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Article

Reactions of $(CF_3)_3BCO$ with Amines and Phosphines

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Reactions of tris(trifluoromethyl)borane carbonyl, $(CF_3)_3BCO$, with ammonia yielded either a mixture of $[NH_4][(CF_3)_3BC(O)NH_2]$, $[NH_4][(CF_3)_3BCN]$, and $[NH_4]_2[\{(CF_3)_3BC(O)\}_2NH]$ or neat $[NH_4]_2[\{(CF_3)_3BC(O)\}_2NH]$ depending on the reaction conditions. The salt $K[(CF_3)_3BC(O)NH_2]$ was obtained as the sole product from the reaction of NH_3 with $K[(CF_3)_3BC(O)F]$. A simple synthesis for cyanotris(trifluoromethyl)borates, $M[(CF_3)_3BCN]$, was developed by dehydration of $M[(CF_3)_3BC(O)NH_2]$ ($M = [NH_4]$, K) using phosgene. In addition, syntheses of the tris(trifluoromethyl)boron species $[(CF_3)_3BC(O)NH^nPr]^-$, $[(CF_3)_3BC(O)NMe_2]^-$, and $(CF_3)_3BC(O)NMe_3$, as well as of $(CF_3)_3BC(O)PMe_3$, were performed. All species were characterized by multinuclear NMR spectroscopy. As far as neat substances resulted, IR and Raman spectra were recorded and their thermal behaviors were studied by differential scanning calorimetry. The interpretation of reaction pathways, structures, and vibrational spectra are supported by DFT calculations. The solid-state structure of $K_2[\{(CF_3)_3BC(O)\}_2NH]\cdot 2MeCN$ was determined by single-crystal X-ray diffraction.

Introduction

Chemical and thermal stable borate anions are of growing interest because they are applied in many fields of chemistry, biology, and physics.[1−4] They can serve as ligands with tunable properties in transition metal chemistry, for example, $[(C_6F_5)_3BCN]^-$,[5] $[(CF_3)_3BCN]^-$,[6] $[B(CN)_4]^-$,[6−8] and $[CB_{11}F_{11}]^{2-}$,[9] or as weakly coordinating anions,[1,3,4,10] e.g., $[B(C_6F_5)_4]^-$,[3] $[B(CF_3)_4]^-$,[11] $[CHB_{11}Cl_{11}]^-$,[12] and $[CB_{11}F_{12}]^-$.[13]

Acidic solvolysis of one trifluoromethyl group of the tetrakis(trifluoromethyl)borate anion, $[B(CF_3)_4]^-$, in concentrated H_2SO_4 yields the unusual borane carbonyl, $(CF_3)_3BCO$, in 88% yield.[14,15] In a series of recent publications, $(CF_3)_3BCO$ was used as a versatile starting material for the synthesis of new borates and boranes with the $(CF_3)_3B$ fragment.[14,16−20] The borane carbonyl reacts with nucleophiles either under addition to the C atom of the carbonyl ligand

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or in a ligand-exchange reaction under loss of CO.[14] With hydrogen cyanide, $(CF_3)_3BCO$ reacts to $(CF_3)_3BNCH$, which is further deprotonated to the isocyanoborate anion $[(CF_3)_3BNC]^-$ according to (eq 1).[16]

$$(CF_3)_3BCO \xrightarrow[-80\ °C \rightarrow RT,\ CH_2Cl_2]{+HCN,\ -\ CO} (CF_3)_3BNCH \xrightarrow[-20\ °C \rightarrow RT,\ toluene]{+Li[N(SiMe_3)_2],\ -\ HN(SiMe_3)_2} Li[(CF_3)_3BNC] \quad (1)$$

This isocyanoborate anion quantitatively isomerizes to its cyano isomer $[(CF_3)_3BCN]^-$ at elevated temperatures (eq 2).[16]

$$K[(CF_3)_3BNC] \xrightarrow{\Delta} K[(CF_3)_3BCN] \quad (2)$$

Both anions are isoelectronic to the parent borane carbonyl $(CF_3)_3BCO$, and their use as ligands was demonstrated by the synthesis of the Rh(I) complexes $(PPh_3)_3RhCNB(CF_3)_3$ and $(PPh_3)_3RhNCB(CF_3)_3$.[21]

A different route to $[(CF_3)_3BCN]^-$ was found in the reaction of $[(CF_3)_3BC(O)\mathit{Hal}]^-$ (Hal = Cl, Br) with $K[N(SiMe_3)_2]$ which was also extented to its higher homologues $[(CF_3)_3BC\mathit{Pnic}]^-$ (Pnic = P, As) according to (eq 3).[18]

$$[(CF_3)_3BC(O)\mathit{Hal}]^- + K[\mathit{Pnic}(SiMe_3)_2] \xrightarrow[-20\ °C \rightarrow RT]{\mathit{Pnic}(SiMe_3)_3} [(CF_3)_3BC\mathit{Pnic}]^- + (Me_3Si)_2O + K\mathit{Hal} \quad (\mathit{Hal} = Cl, Br;\ \mathit{Pnic} = N, P, As) \quad (3)$$

In this contribution we report on (i) the synthesis of the carbamoyl complexes $[(CF_3)_3BC(O)NR^1R^2]^-$ (R^1 = H, Me, ^{n}Pr; R^2 = H, Me), $[\{(CF_3)_3BC(O)\}_2NH]^{2-}$ and $(CF_3)_3BC(O)\mathit{Pnic}Me_3$ (Pnic = N, P), (ii) the dehydration of $K[(CF_3)_3BC(O)NH_2]$ yielding $K[(CF_3)_3BCN]$, (iii) the solid-state structure of $K_2[\{(CF_3)_3BC(O)\}_2NH]\cdot 2MeCN$ determined by X-ray diffraction, and (iv) DFT calculations supporting the interpretation of reaction pathways and the assignments of the vibrational spectra.

The new borate anions may be used as ligands in organometallic chemistry.

Experimental Section

General Procedures and Reagents. 1. Apparatus. Volatile materials were manipulated in glass vacuum lines of known volume equipped with valves with PTFE stems (Young, London) and with a capacitance pressure gauge (Type 280E, Setra Instruments, Acton, MA). The reactions involving air-sensitive compounds were performed under a N_2 or Ar atmosphere using standard Schlenk line techniques. Solid materials were manipulated inside an inert atmosphere box (Braun, Munich, Germany) filled with argon, with a residual moisture content of less than 1 ppm. Reactions were performed either in round-bottom flasks equipped with valves with PTFE stems (Young, London) and fitted with PTFE-coated magnetic stirring bars or in 5 mm o.d. NMR tubes attached to rotational symmetric valves (Young, London).[22] Volatile compounds were stored in flame-sealed glass ampules under liquid nitrogen in a storage Dewar vessel. The ampules were opened and flame-sealed again by using an ampule key.[23]

2. Chemicals. $(CF_3)_3BCO$ was synthesized as described previously from $K[B(CF_3)_4]$.[14,15] Labeled $^{15}NH_3$ (isotopic enrichment: 99%) was obtained from Euriso-Top GmbH (Saarbrücken, Germany). All dry solvents were obtained from Aldrich and stored under dry N_2 or Ar in 1 L round-bottom flasks equipped with valves with PTFE stems (Young, London) and charged with molecular sieves (4 Å). All other chemicals were obtained from commercial sources and used without further purification.

3. Synthetic Reactions. 3.1. Reaction of $(CF_3)_3BCO$ with NH_3. A 250 mL round-bottom flask was charged at −196 °C with 3.56 g (14.5 mmol) of $(CF_3)_3BCO$ followed by 20 mL of dry liquid ammonia. The reaction vessel was placed into a cold bath kept at −90 °C. The clear, colorless reaction mixture was warmed to −30 °C within 3 h. Subsequently, the excess of NH_3 was removed under reduced pressure. The white product mixture was investigated by NMR spectroscopy in CD_3CN solution: 39% $[NH_4][(CF_3)_3BC(O)NH_2]$, 27% $[NH_4][(CF_3)_3BCN]$, 26% $[NH_4]_2[(CF_3)_3BCO_2]$, and 8% $[NH_4]_2[\{(CF_3)_3BC(O)\}_2NH]$.

