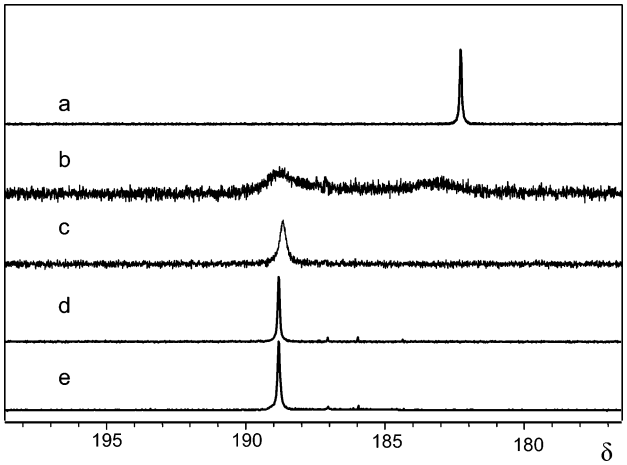


Figure 5. ^{13}C NMR spectra (−30 °C, CD_2Cl_2) of (a) $CH_3CH_2{}^{13}CO_2H$ and of solutions of $B(C_6F_5)_3$ and $CH_3CH_2{}^{13}CO_2H$ in the ratios (b) 0.75:1, (c) 1:1, (d) 1.5:1, and (e) 2:1.

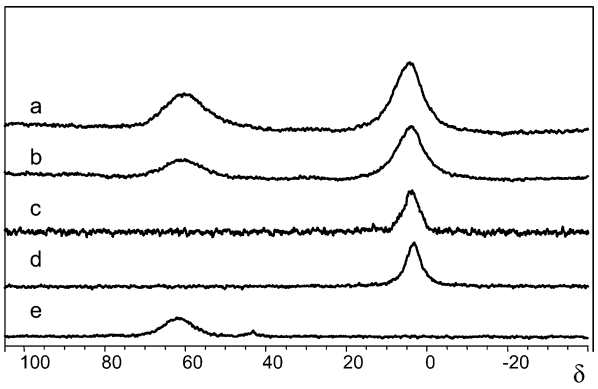


Figure 6. ^{11}B NMR spectra (−30 °C, CD_2Cl_2) for solutions of $B(C_6F_5)_3$ and $CH_3CH_2{}^{13}CO_2H$ in the approximate ratios (a) 2:1, (b) 1.5:1, (c) 1:1, and (d) 0.75:1, (e) 1.0; (e) shows the resonance of free $B(C_6F_5)_3$.

displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and torsion angles are given in the Supporting Information.

Exchange Experiments Involving $C_2H_5CO_2H$, $B(C_6F_5)_3$ and Either $C_2H_5CO_2Me$ or PhCOMe. A solution of 24.1 mg of $C_2H_5CO_2Me{\cdot}B(C_6F_5)_3$ (0.0402 mmol) in 0.5 mL of CD_2Cl_2 was reacted with 2.98 mg of propionic acid (3 μL, 0.0402 mmol), and a ^{1}H NMR spectrum was obtained at room temperature. In the same manner, ^{1}H NMR spectra were obtained for solutions containing various ratios of $C_2H_5CO_2Me{\cdot}B(C_6F_5)_3$ and propionic acid, as well as of $C_2H_5CO_2H$, $B(C_6F_5)_3$, and PhCOMe.

Crystallographic data for $[(\mu\text{-}C_6H_5CO_2)(\mu\text{-OH})\{B(C_6F_5)_2\}_2]$ and $C_2H_5CO_2Me{\cdot}B(C_6F_5)_3$ have been deposited with the Cambridge Crystallographic Data Centre. Copies of these data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. The deposition numbers are CCDC 616968 and CCDC 616969, respectively.

Results and Discussion

For purposes of comparison, the relevant spectral data for $[Me_4N][MeCO_2\{B(C_6F_5)_3\}]$ are as follows. ^{1}H NMR (CD_2Cl_2, 21 °C): δ 1.94 (s, MeC). ^{19}F NMR (CD_2Cl_2, 21 °C): δ −135.9 (*ortho*-F), −163.6 (*para*-F), −168.2 (*meta*-F). ^{11}B NMR (CD_2Cl_2, 21 °C): δ −5.1 (sharp). IR (Fluorolube mull): ν(CO) 1682, 1491 cm^{-1}.[6e] The comparable data for $[Me_4N][MeCO_2\{B(C_6F_5)_3\}_2]$ are as follows. ^{1}H NMR (CD_2Cl_2, 21 °C): δ 2.19 (s, MeC). ^{19}F NMR (CD_2Cl_2, 21 °C): δ −135.6 (*ortho*-F), −161.0 (*para*-F), −167.1 (*meta*-F). ^{11}B NMR (CD_2Cl_2, 21 °C): δ −1.6 (broad). IR (Fluorolube mull): ν(CO) 1566, 1417 cm^{-1}.[6e] The methyl chemical shift of CH_3CO_2H is δ 2.07 in CD_2Cl_2 at 21 °C, falling midway between the methyl resonances of $[MeCO_2\{B(C_6F_5)_3\}]^-$ and $[MeCO_2\{B(C_6F_5)_3\}_2]^-$. Thus the proton appears to have an electron-withdrawing ability approximately midway between that of a single $B(C_6F_5)_3$ and those of two $B(C_6F_5)_3$.

