Syntheses, characterization, and crystal structures of the tetramethylammonium salts of the novel weakly coordinating anions $[MeCO_2\{B(C_6F_5)_3\}]^-$ and $[MeCO_2\{B(C_6F_5)_3\}_2]^-$ [1]

Simona Mitu and Michael C. Baird

Abstract: The novel compounds $[Me_4N][MeCO_2\{B(C_6F_5)_3\}]$ and $[Me_4N][MeCO_2\{B(C_6F_5)_3\}_2]$ are prepared and characterized spectroscopically and crystallographically. The compounds are salts of the unisolable acids $MeCO_2H{\cdot}B(C_6F_5)_3$ and $MeCO_2H{\cdot}2B(C_6F_5)_3$, respectively, which are sufficiently strong that they can protonate isobutene and initiate its carbocationic polymerization. The 1:1 adduct contains a conventional, monodentate acetate ion coordinated to the $B(C_6F_5)_3$, while the 2:1 adduct contains a bridging acetate ligand.

Key words: weakly coordinating anions, carbocationic polymerization, isobutene, polyisobutene.

Résumé : On a préparé les nouveaux composés $[Me_4N][MeCO_2\{B(C_6F_5)_3\}]$ et $[Me_4N][MeCO_2\{B(C_6F_5)_3\}_2]$ et on les a caractérisés sur des bases spectroscopiques et cristallographiques. Les composés sont respectivement des acides $MeCO_2H{\cdot}B(C_6F_5)_3$ et $MeCO_2H{\cdot}2B(C_6F_5)_3$ qui ne peuvent pas être isolés, mais qui sont suffisamment forts pour protoner l'isobutène et initier sa polymérisation carbocationique. L'adduit 1 : 1 contient un ion acétate monodentate conventionnel qui est lié par coordination au $B(C_6F_5)_3$ alors que l'adduit 2 : 1 comporte un ligand acétate qui agit comme pont.

Mots clés : anions faiblement coordinés, polymérisation carbocationique, isobutène, polyisobutène.

[Traduit par la Rédaction]

Recent years have seen extraordinary developments in the once esoteric field of "weakly coordinating anions" (1). For present purposes, weakly coordinating anions may be defined loosely, if narrowly, as anions that, in solution, bind sufficiently weakly to cationic species such as H^+, carbocations, or metal ions that they are readily displaced by such normally poor electron pair donors as unsaturated hydrocarbons (1). Of great relevance here are the clearly similar, important properties of weakly coordinating anions in the complementary fields of the coordination polymerization of olefins such as ethylene and 1-alkenes (2) and of the carbocationic polymerization of, e.g., the more sterically hindered, electron-rich isobutene (3). As well-known examples of coordination polymerization catalysis, active catalysts are often generated from neutral zirconocene precursors, as in Scheme 1 (2).

Since monomer access to the active metal site of $[Cp'_2ZrMe]^+$ may be effectively blocked if the counteranion X^- binds too strongly to the metal, it is clearly important that X^- be an exceedingly poor ligand if olefin coordination and subsequent polymerization are to occur (Scheme 2).

In a similar vein, initiation of carbocationic polymerization of an olefin such as isobutene involves interaction of a molecule of monomer with, e.g., a strong acid, as in Scheme 3.

The carbocationic center so formed is stabilized by solvent and (or) counteranion X^-, and the latter must be a very poor Lewis base, otherwise the ions will combine to give the neutral compound Me_3CX. Chain propagation involves displacement of X^- by monomer and repeated additions of alkene molecules to the carbocationic center, which migrates well away from the site of initial attack (Scheme 4).

Weakly coordinating counteranions result in higher molecular weights (3*d*, 3*e*), and thus, in chemistry reminiscent of coordination polymerization, the C=C bond must be the most nucleophilic species in the system. Indeed, many cationic transition metal complexes function as both coordination catalysts and carbocationic initiators (3*f*, 4).

Much attention has been paid to the development of catalysts utilizing the chemistry of Scheme 1 (2, 5–8), and many new weakly coordinating anions X^- have been designed on the premise that delocalization of negative charge over as many atoms as possible in a large anion should be of advantage (5–8). Thus, there have been reported several very bulky anions in which the perfluorophenyl groups of $[BMe(C_6F_5)_3]^-$ have been substituted by more complex perfluoroaryl groups (5*g*–5*p*). Alternative, synthetically less

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Dedicated to Dr. Arthur Carty, an excellent scientist, a visionary, a bon vivant, and a very generous friend.

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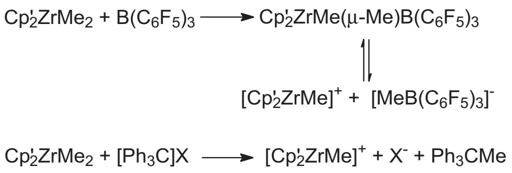
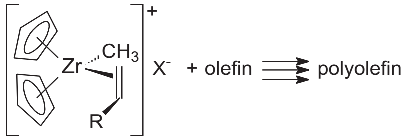
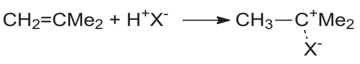
Scheme 1. Cp′ = substituted cyclopentadienyl, X^- = weakly coordinating anion.