3.2. Synthesis of $K[(CF_3)_3BCN]$ Using the Product Mixture of Reaction 3.1. The product mixture of 3.1. was dissolved in 100 mL of dry acetonitrile in a 250 mL round-bottom flask. Phosgene (60 mmol) and 9 mL of triethylamine were added in vacuo. Overnight the stirred reaction mixture was allowed to warm to room temperature. All volatiles were removed under reduced pressure. Water (20 mL) and 30 mL of dichloromethane were added to the residue. Subsequently, the mixture was treated with 2 mL of Et_3N and 1 mL of concentrated hydrochloric acid. The dichloromethane layer was separated, and the remaining aqueous solution was extracted twice with 25 mL of CH_2Cl_2. The combined colorless dichloromethane phases were dried with anhydrous $MgSO_4$ and filtered. KOH (2 g) was dissolved in 5 mL of water and added to the clear, colorless CH_2Cl_2 solution. The mixture was stirred vigorously for 15 min. Subsequently, the dichloromethane was removed under reduced pressure. After addition of 100 mL of diethyl ether, K_2CO_3 was added until the aqueous phase became greasy. The etheral phase was separated, and the greasy residue was extracted twice with 20 mL of Et_2O. The collected organic layers were dried over K_2CO_3 followed by filtration and removal of the solvent. Colorless pure $K[(CF_3)_3BCN]$ (2.34 g, 8.3 mmol, based on $(CF_3)_3BCO$: 57%) was obtained. Anal. Calcd for C_4BF_9KN: C, 16.98; N, 4.95. Found: C, 16.79; N, 4.97.

3.3. $K[(CF_3)_3BC(O)NH_2]$. Inside a drybox, 679 mg (2.2 mmol) of $K[(CF_3)_3BC(O)F]$ was weighed into a 50 mL round-bottom flask. In vacuo, 5 mL of dry liquid NH_3 was added. The reaction mixture was held at −80 °C, and then it was warmed to −10 °C overnight. The remaining liquid ammonia was removed under reduced pressure, and the colorless residue was dissolved in 30 mL of Et_2O. After addition of a few milliliters of a concentrated aqueous K_2CO_3 solution, the reaction mixture was stirred for 15 min. A small amount of solid K_2CO_3 was added, and then the etheral phase was decanted. The greasy residue was extracted with two portions of diethyl ether (20, 10 mL). The combined organic layers were dried with K_2CO_3 and subsequently filtered. All volatiles were removed under reduced pressure yielding 552 mg (1.8 mmol, 83%) of $K[(CF_3)_3BC(O)NH_2]$. Anal. Calcd for $C_4H_2BF_9KNO$: C, 15.96; H, 0.67; N, 4.65. Found: C, 16.14; H, 0.7; N, 4.64.

3.4. $K[(CF_3)_3BCN]$ by Dehydration of $K[(CF_3)_3BC(O)NH_2]$. The synthesis was performed analogous to reaction 3.2. $K[(CF_3)_3$-

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$BC(O)NH_2]$ (242 mg, 0.9 mmol) was dissolved in 10 mL of dry CH_3CN and 1 mL of Et_3N. At −196 °C, 4 mmol of phosgene was added. The workup was performed as described for reaction 3.2. Yield: 213 mg (0.8 mmol, 94%).

3.5. $K_2[\{(CF_3)_3BC(O)\}_2NH]$. A 100 mL round-bottom flask was charged at −196 °C with 1.18 g (4.8 mmol) of $(CF_3)_3BCO$. Subsequently, 50 mL of diethyl ether were added. The reaction mixture was warmed to −80 °C. A 250 mL round-bottom flask filled with 29 mmol of NH_3 was kept at −196 °C and connected to the other reaction vessel. The valves between the two flasks were opened, and subsequently, the ammonia was allowed to warm to room temperature and to diffuse into the reaction mixture. Under vigorous stirring, the reaction mixture was warmed to room temperature overnight. A clear, colorless two-phase system was obtained. The solvent and the excess of NH_3 were removed under reduced pressure, and pure colorless $[NH_4]_2[\{(CF_3)_3BC(O)\}_2NH]$ remained in the flask. Analogous to synthesis 3.3., $[NH_4]_2[\{(CF_3)_3BC(O)\}_2NH]$ is transformed in Et_2O into the corresponding potassium salt using aqueous solutions of KOH and K_2CO_3. Yield: 552 mg (1.8 mmol, 83%). Anal. Calcd for $C_8HB_2F_{18}K_2NO_2$: C, 16.43; H, 0.17; N, 2.39. Found: C, 16.52; H, < 0.2; N, 2.40.

3.6. $K[(CF_3)_3BC(O)^{15}NH_2]$ and $K_2[\{(CF_3)_3BC(O)\}_2{}^{15}NH]$. The isotopically labeled compounds were synthesized by the same procedures as described for the natural compounds.

3.7. $K[(CF_3)_3BC(O)NH^nPr]$. A NMR tube[22] was charged with 100 mg (0.33 mmol) of $K[(CF_3)_3BC(O)F]$. $^nPrNH_2$ (1.3 mmol) and 1 mL of CD_2Cl_2 were added in a vacuum at −196 °C. The reaction mixture was warmed to room temperature and shaken subsequently. After a small portion of solid K_2CO_3 was added, the NMR tube was shaken again. According to the NMR spectra, $K[(CF_3)_3BC(O)NH^nPr]$ was the only product.

3.8. $K[(CF_3)_3BC(O)NMe_2]$. $K[(CF_3)_3BC(O)F]$ (94 mg, 0.31 mmol) was transferred into a NMR tube,[22] and at −196 °C, 1 mL of CD_3CN was added in vacuo. Under a N_2 atmosphere, 0.5 mL of Me_2NSiMe_3 was transferred into the NMR tube using a syringe. The reaction mixture was shaken and then investigated by NMR spectroscopy. $K[(CF_3)_3BC(O)NMe_2]$ was identified as the sole product.

3.9. Reaction of $(CF_3)_3BCO$ with $HN(SiMe_3)_2$. A 50 mL round-bottom flask was charged at −196 °C with 430 mg (1.8 mmol) of $(CF_3)_3BCO$ and 5 mL of $HN(SiMe_3)_2$. The reaction mixture was warmed from −50 °C to room temperature and stirred overnight. The excess of disilazane was removed under reduced pressure. The NMR spectroscopic investigation revealed the following products: 27% $[(CF_3)_3BCN]^-$ and 73% further unidentified $(CF_3)_3B$ derivatives. The assigned NMR data of the main product (59%) are ^{19}F NMR: $\delta = -61.2$ ppm (q, $^2J_{B,F} = 26.6$ Hz); $^{11}B-NMR$: $\delta = -18.3$ ppm (decet, $^2J_{B,F} = 26.6$ Hz).

3.10. $K[(CF_3)_3BC(O)NHMe]$. Inside a drybox, 98 mg (0.38 mmol) of $(CF_3)_3BCNMe$ was weighed into a beaker with a magnetic stirring bar. After the addition of 5 mL of CH_2Cl_2, 1 mL of a concentrated aqueous K_2CO_3 solution was added while stirring. The dichloromethane layer was discarded, and the aqueous phase was extracted three times with diethyl ether (20, 20, 10 mL). The combined etheral phases were predried with K_2CO_3, filtered, and then dried with molecular sieves (4 Å) in a N_2 atmosphere. After filtration, the solvent was removed under reduced pressure. Yield: 64 mg (0.2 mmol, 53%). In an analogous manner, the ^{15}N-labeled compound was obtained.

3.11. $(CF_3)_3BC(O)NMe_3$. $(CF_3)_3BCO$ (145 mg, 0.59 mmol), 5 mL of CH_2Cl_2, and 1.8 mmol of NMe_3 were condensed into a cylindrical reaction vessel ($V = 15$ mL) equipped with a valve with a PTFE stem (Young, London) and fitted with a PTFE-coated magnetic stirring bar. The reaction mixture was first warmed to −30 °C and then under stirring to room temperature. A colorless solid precipitated from the solution. After 2 h at room temperature, all volatiles were removed in vacuo. $(CF_3)_3BC(O)NMe_3$ was identified as the main product by NMR spectroscopy (78%). Slow decomposition of the trimethylamine adduct in acetonitrile solution to unknown products was observed by NMR spectroscopy.

Table 1. Crystallographic Data of $K_2[\{(CF_3)_3BC(O)\}_2NH]\cdot 2MeCN$ at 100 K

empirical formula	$C_{12}H_7B_2F_{18}K_2N_3O_2$
fw [g mol^{-1}]	667.03
color	colorless
cryst syst, space group	monoclinic, $C2/c$ (no. 15)
unit cell dimensions	
a [Å]	14.4824(2)
b [Å]	11.0174(1)
c [Å]	29.0305(3)
β [deg]	90.17(1)
V [Å^3]	4632.04(9)
Z	8
ρ_{calc} [Mg m^{-3}]	1.910
θ range [deg]	4.21−30.70
R_1, $[I > 2\sigma(I)]^a$	0.0468
wR_2, all data^b	0.1013
GOF on F^2	1.067

[a] $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, weight scheme $w = [\sigma^2(F_o) + (0.0352P)^2 + 7.6786P]^{-1}$; $P = (\max(0,F_o^2) + 2F_c^2)/3)$.