Room-Temperature IR and ^{1}H NMR Studies. To begin, we obtained IR and NMR data at room temperature for CH_2Cl_2 solutions containing $B(C_6F_5)_3$ and propionic acid, *n*-butanoic acid, *n*-decanoic acid, or *n*-octadecanoic acid in various $B(C_6F_5)_3$:acid ratios. The IR spectrum of a solution of propionic acid exhibits a significantly broadened OH stretching band (∼2400 to ∼3400 cm^{-1}) because of the hydrogen bonding.[10a] This band disappears on the addition of an equimolar amount of $B(C_6F_5)_3$, and no new band attributable to ν(OH) appears, a finding that can probably be interpreted in terms of extreme broadening in the presumed adduct(s) because of strong hydrogen bonding.

We show in Figures 1a,b the IR spectra of 0.04 M CH_2Cl_2 solutions of propionic acid and $B(C_6F_5)_3$, respectively, in the range 1300−1800 cm^{-1}. The peaks at 1749 and 1715 cm^{-1} in the spectrum of propionic acid are the C═O stretching modes of respectively the monomeric and hydrogen-bonded dimeric

(10) (a) Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*; Wiley & Sons: New York, 1998; pp 95, 96. (b) Lascombe, J.; Haurie, M.; Josien, M.-L. *J. Chim. Phys.* **1962**, *59*, 1233. (c) Collings, A. J.; Morgan, K. J. *J. Chem. Soc.* **1963**, 3437.

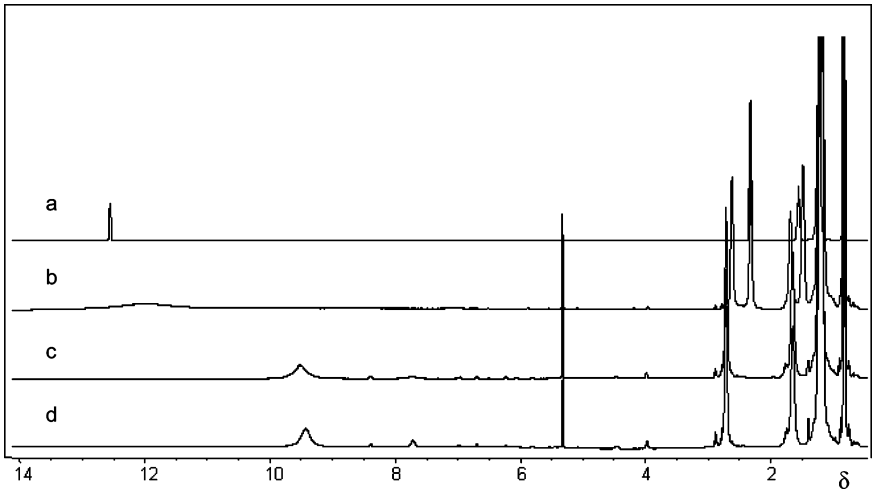


Figure 7. ^{1}H NMR spectra (−30 °C, CD_2Cl_2) of solutions of (a) *n*-decanoic acid, (b) containing $B(C_6F_5)_3$ and *n*-decanoic acid in a 0.5:1 ratio, (c) containing $B(C_6F_5)_3$ and *n*-decanoic acid in a 1.5:1 ratio, and (d) containing $B(C_6F_5)_3$ and *n*-decanoic acid in a 2:1 ratio.

Table 1. Crystal Data and Structure Refinement of $[(\mu\text{-}C_6H_5CO_2)(\mu\text{-}OH)\{B(C_6F_5)_2\}_2]$ and $C_2H_5CO_2Me{\cdot}B(C_6F_5)_3$

	$[(\mu\text{-}C_6H_5CO_2)(\mu\text{-}OH)\{B(C_6F_5)_2\}_2]$	$C_2H_5CO_2Me{\cdot}B(C_6F_5)_3$
empirical formula	$C_{31}H_6B_2F_{20}O_3$	$C_{22}H_8BF_{15}O_2$
fw	827.98	600.09
temperature	180(2) K	180(2) K
wavelength	0.71073 Å	0.71073 Å
cryst syst	monoclinic	monoclinic
space group	*C*2/*c*	*P*2(1)/*c*
unit cell dimens	$a = 21.429(12)$ Å, $\alpha = 90°$	$a = 10.1619(11)$ Å, $\alpha = 90°$
	$b = 14.402(8)$ Å, $\beta = 118.519(8)°$	$b = 14.3044(14)$ Å, $\beta = 91.076(2)°$
	$c = 22.384(18)$ Å, $\gamma = 90°$	$c = 15.1871(15)$ Å, $\gamma = 90°$
volume	6070(7) Å^3	2207.2(4) Å^3
Z	8	4
density (calcd)	1.812 Mg/m^3	1.806 Mg/m^3
absorp coeff	0.198 mm^{-1}	0.200 mm^{-1}
F(000)	3248	1184
cryst size	0.35 × 0.30 × 0.28 mm^3	0.25 × 0.10 × 0.10 mm^3
θ range for data collection	1.78 to 25.00°	1.96 to 25.00°
index ranges	$-25 \le h \le 24$, $-17 \le k \le 17$, $-23 \le l \le 26$	$-12 \le h \le 11$, $-17 \le k \le 16$, $-18 \le l \le 18$
no. of reflns collected	14 201	12 715
no. of indep reflns	5333 [*R*(int) = 0.1030]	3874 [*R*(int) = 0.0322]
completeness to $\theta = 28.18°$	99.8%	99.9%
absorp corr	empirical (Bruker SADABS)	empirical (Bruker SADABS)
max. and min. transmn	0.6374 and 0.3808	1.0000 and 0.8584
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	5333/0/528	3874/0/381
goodness-of-fit on F^2	0.922	1.000
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0551$, $wR_2 = 0.0651$	$R_1 = 0.0329$, $wR_2 = 0.0562$
R indices (all data)	$R_1 = 0.1321$, $wR_2 = 0.0725$	$R_1 = 0.0559$, $wR_2 = 0.0596$
largest diff peak and hole	0.228 and −0.264 e/Å^{-3}	0.172 and −0.234 e/Å^{-3}