Scheme 2. R = H, alkyl.

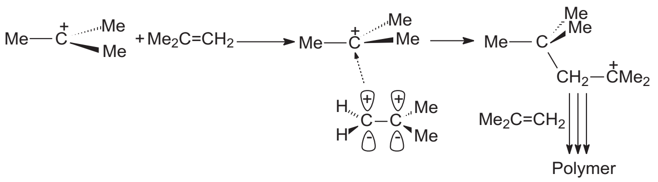


Scheme 3.



$$CH_2{=}CMe_2 + H^+X^- \longrightarrow CH_3{-}\overset{}{\underset{X^-}{C^+}}Me_2$$

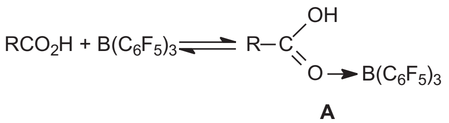
Scheme 4.



challenging procedures involve interaction of $B(C_6F_5)_3$ with various anions Y^- (Y^- = e.g., OH^- (6), CN^- (*5f*, *7a*), N_3^- (*7b*), OR^- (*6b*–*6d*, *6j*), SR^- (*6b*–*6d*), imidazolate (*7c*)) to form complex anions of the types $[YB(C_6F_5)_3]^-$ and $[(\mu\text{-}Y)\{B(C_6F_5)_3\}_2]^-$. In addition, we have recently reported utilization of $[Me_3CH_2B(C_6F_5)_3]^-$ in which the sterically demanding neopentyl group renders the borate anion much less weakly coordinating than is the above-mentioned methyl analogue, $[BMe(C_6F_5)_3]^-$ (8).

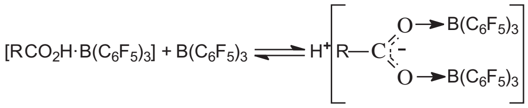
Complementing aspects of the above-mentioned research, we have reported the synthesis and utilization for isobutene polymerization of strong acids of the types $[ROH\{B(C_6F_5)_3\}_{1,2}]$ and $[RCO_2H\{B(C_6F_5)_3\}_{1,2}]$ (R = alkyl, aryl) (9, 10). Carboxylic acids, RCO_2H, do not by themselves initiate isobutene polymerization but are apparently activated via formation of adducts with $B(C_6F_5)_3$, as in eqs. [1] and [2].

[1]



A

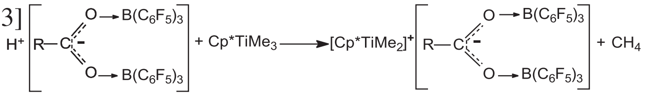
[2]



B

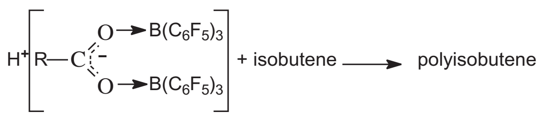
These can then react with metallocene-type compounds, as in eq. [3], generating the cationic $[Cp^*TiMe_2]^+$, a known initiator for both coordination and carbocationic olefin polymerization reactions (10*a*), or they can be used directly to initiate the carbocationic polymerization of, e.g., isobutene and similarly polymerizable olefins (eq. [4]) (10*b*–10*d*).

[3]



C

[4]



The species formed when a carboxylic acid is combined with 2 equiv. of the borane is thus a novel type of Brønsted acid, sufficiently strong to protonate isobutene; presumably its conjugate base, $[RCO_2\{B(C_6F_5)_3\}_2]^-$, is stabilized by extensive delocalization of the negative charge. However, to this point the nature of the species in solution had been inferred only from the chemistry observed, and we have possessed only spectroscopic information concerning the structures of the putative products of eqs. [1] and [2].

Complicating our attempts to investigate spectroscopically the nature of the species in solution, we have found that the 1:1 and 2:1 adducts **A** and **B** are sufficiently acidic that cleavage of the B—C_6F_5 bonds occurs readily above about –30 °C to give pentafluorobenzene. We wished, however, to determine unequivocally the nature of the borane–carboxylate species in solution, and we have now accomplished this by isolating and characterizing salts of the conjugate bases of the products of eqs. [1] and [2]. Although the best carbocationic polymerization initiators found previously have involved long-chain carboxylic acids (10), we decided that we might have better success obtaining crystalline materials if we were to use short-chain carboxylic acids, and we have now accomplished the successful syntheses and characterization of the 1:1 and 2:1 acetato compounds $[Me_4N][MeCO_2\{B(C_6F_5)_3\}]$ and $[Me_4N][MeCO_2\{B(C_6F_5)_3\}_2]$. Crystal structures of both tetramethylammonium salts confirm their structures. A subsequent paper will consider the nature of the conjugate acids of these types of anions and their roles in initiating carbocationic polymerization of isobutene.