3.12. $(CF_3)_3BC(O)PMe_3$. Analogous to reaction 3.11., $(CF_3)_3BC(O)PMe_3$ was synthesized from the borane carbonyl and PMe_3. Yield: 520 mg (1.6 mmol, 99%). Anal. Calcd for $C_7H_9BF_9PO$: C, 26.12; H, 2.82. Found: C, 26.75; H, not observed. An analysis of the hydrogen content was not possible because the peak was interfered by an artifact.

3.13. $(CF_3)_3BCNMe$. $K[(CF_3)_3BCN]$ (205 mg, 0.7 mmol) was weighed into a cylindrical reaction vessel ($V = 10$ mL) equipped with a valve with a PTFE stem (Young, London), fitted with a PTFE-coated magnetic stirring bar. At −196 °C, 5 mL of $CF_3S(O)_2OMe$ was added. The reaction mixture was allowed to warm to room temperature, yielding a colorless solution. During the course of the reaction, a solid slowly precipitated from the solution. After 5 h at room temperature, the excess of methyltriflate was removed in vacuo. The colorless residue was extracted three times with CH_2Cl_2 (20, 20, 10 mL), and the organic phases were filtered through a glass frit packed with Celite. After removal of the solvent, a colorless solid was obtained. Yield: 127 mg (0.5 mmol, 71%). Anal. Calcd for $C_5H_3BF_9N$: C, 23.20; H, 1.17; N, 5.41. Found: C, 22.75; H, 0.8; N, 4.66. In a similar way, the ^{15}N-labeled compound was obtained.

4. Instrumentation. 4.1. Single-Crystal X-Ray Diffraction. Crystals of $K_2[\{(CF_3)_3BC(O)\}_2NH]\cdot 2MeCN$ suitable for X-ray diffraction were obtained by slow diffusion of dichloromethane vapor into an acetonitrile solution. Diffraction data were collected at 100 K on a KappaCCD diffractometer (Bruker AXS) using Mo K_α radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. Crystal structures were determined using SHELXS-97,[24] and full-matrix least-squares refinements based on F^2 were performed using SHELXL-97.[25] Integration and empirical absorption corrections (DENZO scalepack)[26] were applied. Figures of the molecular structure were drawn using the program Diamond.[27] A summary

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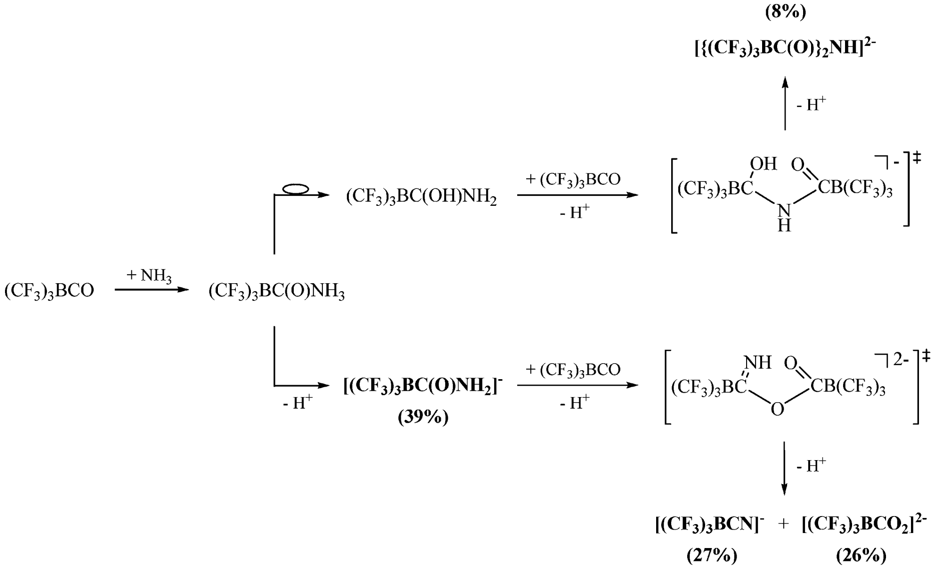
Scheme 1. Reaction of $(CF_3)_3BCO$ with Liquid Ammonia (Observed Borates Are Printed in Bold Letters)



of experimental details and crystal data is collected in Table 1. An X-ray crystallographic file in CIF format for $K_2[\{(CF_3)_3BC(O)\}_2NH]\cdot 2MeCN$ has been deposited at the Cambridge Crystallographic Data Center under the deposition number CCDC-253572. A copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

4.2. Vibrational Spectroscopy. Infrared spectra were recorded at room temperature on an IFS 66v FTIR instrument (Bruker, Karlsruhe, Germany). A DTGS detector, together with a KBr/Ge beam splitter was used in the region of 5000−400 cm^{-1}. Raman spectra were recorded on a Bruker RFS 100/S FT Raman spectrometer using the 1064 nm excitation (500 mW) of a Nd:YAG laser.

4.3. NMR Spectroscopy. ^1H, ^{19}F, ^{31}P, and ^{11}B NMR spectra were recorded at room temperature on a Bruker Avance DRX-300 spectrometer operating at 300.13, 282.41, 121.49, or 96.29 MHz for ^1H, ^{19}F, ^{31}P, and ^{11}B nuclei, respectively. ^{13}C and ^{15}N NMR spectroscopic studies were performed at room temperature on a Bruker Avance DRX-500 spectrometer, operating at 125.758 or 50.678 MHz for ^{13}C and ^{15}N nuclei, respectively. The NMR signals were referenced against TMS and $CFCl_3$ as internal standards and $BF_3\cdot OEt_2$ in CD_3CN, H_3PO_4 in H_2O and $MeNO_2$ in CD_3CN as external standards. Concentrations of the investigated samples were in the range of 0.1−1 mol L^{-1}. ^{15}N NMR spectra were obtained by direct measurements or for compounds having a hydrogen available for polarization transfer with the INEPT method.[28,29]

4.4. DSC Measurements. Thermoanalytical measurements were made with a Netzsch DSC204 instrument. Temperature and sensitivity calibrations in the temperature range of 20−500 °C were carried out with naphthalene, benzoic acid, KNO_3, $AgNO_3$, $LiNO_3$, and CsCl. About 5−10 mg of the solid samples were weighed and contained in sealed aluminum crucibles. They were studied in the temperature range of 20−500 °C with a heating rate of 5 K min^{-1}; throughout this process, the furnace was flushed with dry nitrogen. For the evaluation of the output, the Netzsch Protens4.0 software was employed.

4.5. Computational Calculations. Quantum chemical calculations were performed to support the interpretation of the experimental results in this study. DFT calculations[30] were carried out using Becke's three-parameter hybrid functional and the Lee−Yang−Parr correlation functional (B3LYP)[31−33] with the Gaussian 98 program suite.[34] Geometries were optimized and energies were calculated with the 6-311++G(d) basis set, and all structures represent true minima on the respective hypersurface (no imaginary frequency). Diffuse functions were incorporated because improved energies are obtained for anions.[35] All energies presented herein are zero-point corrected, and for enthalpies and free energies, the thermal contributions are included for 298 K.