forms of the acid and are typical for aliphatic carboxylic acids.[10b,c] On the basis of data for 1:1 adducts of $B(C_6F_5)_3$ with the carbonyl Lewis bases benzaldehyde, acetophenone, ethyl benzoate, and *N*,*N*-diisopropylbenzamide,[11] one would anticipate that the IR spectrum of a 1:1 adduct of the propionic acid monomer, with a structure as in **A**, would exhibit ν(C═O) some 49−83 cm^{-1} lower than ν(C═O) of the free, monomeric acid, i.e., in the range 1666−1700 cm^{-1}. On the other hand, a 1:1 adduct with a structure as in **A′** might be expected to exhibit a ν(C═O) perturbed relatively little from that of the free acid. The IR spectrum of $B(C_6F_5)_3$ exhibits peaks at 1647, 1523, and 1481 cm^{-1}; these are attributed to ring vibrational modes[12a] and would reasonably be expected to shift relatively little on formation of an adduct.

In Figure 1c we show a spectrum in the carbonyl region of a solution containing propionic acid and $B(C_6F_5)_3$ in a 1:1 ratio, both 0.02 M; a very similar spectrum is observed when a second molar equivalent of $B(C_6F_5)_3$ is added. As can be seen, the two ν(C═O) of the free propionic acid have disappeared completely, consistent with essentially quantitative formation of one or more adducts of the acid with $B(C_6F_5)_3$. However there are no well-defined new peaks, attributable to species such as **A** or **A′**, in the region 1660−1800 cm^{-1}; one observes only those at 1561, 1533, and 1520 cm^{-1}, the latter two of which are probably attributed to C_6F_5 vibrational modes.[12b]

Room-temperature ^{1}H NMR spectra were obtained for mixtures of propionic, *n*-butanoic acid, and *n*-octadecanoic acids with $B(C_6F_5)_3$ in CD_2Cl_2, and it was found in all cases that resonances of RCH_2CO_2H and R$CH_2CH_2CO_2H$ groups shifted to

(11) Parks, D. J.; Piers, W. E.; Parvez, M.; Atencio, R.; Zawarotko, M. J. *Organometallics* **1998**, *17*, 1369.

(12) (a) Frankiss, S. G.; Harrison, D. J. *Spectrochim. Acta* **1975**, *31A*, 1839. (b) While a peak is also observed at 1533 cm^{-1} in the spectrum of the 1:1 mixture, this peak gains in intensity with time and, consistent with the NMR data, may be assigned to pentafluorobenzene, a product of protic cleavage of the B−C_6F_5 bond. The peaks at 1520, 1485, and 1473 cm^{-1} may all be assigned to vibrational modes of $B(C_6F_5)_3$.

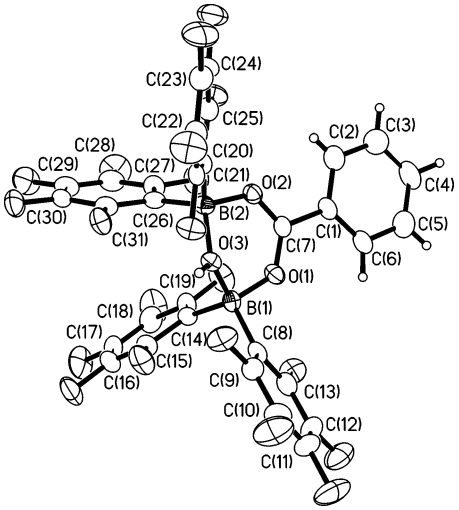


Figure 8. Molecular structure of $[(\mu\text{-}C_6H_5CO_2)(\mu\text{-OH})\{B(C_6F_5)_2\}_2]$.

Table 2. Important Bond Lengths and Bond Angles of $[(\mu\text{-}C_6H_5CO_2)(\mu\text{-OH})\{B(C_6F_5)_2\}_2]$

Bond Lengths (Å)	
C(1)−C(7)	1.463(5)
C(7)−O(1)	1.272(4)
C(7)−O(2)	1.271(4)
B(1)−O(1)	1.509(4)
B(2)−O(2)	1.494(5)
B(1)−O(3)	1.522(5)
B(2)−O(3)	1.527(4)
Bond Angles (deg)	
C(1)−C(7)−O(1)	118.3(4)
C(1)−C(7)−O(2)	118.1(3)
O(1)−C(7)−O(2)	123.6(3)
C(7)−O(1)−B(1)	126.1(3)
C(7)−O(2)−B(2)	125.8(3)

lower field, consistent with coordination. However, within minutes these resonances decreased in intensity as others appeared in the same region; a multiplet at δ 6.96, attributed to C_6F_5H, also appeared and is indicative of protic cleavage of B−C bonds.