We note reports elsewhere of isobutene polymerizations being effected in the presence of other dinuclear counteranions (4*g*, 11), and it seems clear that counteranions, which are weakly coordinating because of combinations of steric factors and extensive delocalization of charge, do indeed play a role similar to those mentioned above for coordination polymerization catalysts.

Experimental

Most synthetic procedures, unless otherwise noted, were carried out under an atmosphere of nitrogen or argon purified by passing through a column of BASF catalyst heated to 140 °C and a column of 5 Å molecular sieves. Manipulation of air-sensitive materials employed standard Schlenk line techniques and an Mbraun Labmaster glovebox. Solvents were dried by passing them through activated alumina col-

Table 1. Crystallographic data for $[Me_4N][MeCO_2\{B(C_6F_5)_3\}]$ and $[Me_4N][MeCO_2\{B(C_6F_5)_3\}_2]$.

	$[Me_4N][MeCO_2\{B(C_6F_5)_3\}]$	$[Me_4N][MeCO_2\{B(C_6F_5)_3\}_2]$
Empirical formula	$C_{25}H_{17}BCl_{2}F_{15}NO_2$ $(C_{24}H_{15}BF_{15}NO_2{\cdot}CH_2Cl_2)$	$C_{44.72}H_{20.43}B_2Cl_{5.43}F_{30}NO_2$ $([N(CH_3)_4]\{[(C_6F_5)_3B]_2(OOCCH_3)\}{\cdot}2.72CH_2Cl_2)$
Formula weight	730.11	1 387.99
Temperature (K)	180(2)	150(2)
Wavelength (Å)	0.710 73	0.710 73
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\overline{1}$
Unit cell dimensions		
a (Å)	9.659(2)	11.682(2)
b (Å)	14.080(3)	15.629(3)
c (Å)	21.244(5)	17.363(3)
α (°)	90	100.132(3)
β (°)	90.137(4)	108.095(3)
γ (°)	90	108.198(3)
Volume ($Å^3$)	2 889.1(12)	2 728.7(8)
Z	4	2
Density (calcd.) (Mg/m^3)	1.679	1.689
Absorption coefficient (mm^{-1})	0.349	0.429
$F(000)$	1 456	1 368
Crystal size (mm^3)	0.3 × 0.3 × 0.2	0.4 × 0.4 × 0.3
θ Range for data collection (°)	1.74–28.24	1.44–28.30
Index ranges	$-12 \le h \le 12$, $-17 \le k \le 17$, $-28 \le l \le 27$	$-14 \le h \le 14$, $-20 \le k \le 19$, $-22 \le l \le 21$
Reflections collected	20 046	19 369
Independent reflections	6 686 [R(int) = 0.033 1]	12 259 (R(int) = 0.016 9]
Completeness to θ = 25.00° (%)	100.0	99.5
Absorption correction	Empirical (Bruker SADABS)	Empirical (Bruker SADABS)
Max. and min. transmission	1.000 0 and 0.744 7	1.000 0 and 0.912 1
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6 686 / 0 / 474	12 259 / 667 / 871
Goodness-of-fit on F^2	0.844	1.103
Final R indices $I > 2\sigma(I)$	R_1 = 0.038 1, wR_2 = 0.077 4	R_1 = 0.062 6, wR_2 = 0.194 9
R indices (all data)	R_1 = 0.083 9, wR_2 = 0.087 4	R_1 = 0.086 5, wR_2 = 0.208 4
Largest diff. peak and hole (e $Å^{-3}$)	0.233 and –0.307	1.246 and –0.994

umns (Innovative Technology). All chemicals were purchased from Aldrich and were purified as appropriate before use. The compound $B(C_6F_5)_3$ was prepared as described in the literature (12).