Results and Discussion

1. Synthetic Aspects. The reaction of $(CF_3)_3BCO$ with liquid ammonia results in a mixture of the borates $[NH_4][(CF_3)_3BC(O)NH_2]$, $[NH_4][(CF_3)_3BCN]$, $[NH_4]_2[(CF_3)_3BCO_2]$, and $[NH_4]_2[\{(CF_3)_3BC(O)\}_2NH]$, as rationalized in Scheme 1. Ammonia adds to the carbonyl C atom of $(CF_3)_3BCO$ yielding $(CF_3)_3BC(O)NH_3$ as the intermediate. Subsequently, most of the $(CF_3)_3BC(O)NH_3$ is deprotonated by ammonia, yielding $[NH_4][(CF_3)_3BC(O)NH_2]$. Similar reactions of NH_3 with other borane carbonyls yielding carbamoyl complexes have been observed, for example, $[NH_4][H_3BC(O)NH_2]$[36,37] and $[NH_4]_2[1,12\text{-}B_{12}H_{10}\{C(O)NH_2\}_2]$.[38,39]

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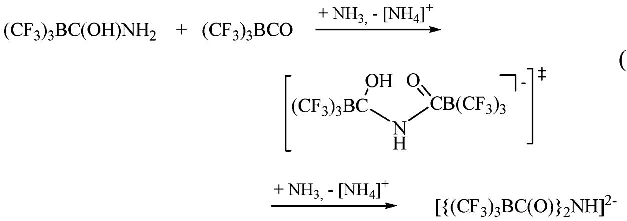
The $[(CF_3)_3BC(O)NH_2]^-$ anion is dehydrated by unreacted $(CF_3)_3BCO$, resulting in $[NH_4][(CF_3)_3BCN]$ and $[NH_4]_2[(CF_3)_3BCO_2]$ in equimolar amounts. The postulated transient $[(CF_3)_3BC(NH)OC(O)B(CF_3)_3]^{2-}$ is very likely, since this dimeric borate anion is similar to the known $[\{(CF_3)_3BC(O)\}_2O]^{2-}$ dianion.[17]

The formation of $[NH_4]_2[\{(CF_3)_3BC(O)\}_2NH]$ as side product is rationalized by deprotonation of the intermediate $[(CF_3)_3BC(OH)NHC(O)B(CF_3)_3]^-$. Due to a low local concentration of NH_3, the deprotonation of $(CF_3)_3BC(O)NH_3$ is incomplete. Hence, $(CF_3)_3BC(O)NH_3$ rearranges to $(CF_3)_3BC(OH)NH_2$, which reacts with $(CF_3)_3BCO$ to the $[\{(CF_3)_3BC(O)\}_2NH]^{2-}$ dianion. The selective synthesis of salts with the $[\{(CF_3)_3BC(O)\}_2NH]^{2-}$ anion were achieved by diffusion of gaseous ammonia into solutions of $(CF_3)_3BCO$ in diethyl ether (eq 4).



(4)

Due to the lower basicity of diethyl ether in comparison to ammonia, the carbene complex $(CF_3)_3BC(OH)NH_2$ is present in the reaction mixture instead of $[(CF_3)_3BC(O)NH_2]^-$. Hence, $(CF_3)_3BCO$ reacts with the N atom of $(CF_3)_3BC(OH)NH_2$ and after deprotonation $[\{(CF_3)_3BC(O)\}_2NH]^{2-}$ is obtained and isolated as the colorless salt $K_2[\{(CF_3)_3BC(O)\}_2NH]$, which according to DSC measurements undergoes a phase transition at 104 °C and decomposes at 185 °C. The close relationship to the acetylacetonate anion, $[\{MeC(O)\}_2CH]^-$, whose coordination chemistry is well studied,[40,41] makes $[\{(CF_3)_3BC(O)\}_2NH]^{2-}$ a possible candidate as a bidentate ligand.

Pure $K[(CF_3)_3BC(O)NH_2]$ was obtained from the reaction of $K[(CF_3)_3BC(O)F]$ with liquid NH_3 (eq 5).

$$[(CF_3)_3BC(O)F]^- + 2NH_3 \xrightarrow[-80 \rightarrow -10\ ^{\circ}C]{NH_3} [(CF_3)_3BC(O)NH_2]^- + [NH_4]F \quad (5)$$

$K[(CF_3)_3BC(O)NH_2]$ is a colorless solid which undergoes a phase transition at 74 °C and decomposes at 215 °C. The main thermal decomposition product is $K[(CF_3)_3BCN]$ (60%, NMR spectroscopy), besides the borates $K[C_2F_5BF_3]$ (32%), $K[(CF_3)_3BF]$ (5%), and $K[BF_4]$ (3%). The latter three salts were observed also when reacting KF with the gas-phase decomposition products of $(CF_3)_3BCO$.[42] The dehydration of the $[(CF_3)_3BC(O)NH_2]^-$ anion is quantitative by treatment with phosgene in the presence of triethylamine (eq 6).

$$[(CF_3)_3BC(O)NH_2]^- + OCCl_2 + 2Et_3N \xrightarrow[RT]{CH_3CN} [(CF_3)_3BCN]^- + 2[Et_3NH]Cl + CO_2 \quad (6)$$

N-Alkylamide derivatives of the type $[(CF_3)_3BC(O)NR^1R^2]^-$ were obtained by three different routes: (i) reaction of amines with $K[(CF_3)_3BC(O)F]$ (eq 7),

$$[(CF_3)_3BC(O)F]^- + 2^nPrNH_2 \xrightarrow[RT]{CH_3CN} [(CF_3)_3BC(O)NH\,^nPr]^- + [^nPrNH_3]F \quad (7)$$

(ii) reaction of R_2NSiMe_3 with $K[(CF_3)_3BC(O)F]$ (eq 8) and

$$[(CF_3)_3BC(O)F]^- + Me_2NSiMe_3 \xrightarrow[RT]{CD_3CN} [(CF_3)_3BC(O)NMe_2]^- + Me_3SiF \quad (8)$$

(iii) alkylation of $[(CF_3)_3BCN]^-$ (eq 9) followed by hydrolysis (eq 10).

$$K[(CF_3)_3BCN]\ CF_3S(O)_2OMe \xrightarrow{CF_3\ S(O)_2OMe} (CF_3)_3BCNMe + KCF_3SO_3 \quad (9)$$

$$2(CF_3)_3BCNMe + K_2CO_3 + H_2O \xrightarrow{H_2O} 2K[(CF_3)_3BC(O)NHMe] + CO_2 \quad (10)$$

$(CF_3)_3CC(O)NMe_2$, which is isoelectronic to the $[(CF_3)_3BC(O)NMe_2]^-$ anion, is formed by the reaction of $(CF_3)_3CC(O)Cl$ with Me_2NH,[43,44] analogous to the synthesis of $[(CF_3)_3BC(O)NH^nPr]^-$ shown in eq 7.

The main product of the reaction of $(CF_3)_3BCO$ with trimethylamine is the colorless inner salt $(CF_3)_3BC(O)NMe_3$. PMe_3 reacts with the borane carbonyl to $(CF_3)_3BC(O)PMe_3$ as the sole product.

$$(CF_3)_3BCO + Me_3\mathit{Pnic} \xrightarrow{CH_2Cl_2} (CF_3)_3BC(O)\,\mathit{Pnic}\,Me_3\ (\mathit{Pnic} = N, P) \quad (11)$$

The adduct $H_3BC(O)NMe_3$ obtained from NMe_3 and H_3BCO,[36,37,45] is stable only at temperatures below −45 °C and decomposes at elevated temperatures to H_3BNMe_3 and CO.[36,37,45] In contrast, $(CF_3)_3BC(O)NMe_3$ decomposes slowly in solution at room temperature but no $(CF_3)_3BNMe_3$[46] is formed, and if triethylamine is used in place of NMe_3, the mixture turns black when warming up (> −30 °C) and slow gas evolution is observed.

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Table 2. Calculated[a] Enthalpies of the Reactions of $(CF_3)_3BCO$ with NH_3 and Me_3*Pnic* (*Pnic* = N, P)

base	$(CF_3)_3BCO + X_3Pnic \rightarrow (CF_3)_3BC(O)PnicX_3$ ΔH(298 K) [kJ mol^{-1}]	$(CF_3)_3BCO + X_3Pnic \rightarrow (CF_3)_3BPnicX_3 + CO$ ΔH(298 K) [kJ mol^{-1}]
NH_3	−46.1	−124.5
Me_3N	−33.6	−87.2
Me_3P	−57.4	−121.8

[a] B3LYP/6-311++G(d).

Table 3. Selected Bond Parameters of the $[\{(CF_3)_3BC(O)\}_2NH]^{2-}$ Ion in the Potassium Salt and from DFT Calculations[a,b]

	exptl	calcd		exptl	calcd
		bond lengths [Å]			
C−O	1.227(2)	1.217	B−C(O)	1.636(3)	1.665
C−N	1.397(2)	1.414	B−CF_3	1.626(4)	1.648
N−H	0.822(26)	1.011	C−F	1.358(5)	1.372
		bond angles [deg]			
O−C−N	120.73(16)	121.7	B−C−N	117.59(16)	117.3
B−C−O	121.59(16)	121.0	(O)C−B−CF_3	109.48(16)	110.0
		torsion angles [deg]			
O−C−N−C(O)	6.6	4.7	O−C−N−H	175.2	175.3

[a] B3LYP/6-311++G(d). [b] Mean values of different bond lengths and angles.