The ^{1}H NMR spectrum of free propionic acid in CD_2Cl_2 at −30 °C exhibits methyl, methylene, and OH resonances at δ 1.06 (t), 2.36 (q), and ∼12.7 (s), respectively (Figure 2a). As can be seen in Figure 2, addition of increasing amounts of $B(C_6F_5)_3$ to a solution of propionic acid resulted in initial broadening of the OH resonance and then narrowing as it shifted from δ ∼12.7 to higher field. Ultimately the resonance leveled off at δ ∼9.7 in the presence of 1.0−1.5 equiv, and little change was observed on the further addition of $B(C_6F_5)_3$. Similar results were obtained in $CDCl_3$, C_6D_6, and toluene-d_8. Several of the reactions were also monitored by ^{19}F NMR spectroscopy, and in all cases several sets of C_6F_5 resonances were observed to form, indicating mixtures of products that included C_6F_5H. Thus it seems in general that $B(C_6F_5)_3$ reacts with carboxylic acids to give adducts that exhibit resonances distinguishable from those of the free acid, but that rapid protic cleavage of B−C_6F_5 bonds results in the formation of C_6F_5H and, presumably, compounds of the type $RCO_2B(C_6F_5)_2$.

In an attempt to identify the latter, $B(C_6F_5)_3$ was reacted with propionic acid and benzoic acid (both 1:1 molar ratio) in CH_2Cl_2 at room temperature for 30 min. Addition of hexanes gave in both cases small amounts of crude products with very similar ^{19}F NMR spectra and broad, low-field resonances in the ^{1}H NMR spectra (see Experimental Section). The latter were ultimately assigned to μ-OH groups on the basis of a crystal

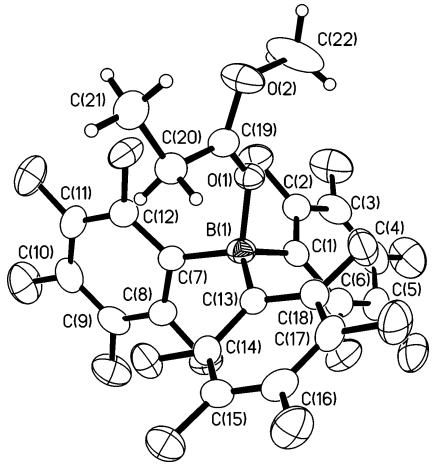


Figure 9. Molecular structure of $C_2H_5CO_2Me{\cdot}B(C_6F_5)_3$.

Table 3. Important Bond Lengths and Bond Angles of $C_2H_5CO_2Me{\cdot}B(C_6F_5)_3$

Bond Lengths (Å)	
C(19)−O(2)	1.292(2)
C(19)−O(1)	1.248(2)
O(2)−C(22)	1.472(2)
C(19)−C(20)	1.477(3)
C(20)−C(21)	1.509(3)
B(1)−O(1)	1.579(2)
B(1)−C(1)	1.628(3)
B(1)−C(7)	1.631(3)
B(1)−C(13)	1.627(3)
Bond Angles (deg)	
C(19)−C(20)−C(21)	115.61(19)
C(20)−C(19)−O(1)	126.45(18)
C(20)−C(19)−O(2)	115.54(18)
O(1)−C(19)−O(2)	118.00(17)
C(19)−O(2)−C(22)	117.24(16)
C(19)−O(1)−B(1)	132.86(15)
O(1)−B(1)−C(1)	101.61(14)
O(1)−B(1)−C(7)	109.99(15)
O(1)−B(1)−C(13)	105.54(15)

structure of the benzoic acid product, which showed that the compound was $[(\mu\text{-}C_6H_5CO_2)(\mu\text{-OH})\{B(C_6F_5)_2\}_2]$ (Tables 1, 2; Figure 8). Thus the compound obtained was not the anticipated $C_6H_5CO_2B(C_6F_5)_2$, but rather a secondary product resulting presumably from hydrolysis by adventitious water. The bond lengths and angles shown in Table 2 are generally unexceptional where precedents exist,[13] but the structure does serve to confirm the presence among the products of a species containing a $B(C_6F_5)_2$ moiety. We note that, as might be anticipated, the two B−OH bond lengths (1.516(6), 1.529(6) Å) are significantly longer than are the two B−O bond lengths (1.496(2), 1.306(2) Å) of the complex anion $[(C_6F_5)_3B(\mu\text{-O})B(C_6F_5)_2]^-$.[13d]

Low-Temperature NMR studies. In an effort to circumvent the B−C_6F_5 cleavage problem, we investigated reactions of $B(C_6F_5)_3$ with propionic and *n*-decanoic acid at lower temperatures, down to −50 °C. We found that temperatures of about −30 °C were optimal, the rates of B−C_6F_5 cleavage being slow, while reasonable solubilities and usable resonance line widths were still generally attainable.