The ^1H, ^{11}B, and ^{19}F NMR spectra were run on an Avance 400 NMR spectrometer, the residual proton resonances of the deuterated solvents serving as internal references. Mass spectra were obtained on a Quatro Fisons Pro Quadrupole mass spectrometer in EI mode with CH_2Cl_2 as solvent. Canadian Microanalytical Services of Delta, British Columbia, performed elemental analyses. X-ray crystallographic structure determinations were carried out using a Siemens P4 diffractometer with a Bruker SMART CCD 1000 detector and graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) controlled with a Crysostream controller 700. Typically a crystal was mounted on a glass fibre with epoxy glue. No significant decay was observed during data collection, and the data were processed on a Pentium PC using the Bruker AXS Windows NT SHELXTL software package (version 5.10) (13*a*). Neutral atom scattering factors were taken from Cromer and Waber (13*b*). The raw intensity data were converted to structure amplitudes and their esds using the program SAINT-plus, which corrects for *L*p and decay. Absorption corrections were applied using the program SADABS. The crystals are monoclinic space group $P2_1/c$ for $[Me_4N][MeCO_2\{B(C_6F_5)_3\}]$ and triclinic space group $P\overline{1}$ for $[Me_4N][MeCO_2\{B(C_6F_5)_3\}_2]$ based on the systematic absences, *E* statistics, and successful refinement of the structure. The structure was solved by direct methods. Full-matrix least-square refinements minimizing the function $\sum w(F_o^2 - F_c^2)^2$ were applied to the compound. For the structure of $[Me_4N][MeCO_2\{B(C_6F_5)_3\}]$, all non-hydrogen atoms in the structure were refined anisotropically, and only the hydrogen atoms of the solvent molecule were calculated; all the other hydrogen atoms were located directly from the difference Fourier map. For the structure of $[Me_4N][MeCO_2\{B(C_6F_5)_3\}_2]$, the solvent molecules ($2.72CH_2Cl_2$) in the crystal are severely disordered, and the SHELXL commands SIMU, DFIX, SAME, and PART were thus used to refine the structure. All non-hydrogen atoms in the structure (**II**) (except C47, C49, Cl13, and Cl14) were refined anisotropically. All hydrogen atoms were calculated,

Table 2. Important bond lengths and bond angles for $[Me_4N][MeCO_2\{B(C_6F_5)_3\}]$ and $[Me_4N][MeCO_2\{B(C_6F_5)_3\}_2]$.

Compound	$[Me_4N][MeCO_2\{B(C_6F_5)_3\}]$	$[Me_4N][MeCO_2\{B(C_6F_5)_3\}_2]$
Bond lengths (Å)		
C(1)—C(2)	1.499(3)	1.496(4)
C(2)—O(1)	1.324(2)	1.279(4)
C(2)—O(2)	1.217(2)	1.260(4)
B(1)—O(1)	1.514(2)	1.543(4)
B(2)—O(2)	—	1.568(4)
B(1)—C(3)	1.654(3)	1.649(5)
B(1)—C(9)	1.651(3)	1.650(5)
B(1)—C(15)	1.644(3)	1.628(4)
B(2)—C(21)	—	1.644(4)
B(2)—C(27)	—	1.636(5)
B(2)—C(33)	—	1.645(5)
Bond angles (°)		
C(1)-C(2)-O(1)	112.84(18)	114.8(3)
C(1)-C(2)-O(2)	123.32(19)	124.5(3)
O(1)-C(2)-O(2)	123.84(17)	120.7(3)
C(2)-O(1)-B(1)	119.74(14)	128.0(2)
C(2)-O(2)-B(2)	—	127.8(2)
O(1)-B(1)-C(15)	112.20(14)	108.8(2)
O(1)-B(1)-C(9)	105.93(14)	103.3(2)
O(1)-B(1)-C(3)	106.33(14)	109.9(2)
O(2)-B(2)-C(27)	—	105.9(2)
O(2)-B(2)-C(33)	—	103.7(2)
O(2)-B(2)-C(21)	—	112.1(3)
C(15)-B(1)-C(9)	116.35(15)	111.3(2)
C(15)-B(1)-C(3)	104.42(14)	116.7(2)
C(9)-B(1)-C(3)	111.28(15)	105.9(2)
C(21)-B(2)-C(27)	—	116.3(2)
C(21)-B(2)-C(33)	—	104.0(2)
C(27)-B(2)-C(33)	—	114.3(3)

and their contributions were included in the structure factor calculations with isotropic thermal parameters 1.2 times that of the attached carbon atoms (1.5 times for methyl hydrogens). Crystallographic data for the two compounds studied are summarized in Table 1, with selected bond distances and angles in Table 2. Molecular structures are shown in Figs. 1 and 2, and complete crystallographic data are given in the supporting information.[3]