Solid $(CF_3)_3BC(O)PMe_3$ is thermally stable up to 142 °C. The residue of the decomposition contains no $(CF_3)_3BPMe_3$. The reaction of PH_3 with the borane carbonyl yields a light yellow solid, which is insoluble in acetonitrile and in water. In contrast to PMe_3 and PH_3, PF_3 does not react with $(CF_3)_3BCO$, neither in the gas phase ($p(PF_3) = 3$ bar) nor in CD_2Cl_2 solution at room temperature.

2. DFT Calculations. Thermochemical data derived from DFT calculations (B3LYP/6-311++G(d)) of CO exchange reactions and additions to the carbonyl C atom of $(CF_3)_3BCO$ with ammonia, NMe_3, and PMe_3, respectively, are listed in Table 2. All six reactions are exothermic. For all examples, the exchange reactions are thermochemically favored over the respective addition reactions, in sharp contrast to the experimental findings. The formation of stable adducts is kinetically favored, and so no ligand exchange occurs. If no stable adduct is formed, e.g., with acetonitrile, immediately CO is released and $(CF_3)_3BNCMe$ is obtained.[14]

The increased enthalpy of the reaction of the borane carbonyl with PMe_3 in comparison to NMe_3 parallels the trend in thermal stability: while $(CF_3)_3BC(O)PMe_3$ is stable in acetonitrile solution at room temperature and up to 142 °C in the solid state, $(CF_3)_3BC(O)NMe_3$ slowly decomposes in MeCN solution at room temperature.

3. Solid State Structure of $K_2[\{(CF_3)_3BC(O)\}_2NH]\cdot 2MeCN$. The potassium salt of the $[\{(CF_3)_3BC(O)\}_2NH]^{2-}$ anion crystallizes as solvate with two molecules of acetonitrile per formula unit in the monoclinic space group *C*2/*c* (no. 15). Selected bond parameters are collected in Table 3 and are compared to values derived from DFT calculations (B3LYP/6-311++G(d)). In Figure 1, an anion in the crystal structure is depicted. In the solid state, the anions have no symmetry (C_1), whereas for the energy minimum of the gas-phase structure, C_2 symmetry is calculated. However, the deviations between experimental and theoretical bond parameters are small.

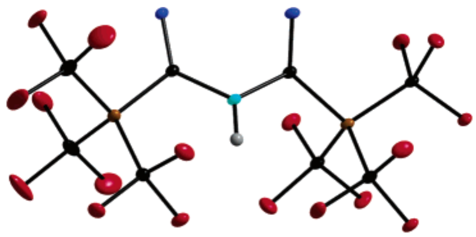

Figure 1. View of the $[\{(CF_3)_3BC(O)\}_2NH]^{2-}$ anion in the crystal structure of $K_2[\{(CF_3)_3BC(O)\}_2NH]\cdot 2MeCN$.

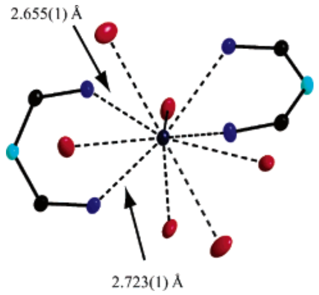

Figure 2. Coordination sphere of one K^+ chelated by two $[\{(CF_3)_3BC(O)\}_2NH]^{2-}$ anions in the crystal structure of $K_2[\{(CF_3)_3BC(O)\}_2NH]\cdot 2MeCN$.

In the crystal lattice, the borate anions form layers parallel to the *c* axis which are rotated (Figure S1). Two different types of potassium cations are present in the crystals which are both located on the C_2 axis. One-half of the cations are coordinated by four O atoms of two chelating borate anions with distances of 2.655(1) and 2.723(1) Å, as well as six fluorine atoms (2.861(1)−2.970(1) Å) (Figure 2). The second half of the K^+ cations are coordinated by two N atoms of two acetonitrile molecules (2.852(2) Å), two nonchelating oxygen atoms (2.802(2) Å), and six fluorine atoms (2.991(2)−3.183(2) Å). All contacts represent weak interionic interactions.[47]

4. Vibrational Spectroscopy. $K[(CF_3)_3BC(O)NH_2]$, $K_2[\{(CF_3)_3BC(O)\}_2NH]$ (Figure 3), and $(CF_3)_3BC(O)PMe_3$ (Figure 4), as well as the reaction mixture obtained from $(CF_3)_3BCO$ and NMe_3, were investigated by IR and Raman spectroscopy. Due to the large number of vibrational modes, the spectra are complex and only those of the simplest $[(CF_3)_3BC(O)NH_2]^-$ anion were assigned in detail with the aid of the predicted spectrum obtained from DFT calculations (Table S1).

Especially the vibrational spectra of $K[(CF_3)_3BC(O)NH_2]$ and $K_2[\{(CF_3)_3BC(O)\}_2NH]$ display in the range of 100−1300 cm^{-1} the band pattern typical for $(CF_3)_3B$ species.[11,14,48,49] In the Raman spectrum of $(CF_3)_3BC(O)PMe_3$, this trend is not as clear due to additional strong bands associated with the PMe_3 moiety (Figure 4).

Characteristic bands for the carbamoyl complexes are the CO stretches which are observed (calculated) at 1696 cm^{-1} (1624 cm^{-1}) for $K[(CF_3)_3BC(O)NH_2]$, at 1756 (1694) and 1725 cm^{-1} (1662 cm^{-1}) for $K_2[\{(CF_3)_3BC(O)\}_2NH]$, at 1993

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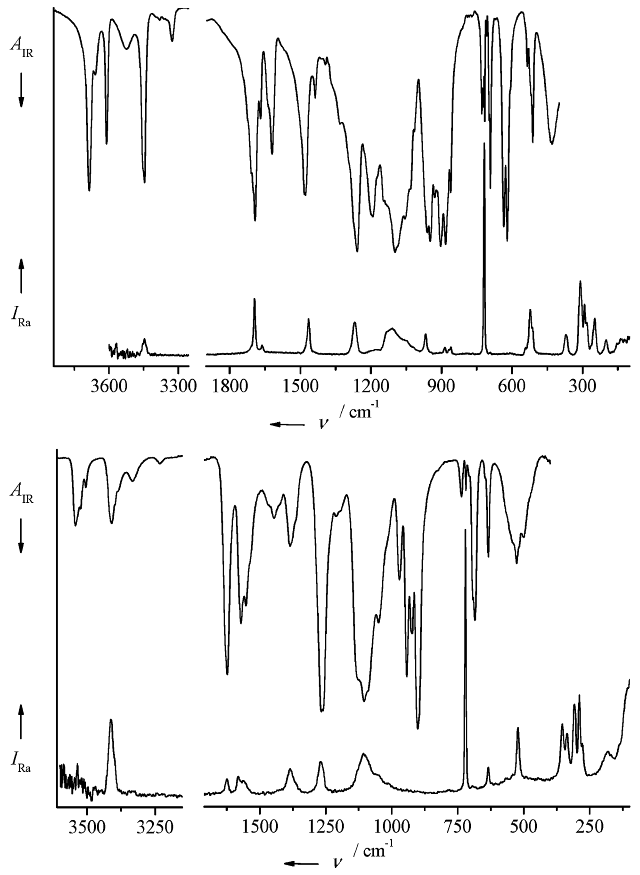

Figure 3. IR and Raman spectra of $K_2[\{(CF_3)_3BC(O)\}_2NH]$ (top) and $K[(CF_3)_3BC(O)NH_2]$ (bottom).

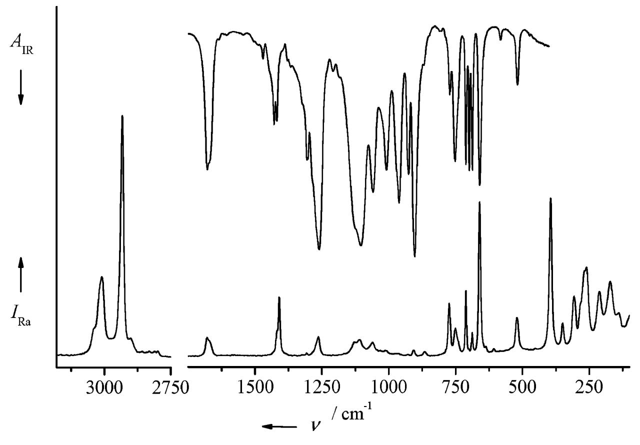

Figure 4. IR and Raman spectra of $(CF_3)_3BC(O)PMe_3$ (IR spectrum as Nujol mull).

cm^{-1} (1800 cm^{-1}) for $(CF_3)_3BC(O)NMe_3$, and at 1815 cm^{-1} (1679 cm^{-1}) for $(CF_3)_3BC(O)PMe_3$. As a first approximation, ν(CO) is a measure for the bonding between the carbonyl C atom and the N or P base: the stronger the C(O)−X bond becomes, the lower is ν(CO). Hence, trimethylamine is weakest bound, and in $(CF_3)_3BC(O)PMe_3$, the C−P bond strength is significantly increased in accordance with their thermal behaviors. The strongest C−N interactions are present in the borate anions $[(CF_3)_3BC(O)NH_2]^-$ and $[\{(CF_3)_3BC(O)\}_2NH]^{2-}$.