(13) (a) Doerrer, L. H.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1999**, 4325. (b) Vagedes, D.; Fröhlich, R.; Erker, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 3362. (c) Barrado, G.; Doerrer, L.; Green, M. L. H.; Leech, M. A. *J. Chem. Soc., Dalton Trans.* **1999**, 1061. (d) Di Saverio, A.; Focante, F.; Camurati, I.; Resconi, L.; Beringhelli, T.; D'Alfonso, G.; Donghi, D.; Maggioni, D.; P.; Mercandelli, P.; Sironi, A. *Inorg. Chem.* **2005**, *44*, 5030. (e) Beringhelli, T.; D'Alfonso, G.; Donghi, D.; Maggioni, D.; Mercandelli, P.; Sironi, A. *Organometallics* **2004**, *23*, 5493.

Propionic Acid. A series of ^{1}H NMR experiments in CD_2Cl_2 and involving $B(C_6F_5)_3$ and propionic acid in various $B(C_6F_5)_3$:$CH_3CH_2CO_2H$ molar ratios (0.25:1−2.75:1) were carried out at −30 °C. Representative spectra in the range δ 1−14 are shown in Figure 2, and expanded spectra in the range δ 1−3 in Figure 3. In view of the errors involved in measuring the miniscule quantities of reagents involved, the ratios varied somewhat from the nominal ratios stated in the Experimental Section and in Figure 2; however, the trends in the ratios are undoubtedly as stated.

Changes in the aliphatic region were more subtle but, as can be seen in Figure 3a, addition of ∼0.25 molar equivalent of $B(C_6F_5)_3$ to a solution of propionic acid resulted in the appearance of very broad, weak methyl and methylene resonances at δ ∼1.18 and ∼2.56, respectively. Both exhibited intensities approximately one-third those of the corresponding methyl and methylene resonances of the free acid although the breadth of the lines made accurate measurements impossible. When the $B(C_6F_5)_3$:propionic acid ratio was increased to ∼0.5:1, the new resonances shifted to δ 1.26 and 2.74 and gained in intensity such that the ratio of their intensities to those of the free acid resonances was now ∼0.5:1 (Figure 3b). (If, as is concluded below, the new species is a 1:1 adduct, then these relative integrations suggest that the nominal 2:1 ratio of reactants had not been achieved exactly.)

Increasing the ratio to ∼1:1 resulted in disappearance of the resonances of the free acid and observation of only the new resonances (Figure 3d), while addition of excess $B(C_6F_5)_3$ (up to a 2.75:1 ratio) resulted in no other changes in the spectrum. Interestingly, when the $B(C_6F_5)_3$:propionic acid ratio was ∼0.75:1, the pairs of methylene and methyl resonances coalesced (Figure 3c).

These experiments were complemented by ^{19}F, ^{13}C, and ^{11}B NMR spectra of solutions (all in CD_2Cl_2 at −30 °C) containing $B(C_6F_5)_3$ and propionic acid in various ratios. On the addition of approximately 1 equiv of propionic acid to a solution of $B(C_6F_5)_3$, the resonances of free $B(C_6F_5)_3$ at δ −128.6 (*ortho*-F), −144.3 (*para*-F), and −158.7 (*meta*-F) (Figure 4a) disappeared and a new set of somewhat broadened resonances at δ −136.9 (*ortho*-F), −158.7 (*para*-F), and −165.4 (*meta*-F) appeared (Figure 4b); these ^{19}F chemical shifts are very similar to those of the acetate adduct $[Me_4N][MeCO_2\{B(C_6F_5)_3\}]$.[6e] The spectrum of a 2:1 reaction mixture (Figure 4c) exhibited both this set of resonances and also those of free $B(C_6F_5)_3$ at δ −128.6 (*ortho*-F), −144.3 (*para*-F), and −158.7 (*meta*-F), the three pairs of *ortho*-, *meta*-, and *para*-resonances being of comparable intensities and somewhat broadened because of exchange. Several sharp, weak resonances were also observed, presumably a result of slow cleavage reactions of the type discussed above.

The ^{13}C NMR experiments were carried out using propionic acid enriched in ^{13}C at the carboxylic carbon. On the addition of ∼0.75 equiv of $B(C_6F_5)_3$ to a solution of propionic acid, the resonance of free acid at δ 182 weakened, broadened, and shifted somewhat while a new, broad resonance at δ ∼189 appeared (Figure 5b). When the ratio of $B(C_6F_5)_3$ to propionic acid was 1:1 and higher, only the (now sharp) resonance at δ 189 remained (Figures 5c−e). Similar ^{11}B NMR experiments (Figure 6) showed that the broad resonance of free $B(C_6F_5)_3$ at δ 62.0 was replaced completely by a new, somewhat narrower resonance at δ 0.2 in the presence of ≥1 equiv of propionic acid, but that the two resonances were present in comparable intensities when the $B(C_6F_5)_3$ to propionic acid ratio was 2:1. Note that the ^{11}B chemical shift of the new species is similar to that of $[Me_4N][MeCO_2\{B(C_6F_5)_3\}]$.[6e]