Preparation of $[Me_4N][MeCO_2\{B(C_6F_5)_3\}]$

$[Me_4N][MeCO_2]$ was prepared by neutralizing tetramethylammonium hydroxide (6 mL, 25 wt% aqueous solution) with glacial acetic acid (1.43 mL, 0.0250 mol) (14). The solution was evaporated to dryness, and the solid residue was recrystallized from acetone and dried under reduced pressure for 12 h at 150 °C to give 2.1 g of $[Me_4N][MeCO_2]$ (95% yield). IR (Fluorolube mull, cm^{-1}) ν(CO): 1681, 1491. ^1H NMR (CD_2Cl_2) δ: 3.43 (s, 12H, MeN), 1.80 (s, 3H, MeC). To prepare $[Me_4N][MeCO_2\{B(C_6F_5)_3\}]$, a mixture of $B(C_6F_5)_3$ (250 mg, 0.49 mmol) and $[Me_4N][MeCO_2]$ (64.9 mg, 0.49 mmol) in dry CH_2Cl_2 (20 mL) was stirred at room temperature for 1 h, after which the solvent was removed under reduced pressure. The resulting white solid was recrystallized from a mixture of CH_2Cl_2 (5 mL) and hexanes (15 mL), filtered off, washed with hexanes, and dried to give 253 mg (80% yield) of product. IR (Fluorolube mull, cm^{-1}) ν(CO): 1682, 1491. ^1H NMR (CD_2Cl_2) δ: 3.13 (s, 12H, MeN), 1.94 (s, 3H, MeC). ^{11}B NMR (CD_2Cl_2) δ: –5.1 (sharp). ^{19}F NMR (CD_2Cl_2) δ: –135.9 (*o*-F), –163.6 (*p*-F), –168.2 (*m*-F). HR-MS (EI) calcd. for $[(CH_3)_4N]$: 74.1460; found: 74.0784. HR-MS (EI) calcd. for $[MeCO_2\{B(C_6F_5)_3\}]$: 571.0296; found: 571.0672. Anal. calcd. for $C_{24}H_{15}BF_{15}O_2\cdot CH_2Cl_2$: C 41.13, H 2.35, N 1.92; found: C 41.58, H 2.38, N 1.88. Crystallographic quality crystals were grown by layering a solution of $[Me_4N][MeCO_2\{B(C_6F_5)_3\}]$ in CH_2Cl_2 with hexanes.

Preparation of $[Me_4N][MeCO_2\{B(C_6F_5)_3\}_2]$

A mixture of $B(C_6F_5)_3$ (500 mg, 0.98 mmol) and $[Me_4N][MeCO_2]$ (64.9 mg, 0.49 mmol) in CH_2Cl_2 (30 mL)

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[3] Supplementary data for this article are available on the journal Web site (http://canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 4085. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 275372 and 275373 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

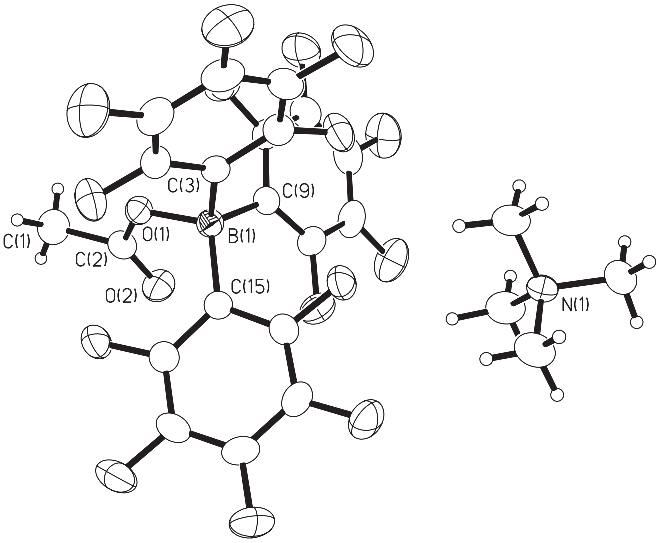


Fig. 1. X-ray structure of $[Me_4N][MeCO_2\{B(C_6F_5)_3\}]$.

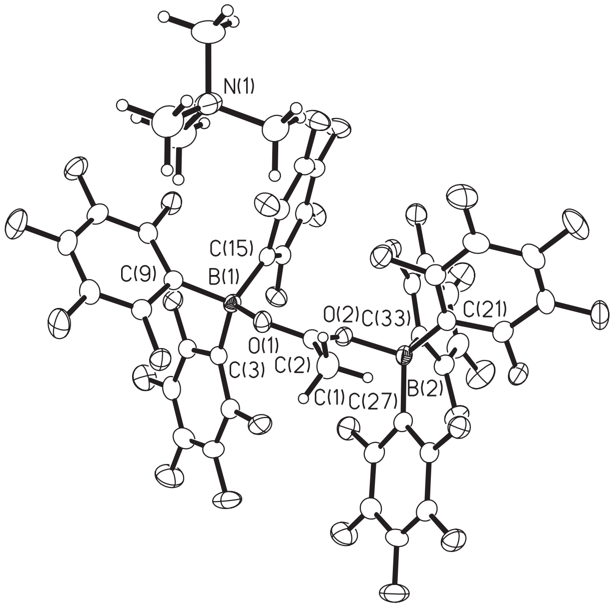


Fig. 2. X-ray structure of $[Me_4N][MeCO_2\{B(C_6F_5)_3\}_2]$.