In the IR spectrum of $K[(CF_3)_3BC(O)NH_2]$, two N−H bands are found at 3707 (ν_{as}(NH)) and 3564 cm^{-1} (ν_s(NH)) (Figure 3, Table S1). In the Raman spectrum, only ν_s(NH) can be observed. In the range from 3300 to 3800 cm^{-1}, a series of bands are found in the spectra of $K_2[\{(CF_3)_3BC(O)\}_2NH]$ due to overtones (Figure 3).

5. NMR Spectroscopy. Multinuclear NMR spectroscopy of the carbamoyl complexes $(CF_3)_3BC(O)NMe_3$ and $(CF_3)_3BC(O)PMe_3$ allowed their detailed characterization due to small line widths (Table S2). This is unexpected, since in general, broad lines are a typical feature for ^{11}B NMR spectra and NMR spectra of nuclei that interact with ^{11}B due the quadrupolar moment of ^{11}B.[50−52] Investigated nuclei are ^1H, ^{11}B, ^{13}C, ^{15}N, ^{19}F, and ^{31}P, and the chemical shifts and coupling constants are collected in Table 4.

In Figure 5 the ^{11}B and in Figure 6 the ^{19}F, as well as $^{19}F\{^{11}B\}$, NMR spectra of $[(CF_3)_3BC(O)NH_2]^-$, $[(CF_3)_3BC(O)NHMe]^-$, $[\{(CF_3)_3BC(O)\}_2NH]^{2-}$, and their ^{15}N isotopomers are depicted. The ^{11}B and ^{19}F NMR chemical shifts of $[(CF_3)_3BC(O)NH_2]^-$, $[(CF_3)_3BC(O)NHR]^-$ (R = Me, ^{n}Pr) and $[\{(CF_3)_3BC(O)\}_2NH]^{2-}$ are similar to those of $[(CF_3)_3BC(O)OH]^-$,[14] while $\delta(^{11}B)$ and $\delta(^{19}F)$ of $[(CF_3)_3BC(O)NMe_2]^-$ are shifted to higher values (Table 4). The ^{11}B NMR signals are split into decets, and the ^{19}F NMR signals into quartets due to the $^2J(^{11}B,^{19}F)$ couplings. The ^{11}B NMR spectra of the three carbamoyl complexes are split into doublets due to $^2J(^{11}B,^{15}N)$ with values of 5.2−6.2 Hz. In the case of $[(CF_3)_3BC(O)NH_2]^-$, only one $^3J(^1H,^{11}B)$ coupling is observed, which is due to the interaction with the trans proton. In general, trans couplings are larger than the respective cis couplings.[53] Similarly, the proton in $[\{(CF_3)_3BC(O)\}_2NH]^{2-}$, which does not couple to ^{11}B, is in the cis position to the B atom. It is further concluded that in $[(CF_3)_3BC(O)NHMe]^-$ the proton is positioned cis to the B atom, in accordance with steric considerations. The ^{19}F nuclei of $[(CF_3)_3BC(O)^{15}NH_2]^-$, $[(CF_3)_3BC(O)^{15}NHMe]^-$, and $[\{(CF_3)_3BC(O)\}_2{}^{15}NH]^{2-}$ couple to the respective ^{15}N nucleus and $^4J(^{15}N,^{19}F)$ range from 0.8 to 1.0 Hz. While for $[(CF_3)_3BC(O)^{15}NHMe]^-$ and $[\{(CF_3)_3BC(O)\}_2{}^{15}NH]^{2-}$ the $^5J(^1H,^{19}F)$ couplings were observed, in the $^{19}F\{^{11}B\}$ NMR spectrum of $[(CF_3)_3BC(O)^{15}NH_2]^-$, no $^5J(^1H,^{19}F)$ coupling was found.

The chemical shifts and coupling schemes in the ^{11}B and ^{19}F NMR spectra of $(CF_3)_3BC(O)PnicMe_3$ (*Pnic* = N, P) are similar to related $(CF_3)_3B{-}C(O)$ derivatives (Table 4, Figure S2).[14] In the trimethylphosphan adduct, $^2J(^{11}B,^{31}P) = 44.5$ Hz and $^4J(^{19}F,^{31}P) = 4.4$ Hz are observed. The much larger line widths in the NMR spectra of $(CF_3)_3BC(O)NMe_3$ are remarkable in comparison to those of its phosphorus analogue.

The ^{15}N NMR spectra of $[(CF_3)_3BC(O)NH_2]^-$, $[(CF_3)_3BC(O)NHMe]^-$, and $[\{(CF_3)_3BC(O)\}_2NH]^{2-}$ display the ^1J couplings between ^1H and ^{15}N (Figure S3). Furthermore, the spectra of $[(CF_3)_3BC(O)NH_2]^-$ and $[(CF_3)_3BC(O)NHMe]^-$

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Table 4. NMR Spectroscopic Data of $[(\mathrm{CF_3})_3\mathrm{BC(O)NR}^{1}\mathrm{R}^{2}]^-$ (R^1 = H, Me; R^2 = H, Me, ^{n}Pr), $(\mathrm{CF_3})_3\mathrm{BC(O)}Pnic\mathrm{Me}_3$ (*Pnic* = N, P), and Related Species[a,b]