***n*-Decanoic Acid.** On treating a CD_2Cl_2 solution of *n*-decanoic acid with $B(C_6F_5)_3$ (nominal $B(C_6F_5)_3$:*n*-decanoic acid ratios ∼0.5:1−2:1) at −30 °C, the OH resonance of the free acid at δ 12.56 first broadened then narrowed and shifted ultimately to δ ∼9.5, as shown in Figure 7. Interestingly, at a $B(C_6F_5)_3$:*n*-decanoic acid ratio of ∼0.5:1, the $CH_3(CH_2)_7CH_2CO_2$ resonance at δ 2.32 decreased in intensity and a new resonance, of comparable intensity and attributable to the $CH_3(CH_2)_7CH_2CO_2$ resonance of the 1:1 adduct, appeared at δ 2.61 (Figure 7b). Similarly the $CH_3(CH_2)_6CH_2CH_2CO_2$ resonance of the free acid at δ 1.55 split into two resonances of comparable intensity at δ 1.68 and 1.48. The resonance at δ 1.68 is presumably attributed to the $CH_3(CH_2)_6CH_2CH_2CO_2$ resonance of the 1:1 adduct, and that at δ 1.48 possibly to free *n*-decanoic acid hydrogen bonded to the adduct since the chemical shift is not identical to that of the free acid. In Figures 7c,d, we show the spectra of *n*-decanoic acid in the presence of 1.5 and 2 equiv of $B(C_6F_5)_3$, respectively. There is in both spectra clearly only single sets of $CH_3(CH_2)_7CH_2CO_2$ and $CH_3(CH_2)_6CH_2CH_2CO_2$ resonances, the chemical shifts of which correspond closely with the chemical shifts of the pair of downfield resonances in Figure 7b and strengthen their assignments to the 1:1 adduct.

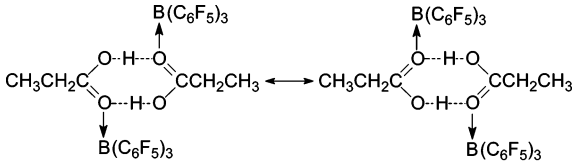
These results are consistent with those discussed above for propionic acid, although the chemical shift differences between the $CH_3(CH_2)_nCH_2CO_2$ and $CH_3(CH_2)_{n-1}CH_2CH_2CO_2$ resonances of the free and coordinated acids are greater for *n*-decanoic acid. ^{19}F NMR spectra of the same $B(C_6F_5)_3$/*n*-decanoic acid solutions (not shown) also exhibited separate resonances for the three pairs of *ortho*-F (δ −136.3), *para*-F (δ −159.7), and *meta*-F (δ −166.0) resonances. These chemical shifts are very similar to those reported above for the 1:1 propionic acid adduct.

Nature of the Adduct(s) in Solution. On the basis of the IR spectroscopic data for propionic acid, it seems that a 1:1 adduct, $C_2H_5CO_2H\cdot B(C_6F_5)_3$, is formed as in Scheme 1 (**A**, R = CH_3CH_2), although slow, proton-induced $B-C_6F_5$ cleavage even at low temperatures impaired all attempts to grow crystallographically useful crystals. The IR spectral data show clearly that ν(OH) and ν(C=O) of free propionic acid disappear completely on the addition of 1 molar equiv of $B(C_6F_5)_3$ and that addition of excess $B(C_6F_5)_3$ results in little further change in the IR spectrum. It was disturbing initially when we found that the adduct did not exhibit ν(C=O) in the range 1666−1700 cm^{-1} as anticipated on the basis of IR data for 1:1 adducts of $B(C_6F_5)_3$ with other carbonyl Lewis bases,[11] but we successfully prepared and characterized spectroscopically and crystallographically the corresponding 1:1 adduct of methyl propionate, $C_2H_5CO_2Me\cdot B(C_6F_5)_3$ (see below). The ester in this compound coordinates to the borane via the carbonyl oxygen atom, as in the corresponding ethyl benzoate adduct,[11] but ν(C=O) shifts from 1746 cm^{-1} in the free ester to 1601 cm^{-1} on coordination, a $\Delta\nu$(C=O) of 145 cm^{-1}, which contrasts markedly with the $\Delta\nu$(C=O) of 49 cm^{-1} reported previously for the 1:1 adduct of ethyl benzoate.[11] The reasons for this apparent discrepancy are discussed below, but observation of an apparent ν(C=O) of $C_2H_5CO_2H\cdot B(C_6F_5)_3$ at 1561 cm^{-1} now seems quite reasonable.

Turning now to the ^{1}H, ^{19}F, ^{11}B, and ^{13}C NMR spectroscopic evidence for the carboxylic acid systems, the data support the conclusion that 1:1 adducts are formed essentially quantitatively. For both propionic and *n*-decanoic acids, addition of ∼0.5 equiv of $B(C_6F_5)_3$ to a CD_2Cl_2 solution of the acid at −30 °C resulted in spectra that exhibited resonances of free and coordinated acid

(^{1}H, ^{13}C), but no resonances of free borane (^{19}F, ^{11}B). On the other hand, similar experiments using 1:1 ratios of $B(C_6F_5)_3$ and carboxylic acid resulted in NMR spectra (^{1}H, ^{19}F, ^{11}B) exhibiting only resonances of the adduct, and experiments using a 2:1 ratio of $B(C_6F_5)_3$ and carboxylic acid resulted in NMR spectra (^{1}H, ^{19}F, ^{11}B) exhibiting resonances of free borane and adduct, but not of free carboxylic acid. Although all spectra where resonances of adduct and a reactant were observed were integrated, the results were not always useful. As indicated above, the fact that very small amounts of reactants were being measured meant that the nominal ratios of reactants were not always achieved. In addition resonances were in some cases quite broad and difficult to integrate accurately.