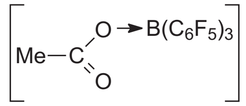
was stirred at room temperature for 1 h, after which the solvent was removed under reduced pressure. The resulting white solid was recrystallized from a mixture of CH_2Cl_2 (5 mL) and hexanes (15 mL), filtered off, washed with hexanes, and dried to give 398 mg (70% yield) of product. IR (Fluorolube mull, cm^{-1}) ν(CO): 1566, 1417. ^1H NMR (CD_2Cl_2) δ: 3.22 (s, 12H, MeN), 2.19 (s, 3H, MeC). ^{11}B NMR (CD_2Cl_2) δ: –1.6 (broad). ^{19}F NMR (CD_2Cl_2) δ: –135.6 (*o*-F), –161.0 (*p*-F), –167.1 (*m*-F). HR-MS (EI) calcd. for $[(CH_3)_4N]$: 74.1460; found: 74.0832. HR-MS (EI) calcd. for $[MeCO_2\{B(C_6F_5)_3\}_2]$: 1083.0147; found: 1083.0642. Anal. calcd. for $C_{42}H_{15}B_2F_{30}O_2$: C 43.59, H 1.31, N 1.21; found: C 43.28, H 1.26, N 1.52. Crystallographic quality crystals were grown by layering a solution of $[Me_4N][MeCO_2\{B(C_6F_5)_3\}_2]$ in CH_2Cl_2 with hexanes.

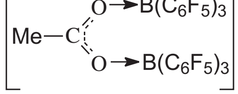
Results and discussion

The combination of carboxylic acids and $B(C_6F_5)_3$, especially in a 2:1 $B(C_6F_5)_3$ – carboxylic acid ratio, results in an acid system sufficiently strong to protonate isobutene (IB) and to initiate its carbocationic polymerization (10). Carboxylic acids themselves are too weak to effect this chemistry, of course, and furthermore carboxylate anions are expected to bind very effectively to the carbocation intermediates. However, the inductive effects of carboxylic acid coordination to the strongly electrophilic borane in a species such as **B** would very likely result in an acid much stronger than the free carboxylic acid itself (10), as has been observed elsewhere with other potentially acidic Lewis base donors (6*j*, 15), and it seemed very likely that the reactions described in eqs. [1] and [2] would pertain. The purpose of this research was to prepare, characterize, and determine the structures of salts of the putative counteranions of species **A** and **B**.

Syntheses of $[Me_4N][MeCO_2\{B(C_6F_5)_3\}]$ and $[Me_4N][MeCO_2\{B(C_6F_5)_3\}_2]$

These two compounds were synthesized by reacting $[Me_4N][MeCO_2]$ with 1 and 2 molar equiv. of $B(C_6F_5)_3$, respectively. Both compounds were characterized fully by elemental analyses and IR and NMR spectroscopy; the crystals of the 1:1 adduct contained one molecule of CH_2Cl_2, as shown by the elemental analyses and X-ray crystallography. The IR spectra are illustrated in Figs. 3 and 4, and we note especially that the observed values of ν(CO) of 1682 and 1491 cm^{-1} for the 1:1 adduct and of 1566 and 1417 cm^{-1} for the 2:1 adduct are consistent with the literature for monodentate and bridging acetato ligands as in **D** and **E**, respectively (16).


D


E

The positions of the symmetric stretches are in both cases uncertain because absorptions of the $B(C_6F_5)_3$ (indicated in the spectra by **B**) and the $[Me_4N]^+$ ion also appear in the region 1300–1800 cm^{-1}.

The ^1H, ^{19}F, and ^{11}B NMR spectra are shown in Figs. 5, 6, and 7, respectively, where they are compared with the spectra of $[Me_4N][MeCO_2]$ (^1H) and $B(C_6F_5)_3$ (^{19}F, ^{11}B). The electron-withdrawing power of the borane is evident in the acetate methyl ^1H resonances, and the changes in the ^{19}F chemical shifts on going from free to coordinated $B(C_6F_5)_3$ are characteristic (5–10). The ^{11}B chemical shifts of the adducts are similar to those of other adducts with O-donors, and the observed narrowing of the resonances is consistent with tetrahedral structures (6*h*, 17*b*–17*d*), although it is not at all clear why the 2:1 complex has a much broader resonance than does the 1:1 complex.

Crystal structures of $[Me_4N][MeCO_2\{B(C_6F_5)_3\}]$ and $[Me_4N][MeCO_2\{B(C_6F_5)_3\}_2]$

Crystal structures were obtained for both compounds, with the 1:1 complex containing a molecule of CH_2Cl_2. Selected bond distances and angles are shown in Table 2, and

Fig. 3. IR spectrum (Fluorolube mull) of $[Me_4N]\{[MeCO_2][B(C_6F_5)_3]\}$: * identifies ν(CO); **B** identifies peaks assignable to $B(C_6F_5)_3$.