compd	$[(\mathrm{CF_3})_3\mathrm{BC(O)NH_2}]^-$	$[(\mathrm{CF_3})_3\mathrm{BC(O)NHMe}]^-$	$[(\mathrm{CF_3})_3\mathrm{BC(O)NH}^n\mathrm{Pr}]^-$[c]	$[(\mathrm{CF_3})_3\mathrm{BC(O)NMe_2}]^-$	$[\{(\mathrm{CF_3})_3\mathrm{BC(O)}\}_2\mathrm{NH}]^{2-}$	$(\mathrm{CF_3})_3\mathrm{BC(O)NMe_3}$	$(\mathrm{CF_3})_3\mathrm{BC(O)PMe_3}$[d]	$[(\mathrm{CF_3})_3\mathrm{BCN}]^-$	$[(\mathrm{CF_3})_3\mathrm{BC(O)OH}]^-$	$[\mathrm{B(CF_3)_4}]^-$
$\delta(^1\mathrm{H})$ $(\mathrm{N}\boldsymbol{H})$	6.2/6.1[e]	6.6	6.4		9.4					
$\delta(^1\mathrm{H})$ $(\mathrm{NC}\boldsymbol{H}_x)$		2.6	3.1	2.9		3.0	1.8			
$\delta(^{11}\mathrm{B})$	−18.9	−18.8	−18.8	−16.6	−18.5	−16.0	−15.9	−22.3	−18.9	−18.9
$\delta(^{13}\mathrm{C})$ $(\boldsymbol{C}\mathrm{F_3})$	134.4	134.5	134.6	134.7	133.7	131.7	132.3	132.4	133.9	132.9
$\delta(^{13}\mathrm{C})$ $(\boldsymbol{C}\mathrm{(O)}/\boldsymbol{C}\mathrm{N})$	189.5	187.0	185.9	185.2	188.1	186.4	229.7	127.5	186.4	
$\delta(^{13}\mathrm{C})$ $(\mathrm{N}\boldsymbol{C}\mathrm{H}_x)$		25.3	40.1	37.5/35.0[e]		48.8	7.9			
$\delta(^{19}\mathrm{F})$	−60.2	−60.4	−60.0	−57.5	−60.0	−58.8	−59.6	−62.1	−60.4	−61.6
$\delta(^{15}\mathrm{N})/\delta(^{31}\mathrm{P})$	−263.5	−263.1	−250.6	n.o.[f]	−197.8	n.o.	20.4	−103.3		
$^1J(\mathrm{C}^1\boldsymbol{H}_x,{}^{13}\boldsymbol{C}\mathrm{H}_x)$		137.7	136.9	146		144.7	134.9			
$^1J(\mathrm{N}^1\boldsymbol{H},{}^{15}\boldsymbol{N})$	90.0/85.8[e]	92.5	89.8		88.2					
$^1J(^{11}\boldsymbol{B},{}^{13}\boldsymbol{C}\mathrm{F_3})$	71.8	71.7	71.7	71.9	72.5	76.9	74.4	76.2	72.8	73.4
$^1J(^{11}\boldsymbol{B},{}^{13}\boldsymbol{C}\mathrm{(O)})$	61.3	62.3	62.5	65.7	63.2	65.5	57.5	64.0	68.2	
$^1J(^{13}\boldsymbol{C}\mathrm{H}_x,{}^{15}\boldsymbol{N})$		10.7	n.o.	n.o.		n.o.	43.5			
$^1J(^{13}\boldsymbol{C}\mathrm{(O)},{}^{15}\boldsymbol{N})$	6.5	n.o.		n.o.	n.o.[g]	n.o.	32.5	14.7		
$^1J(^{13}\boldsymbol{C}\mathrm{F_3},{}^{19}\boldsymbol{F})$	306.2	305.8	306.3	306.9	306.1	303.1	304.1	303.2	305.5	304.3
$^2J(\mathrm{C}^1\boldsymbol{H}_x,{}^{15}\boldsymbol{N})$		1.1	n.o.	n.o.		n.o.	14.4			
$^2J(\mathrm{N}^1\boldsymbol{H},{}^{13}\boldsymbol{C}\mathrm{H}_x)$		1−2	5.4							
$^2J(\mathrm{N}^1\boldsymbol{H},{}^{13}\boldsymbol{C}\mathrm{(O)})$	4.3[h]	2.9−2.7			∼4					
$^2J(^{11}\boldsymbol{B},{}^{15}\boldsymbol{N})$	5.7	6.2	n.o.	n.o.	5.2	n.o.	44.5	n.o.		
$^2J(^{11}\boldsymbol{B},{}^{19}\boldsymbol{F})$	25.1	24.9	24.7	24.9	25.2	27.5	26.4	29.0	25.8	25.9
$^3J(\mathrm{N}^1\boldsymbol{H},\mathrm{C}^1\boldsymbol{H}_x)$		4.6	5.9							
$^3J(\mathrm{C}^1\boldsymbol{H}_x,{}^{13}\boldsymbol{C}\mathrm{H}_x)$				n.o.		n.o.	2.6			
$^3J(\mathrm{C}^1\boldsymbol{H}_x,{}^{13}\boldsymbol{C}\mathrm{(O)})$		2.9−2.7	3.0	2.9		n.o.	1.6			
$^3J(\mathrm{N}^1\boldsymbol{H},{}^{11}\boldsymbol{B})$	4.2	n.o.	n.o.		n.o.					
$^3J(^{11}\boldsymbol{B},{}^{13}\boldsymbol{C}\mathrm{H}_x)$		1.0	0.7	n.o.		n.o.	n.o.			
$^3J(^{13}\boldsymbol{C}\mathrm{F_3},{}^{19}\boldsymbol{F})$	3.7	4.2	4.2	4.2	4.1	n.o.	4.0	3.6	4.0	3.9
$^3J(^{13}\boldsymbol{C}\mathrm{(O)},{}^{19}\boldsymbol{F})$	2.7	n.o.	2.9	3.0	n.o.[g]	n.o.	3.0	3.5	3.5	
$^4J(^{15}\boldsymbol{N},{}^{19}\boldsymbol{F})$	0.9	0.8	n.o.	n.o.	1.0	n.o.	4.4	n.o.		
$^4J(^{19}\boldsymbol{F},{}^{19}\boldsymbol{F})$	6.2	6.3	6.3	n.o.	6.2	6.8	n.o.	6.3	n.o.	5.8
$^5J(\mathrm{N}^1\boldsymbol{H},{}^{19}\boldsymbol{F})$	n.o.	1.0	0.8		0.8					
$^5J(^{13}\boldsymbol{C}\mathrm{H}_x,{}^{19}\boldsymbol{F})$		n.o.	n.o.	n.o.		n.o.	0.8			
$^6J(\mathrm{C}^1\boldsymbol{H}_x,{}^{19}\boldsymbol{F})$		n.o.	n.o.	n.o.		n.o.	0.3			
ref	[i]	[i]	[i]	[i]	[i]	[i]	[i]	14, 16	14	11

[a] δ in ppm, J in Hz. [b] NMR solvent: $\mathrm{CD_3CN}$. [c] $\delta(^1\mathrm{H}) = 1.4$ ppm $(\mathrm{C}\boldsymbol{H}_2\mathrm{CH_3})$, $\delta(^1\mathrm{H}) = 0.9$ ppm $(\mathrm{C}\boldsymbol{H}_3)$, $\delta(^{13}\mathrm{C}) = 23.7$ ppm $(\boldsymbol{C}\mathrm{H_2CH_3})$, $\delta(^{13}\mathrm{C}) = 11.6$ ppm $(\boldsymbol{C}\mathrm{H_3})$, $^1J(^{13}\boldsymbol{C}\mathrm{H_2CH_3},{}^1\boldsymbol{H}) = 126.7$ Hz, $^1J(^{13}\boldsymbol{C}\mathrm{H_3},{}^1\boldsymbol{H}) = 125.3$ Hz, $^2J(^{13}\boldsymbol{C}\mathrm{H_3},{}^1\boldsymbol{H}) = {}^3J(^{13}\boldsymbol{C}\mathrm{H_3},{}^1\boldsymbol{H}) = 4.2$ Hz, $^3J(\mathrm{NC}^1\boldsymbol{H}_2,\mathrm{C}^1\boldsymbol{H}_2\mathrm{CH_3}) = 6.9$ Hz, $^3J(\mathrm{C}^1\boldsymbol{H}_2\mathrm{CH_3},\mathrm{C}^1\boldsymbol{H}_3) = 7.4$ Hz. [d] Coupling constants with ^{31}P are given in the respective rows of ^{15}N. [e] Protons/methyl groups are not equal. [f] n.o. = not observed. [g] Disturbed by coupling to ^{11}B. [h] Both coupling constants are equal within experimental error. [i] This work.

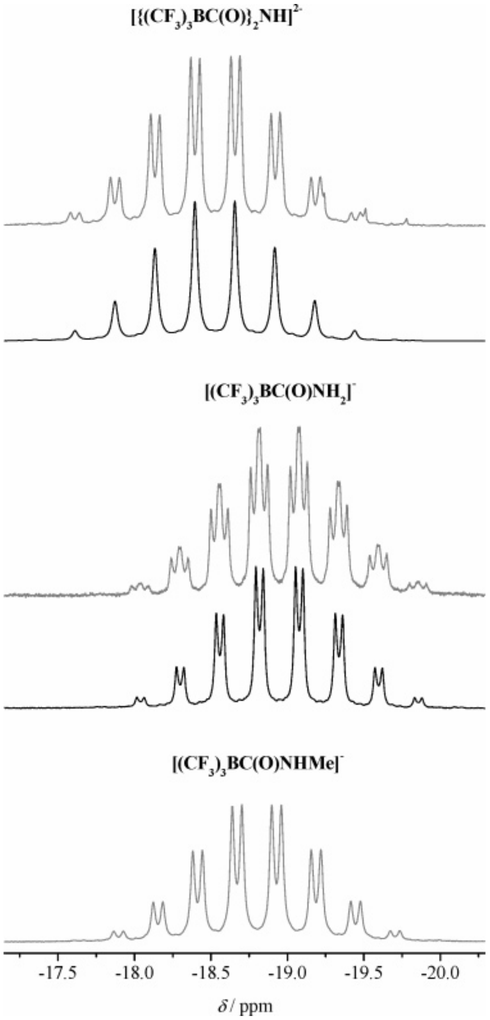

Figure 5. ^{11}B NMR spectra of $[\{(CF_3)_3BC(O)\}_2NH]^{2-}$, $[(CF_3)_3BC(O)NH_2]^-$, and $[(CF_3)_3BC(O)NHMe]^-$ (spectra in gray: ^{15}N-labeled anions).

are split into distorted quartets due to the interaction with ^{11}B. The signal of the $[\{(CF_3)_3BC(O)\}_2NH]^{2-}$ anion is split into a septet with an intensity distribution of 1:2:3:4:3:2:1, in accordance with two equivalent ^{11}B nuclei coupling to ^{15}N.