In no case did addition of excess carboxylic acid or $B(C_6F_5)_3$ result in perturbations, which may be interpreted in terms of significant formation of other products, although evidence for exchange processes was observed in some cases. For instance, the ^{1}H NMR spectrum of the solution containing $B(C_6F_5)_3$ and propionic acid in a 0.75:1 ratio exhibited coalescence of the pairs of methyl and methylene resonances of the free and coordinated acid, while several of the ^{13}C and ^{19}F NMR spectra discussed above exhibited significant line broadening. There presumably exists exchange between coordinated acid and both the monomer and the dimer of the free acid, and the equilibria could in principle also involve hydrogen-bonded dimeric adducts such as **C**, although the formation of **C** perhaps seems unlikely for steric reasons.



C

Broadening of ^{19}F resonances may also arise from hindered rotation about the B−C_6F_5 bonds in some species and perhaps also from quadrupolar effects of the ^{10}B and ^{11}B. We find, for instance, that the ^{19}F resonances of $B(C_6F_5)_3$ are considerably sharper at −20 °C than at 20 °C, an observation that cannot be attributed to hindered rotation. Thus the processes responsible for line broadening in many of the NMR spectra are complicated and were not studied further.

In addition to the above observations, the behavior of the OH resonances suggests that the acidic protons are at all ratios undergoing rapid exchange of some kind. As shown in Figures 2 and 7, addition of ∼0.5 equiv of $B(C_6F_5)_3$ to a solution of a carboxylic acid results in distinct broadening and shifting of the OH resonances from δ ∼12.7 to higher field. As the ratio of $B(C_6F_5)_3$ to carboxylic acid increases, there is a smooth shifting of the OH resonances until they level off as relatively narrow resonances at δ ∼9.5, some 4 ppm from the chemical shift of the free acids. The $-CH_2CO_2H$ resonances shift much less at $B(C_6F_5)_3$:carboxylic acid ratios >1:1, from δ 2.36 to δ 2.75 in the case of propionic acid and from δ 2.32 to δ 2.71 in the case of *n*-decanoic acid.

It is not clear just how to interpret these observations. It seems likely that hydrogen-bonded carboxylic acid dimers (δ ∼12.7) undergo proton exchange with the adducts, which may be monomeric (**A**) or dimeric (**C**). However, it is well established that the ^{1}H NMR spectra of free monomeric carboxylic acids exhibit higher field OH chemical shifts, in the range δ 5.5−8.5 depending on the acid and the solvent used,[14] and thus for simple acids strong hydrogen bonding results in relatively low-field chemical shifts. On this basis, the trends in δ(OH) discussed here would imply *decreased* levels of hydrogen bonding on formation of the adducts, inconsistent with the strongly hydrogen-bonded structure of **C** and providing indirect evidence for the 1:1 adducts being monomeric as in **A**. Indeed, the chemical shifts (δ ∼9.5) of the 1:1 adducts are very similar to those of free monomeric carboxylic acids (δ 5.5−8.5). We also note that autoionization of the 1:1 adducts is possible and may also result in exchange broadening of the OH resonance, but we have not attempted conductivity experiments that might shed light on this issue. The presence of traces of water would also cause complications, but our solvent purification procedures ensure that any adventitious water is a very minor species. Furthermore the reproducibility of our results is inconsistent with the presence of variable amounts of any unrecognized reagent that could affect the results.

Synthesis, Characterization, and Crystal Structure of $C_2H_5CO_2Me\cdot B(C_6F_5)_3$. Having established the existence and the NMR and IR spectroscopic properties of 1:1 adducts of carboxylic acids with $B(C_6F_5)_3$, we felt it desirable to learn more about their chemistry. For instance, we were surprised by our finding that mixtures of adducts $RCO_2H\cdot B(C_6F_5)_3$ and either free RCO_2H or free $B(C_6F_5)_3$ do not generally undergo exchange that is rapid on the NMR time scale, as do the above-mentioned 1:1 adducts of $B(C_6F_5)_3$ with the carbonyl Lewis bases benzaldehyde, acetophenone, and ethyl benzoate.[11] While most of our experiments with carboxylic acid adducts were carried out at lower temperatures, where exchange would in any case be slower, separate ^{1}H and ^{19}F resonances were also observed in room-temperature spectra. It thus seemed worthwhile to make a direct comparison with an ester complex, and we chose methyl propanoate rather than the previously studied ethyl benzoate[11] in order to minimize steric differences between acid (propionic) and ester adducts.

The readily isolable 1:1 adduct $C_2H_5CO_2Me\cdot B(C_6F_5)_3$ was prepared and characterized both spectroscopically and crystallographically (see above). The molecular structure is shown in Figure 9, and the adduct clearly assumes the expected mode of coordination via the carbonyl oxygen atom. Important bond lengths and angles are shown in Table 3, and all are very similar to those of the analogous ethyl benzoate adduct, although the B−O bond of the ethyl benzoate adduct is slightly longer (1.594(6)[11] vs 1.579(2) Å).