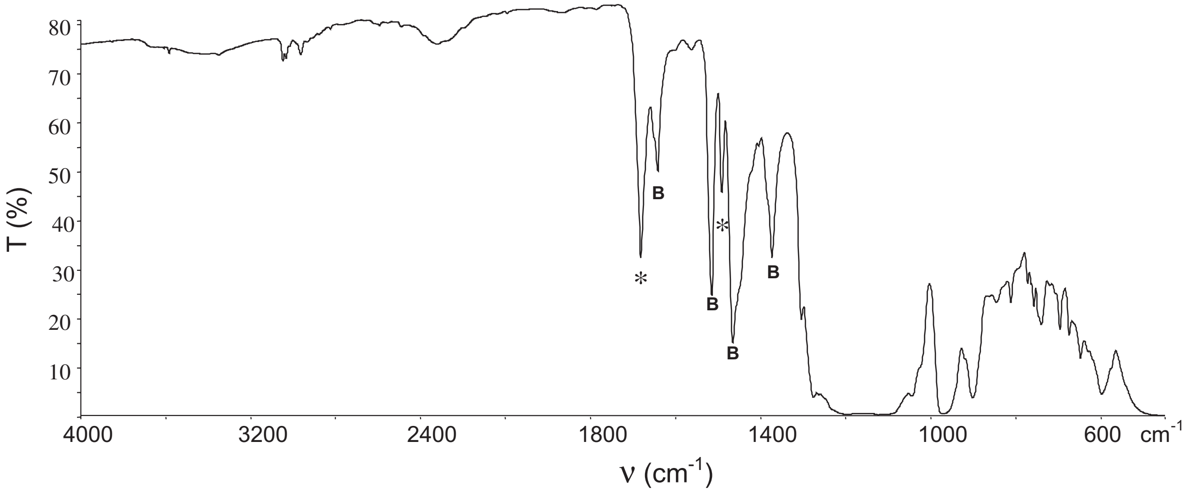


Fig. 4. IR spectrum (Fluorolube mull) of $[Me_4N]\{[MeCO_2][B(C_6F_5)_3]_2\}$: * identifies ν(CO); **B** identifies peaks assignable to $B(C_6F_5)_3$.

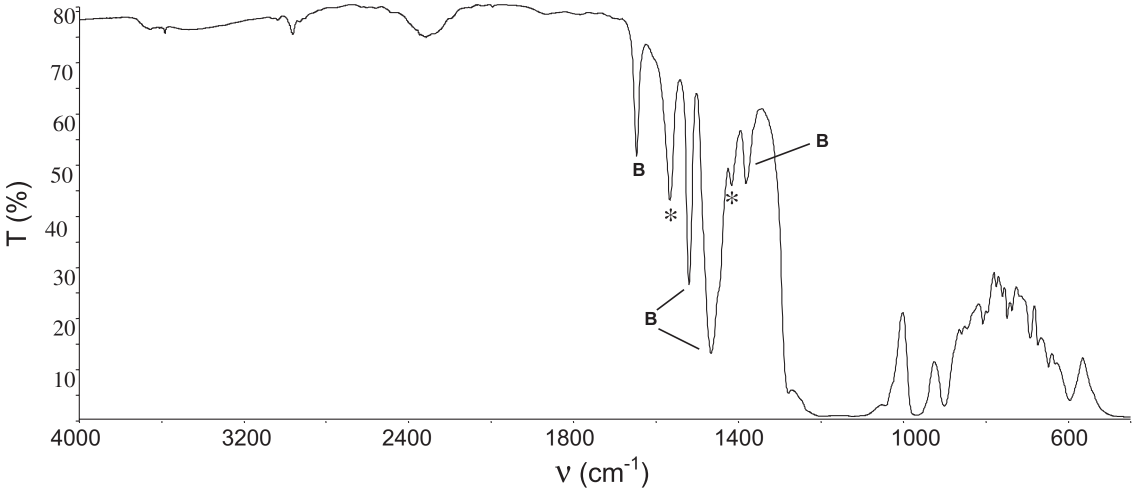
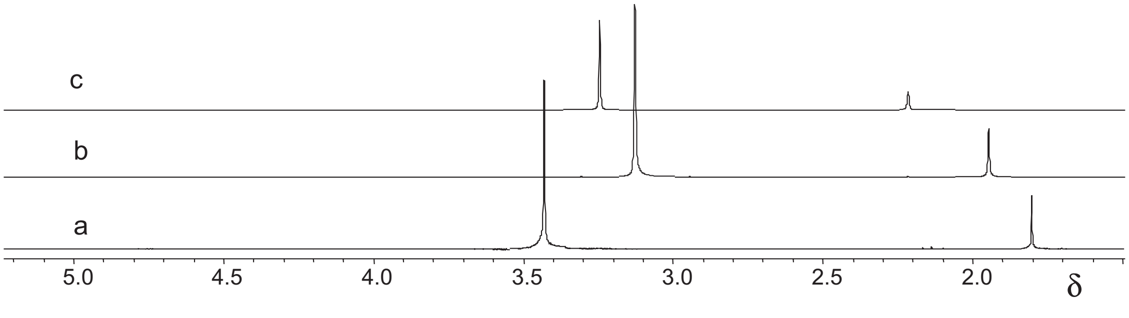