As with the 1:1 adducts of benzaldehyde, acetophenone, and ethyl benzoate, for which the order of basicity toward $B(C_6F_5)_3$ is benzaldehyde > acetophenone > ethyl benzoate,[11] there is also rapid exchange between free and $B(C_6F_5)_3$-coordinated methyl propionate. An approximately equimolar solution containing free methyl propionate and the 1:1 adduct in CD_2Cl_2 exhibited a single, averaged methoxy resonance at δ 3.94, quite distinct from the chemical shifts observed for the pure adduct (δ 4.18) and the free ester (δ 3.62). The nonetheless large change in the chemical shift of the methoxy resonance is consistent with electron withdrawal from the ester, although the methylene and methyl resonances shift much less, about 0.1 and 0 ppm, respectively. As mentioned above, what is particularly interesting is that ν(C═O) shifts from 1746 cm^{-1} in the free ester to 1601 cm^{-1} on coordination, a $\Delta\nu$(C═O) of 145 cm^{-1}, which contrasts markedly with the $\Delta\nu$(C═O) of 82, 83, and 49 cm^{-1} reported previously for the 1:1 adducts of benzaldehyde, aceto-

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phenone, and ethyl benzoate, respectively.[11] On this basis it would seem that methyl propionate coordinates much more strongly to $B(C_6F_5)_3$ than does for instance ethyl benzoate, consistent with the relative B−O bond lengths mentioned above.

Interestingly, in competition experiments involving mixtures of $C_2H_5CO_2Me{\cdot}B(C_6F_5)_3$ and propionic acid, the latter completely displaced the coordinated ester to form the 1:1 complex $C_2H_5CO_2H{\cdot}B(C_6F_5)_3$. This result suggests that the carboxylic acid is a better Lewis base with respect to $B(C_6F_5)_3$, at least, than is the corresponding methyl ester, and is consistent with the greater propensity to dissociation and exchange in the case of the 1:1 ester adduct than with the corresponding propionic acid adduct. Interestingly, since methyl propionate has a significantly higher gas phase proton affinity than does propionic acid,[15] one might anticipate that the acid would be a *poorer* Lewis base. However previous work has shown that steric factors play a major role in determining stabilities of adducts of $B(C_6F_5)_3$,[11] and it seems likely that a decreased steric contribution is an important factor enhancing the stabilities of $B(C_6F_5)_3$ adducts of carboxylic acids.

Formation of stable 1:1 adducts of carboxylic acids, as **A** of Scheme 1, appears to be without precedent, and it is very interesting that the adducts behave as strong acids. Although similar carboxylic acid adducts of, for example, BF_3 are known, they have been little studied because of their corrosive nature,[16] and hence study of carboxylic adducts of $B(C_6F_5)_3$ should shed considerable light on the chemistry of such species.

Role(s) of Carboxylic Acid Adducts in Carbocationic Polymerization Processes. As is clear, the electron-withdrawing power of the highly electrophilic $B(C_6F_5)_3$ increases the Brønsted acidity of coordinated carboxylic acids sufficiently that they are able to protonate isobutene and thereby initiate its carbocationic polymerization. However, although only the 1:1 adducts are observed here, initiation of isobutene polymerization proceeds best when the $B(C_6F_5)_3$:carboxylic acid ratio is 2:1.[6a,d] We interpret this apparent incongruity by positing that the 1:1 adduct is sufficiently acidic to protonate IB and that the anion formed then coordinates a second $B(C_6F_5)_3$ to form the much more sterically hindered and more weakly coordinating 2:1 anionic complex. Certainly the 2:1 anions are capable of existing,[6e] and molecular modeling[6a,f] suggests that the oxygen atoms in the 2:1 anions are sufficiently sterically shielded by aliphatic and $B(C_6F_5)_3$ groups[6a,f] that the anions can indeed behave as weakly coordinating anions.

Summary. Carboxylic acids react with $B(C_6F_5)_3$ in CH_2Cl_2 to form 1:1 adducts, which have been characterized by room-temperature IR and low-temperature (−30 °C) ^1H, ^{19}F, ^{13}C, and ^{11}B NMR spectroscopy. Coordination appears to occur via the carbonyl oxygen atoms, and exchange between an adduct and its components is generally sufficiently slow that ^1H, ^{19}F, ^{13}C, and ^{11}B resonances of the adduct are readily distinguished from the ^1H and ^{13}C resonances of the free corresponding acid or the ^{19}F and ^{11}B resonances of free $B(C_6F_5)_3$. The electron-withdrawing power of the highly electrophilic $B(C_6F_5)_3$ increases the Brønsted acidity of the coordinated acids sufficiently that they induce slow, partial cleavage of $B-C_6F_5$ bonds, and with benzoic acid the compound $[(\mu\text{-}C_6H_5CO_2)(\mu\text{-}OH)\{B(C_6F_5)_2\}_2]$ has been isolated and characterized crystallographically. Because of $B-C_6F_5$ cleavage, crystallographically useful crystals of a 1:1 adduct of a carboxylic acid have not been obtained. However, $C_2H_5CO_2Me{\cdot}B(C_6F_5)_3$, the 1:1 adduct of methyl propionate, has for purposes of comparison been prepared and characterized spectroscopically and crystallographically. In this case coordination occurs unequivocally via the carbonyl oxygen atom.

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Supporting Information Available: Crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and torsion angles for the compounds $[(\mu\text{-}C_6H_5CO_2)(\mu\text{-}OH)\{B(C_6F_5)_2\}_2]$ and $C_2H_5CO_2Me{\cdot}B(C_6F_5)_3$ are available free of charge via the Internet at http://pubs.acs.org.

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