Fig. 5. ^1H NMR spectra of (*a*) $[Me_4N][MeCO_2]$, (*b*) $[Me_4N][MeCO_2\{B(C_6F_5)_3\}]$, and (*c*) $[Me_4N][MeCO_2\{B(C_6F_5)_3\}_2]$ (CD_2Cl_2).



molecular structures are shown in Figs. 1 and 2. As can be seen, the crystal structures are completely in accord with the modes of bonding suggested by **D** and **E**. Thus the carbon–oxygen bond lengths of the 1:1 adduct are 1.216(2) and 1.321(2) Å, as expected for a double and a single bond, respectively. On the other hand, the two carbon–oxygen distances of the 2:1 adduct are intermediate between these two values and are very similar to each other. Interestingly, the boron–oxygen distance in the 1:1 adduct is significantly shorter than that of the 2:1 adduct, consistent with the expected stronger B—O bond in the former. However, all three B—O distances fall in the range established for a variety of adducts of $B(C_6F_5)_3$ with a variety of other O-donors (6*h*, 6*j*, 17).

Possibly complementing the stronger donor–acceptor interaction in the 1:1 adduct, the average of the B—C_6F_5 bond lengths in this adduct is marginally longer than the average of the 2:1 adduct, although steric repulsions should be more

Fig. 6. ^{19}F NMR spectrum of (*a*) $B(C_6F_5)_3$, (*b*) $[Me_4N][MeCO_2\{B(C_6F_5)_3\}]$, and (*c*) $[Me_4N][MeCO_2\{B(C_6F_5)_3\}_2]$ in CD_2Cl_2.

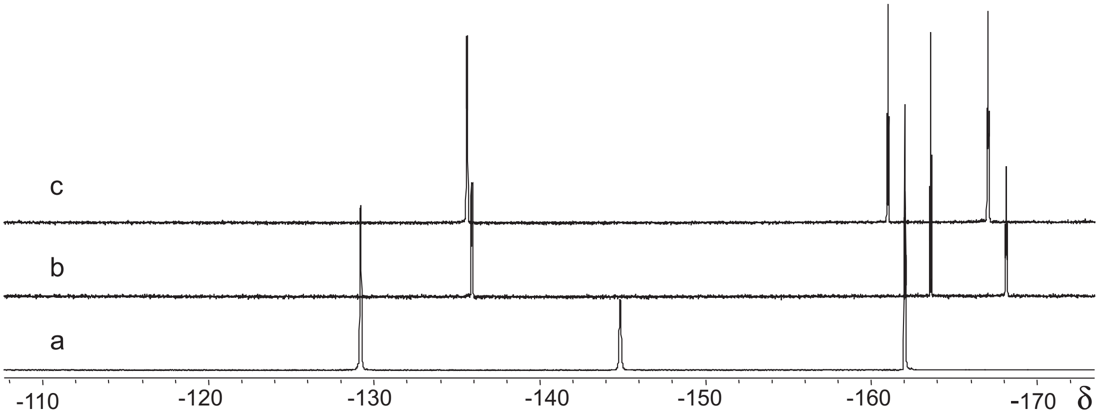
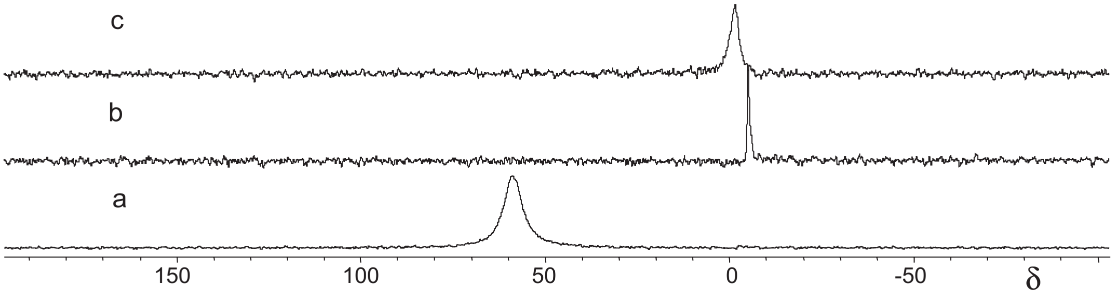


Fig. 7. ^{11}B NMR spectra of (*a*) $B(C_6F_5)_3$, (*b*) $[Me_4N][MeCO_2\{B(C_6F_5)_3\}]$, and (*c*) $[Me_4N][MeCO_2\{B(C_6F_5)_3\}_2]$ (CD_2Cl_2).



important in the latter. The acetate ions are essentially planar in both adducts, but the bond angles vary widely. Thus the O-C-O bond angle of the 1:1 adduct is significantly less than 120°, the two Me-C-O bond angles both being significantly greater. In contrast, the O-C-O bond angle of the 2:1 adduct is 120.7(3)°, while the two (chemically equivalent) Me-C-O bond angles vary widely. The O-B-C_6F_5 and C_6F_5-B-C_6F_5 bond angles vary considerably, but the latter variations seem to be normal (18).

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