The highly coupled ^{31}P NMR spectrum of $(CF_3)_3BC(O)PMe_3$ (Figure 7), consists of a quartet ($^2J(^{11}B,^{31}P) = 44.5$ Hz) of decets ($^2J(^1H,^{31}P) = 14.4$ Hz) of decets ($^4J(^{19}F,^{31}P) = 4.4$ Hz).

In Figure 8 the ^{13}C NMR spectra of $[(CF_3)_3BC(O)NHR]^-$ (R = H, Me), $[(CF_3)_3BC(O)NMe_2]^-$, and $[\{(CF_3)_3BC(O)\}_2NH]^{2-}$ and in Figure S4 in the Supporting Information the ^{13}C NMR spectrum of $(CF_3)_3BC(O)PMe_3$ are presented. The chemical shifts of the CF_3 groups are in the typical region of similar compounds.[11,14] The ^{13}C nuclei of the CF_3 groups couple to three ^{19}F nuclei ($^1J(^{13}C,^{19}F)$, quartet), to ^{11}B ($^1J(^{11}B,^{13}C)$, quartet), and to six ^{19}F nuclei ($^3J(^{13}C,^{19}F)$, septet). The resonance frequency of the carbonyl C atom of $(CF_3)_3BC(O)PMe_3$ ($\delta(^{13}C) = 229.7$ ppm) is shifted to a higher value compared to $(CF_3)_3B$ derivatives with carbamoyl ligands ($\delta(^{13}C) = \sim 187$ ppm). Besides the $^1J(^{11}B,^{13}C)$ coupling of the signals of the carbonyl C atoms, a series of further couplings are assigned (Table 4). For $[(CF_3)_3BC(O)NHMe]^-$ and $[(CF_3)_3BC(O)NMe_2]^-$, the signals of the methyl groups are observed. The very broad signals of the methyl groups of $[(CF_3)_3BC(O)NMe_2]^-$ at 35.0 and

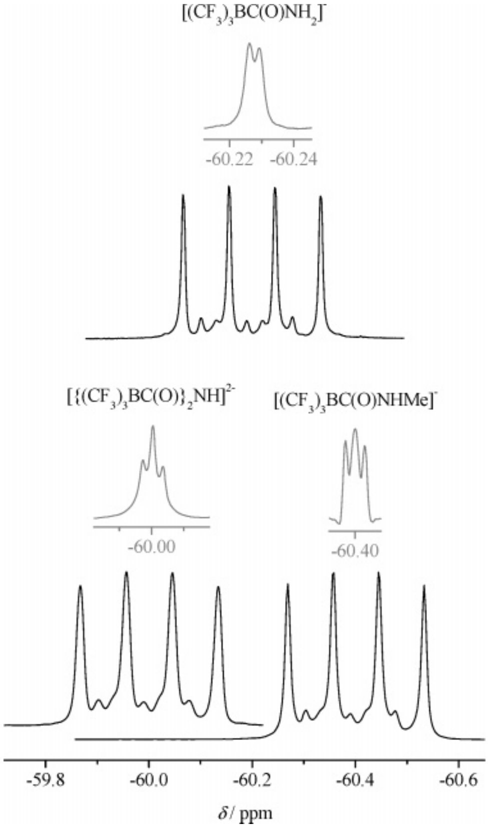

Figure 6. ^{19}F (black) and ^{19}F{^{11}B} NMR spectra (grey) of $[\{(CF_3)_3BC(O)\}_2NH]^{2-}$, $[(CF_3)_3BC(O)NH_2]^-$, and $[(CF_3)_3BC(O)NHMe]^-$ (^{19}F{^{11}B} NMR spectra: ^{15}N-labeled anions).

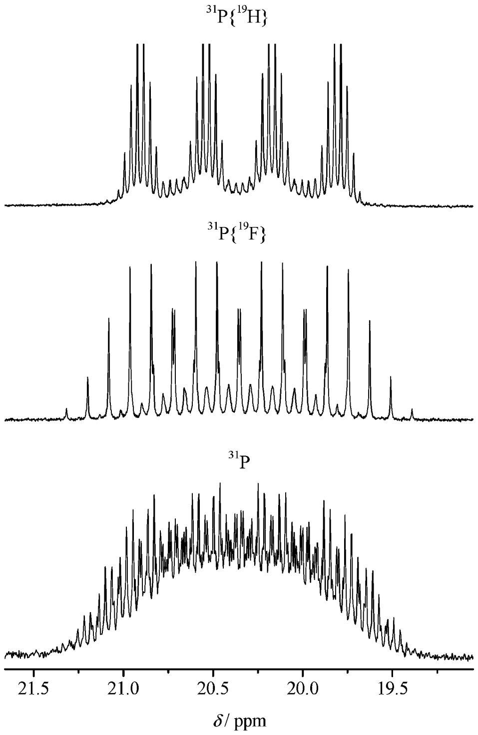

Figure 7. ^{31}P NMR spectra of $(CF_3)_3BC(O)PMe_3$.

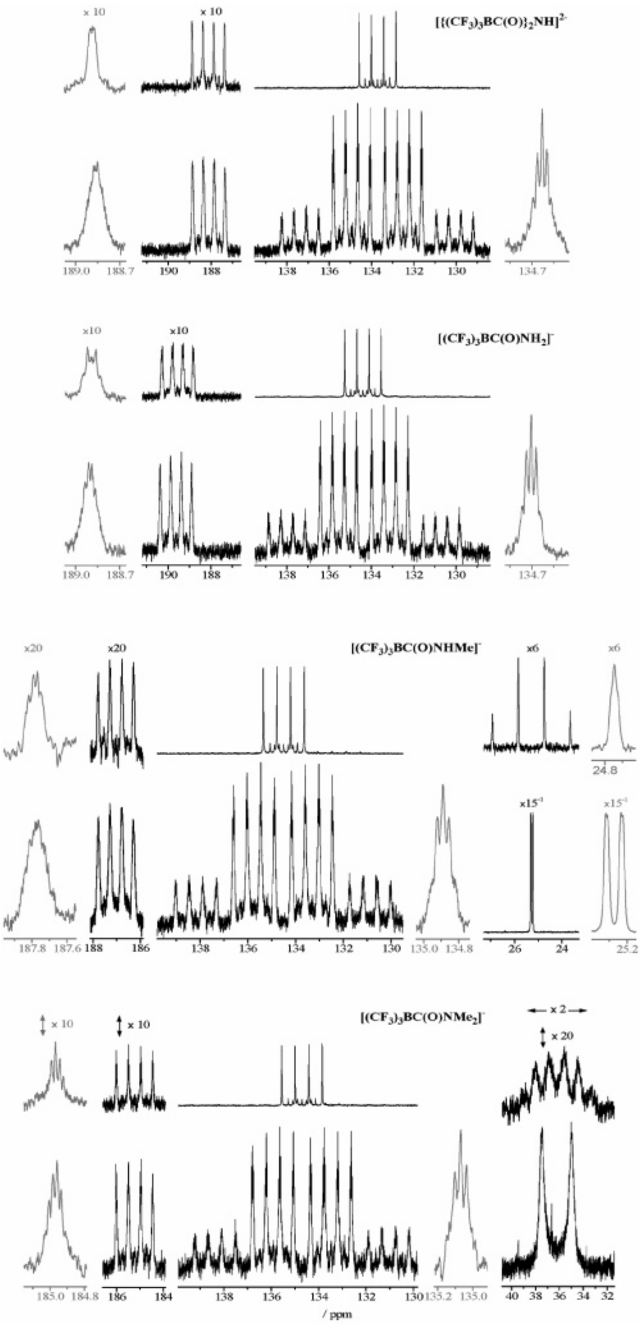

Figure 8. $[\{(CF_3)_3BC(O)\}_2NH]^{2-}$, $^{13}C\{^1H\}$ (top, ^{14}N) and $^{13}C\{^{19}F\}$ NMR spectra (bottom, ^{14}N); $[(CF_3)_3BC(O)NH_2]^-$, $^{13}C\{^1H\}$ (top, ^{14}N) and $^{13}C\{^{19}F\}$ NMR spectra (bottom, ^{15}N); $[(CF_3)_3BC(O)NHMe]^-$, $^{13}C\{^1H\}$ (top, ^{15}N) and $^{13}C\{^{19}F\}$ NMR spectra (bottom, ^{14}N); $[(CF_3)_3BC(O)NMe_2]^-$, $^{13}C\{^1H\}$ (top, ^{14}N) and $^{13}C\{^{19}F\}$ NMR spectra (bottom, ^{14}N).

37.5 ppm, respectively, are explained by slow rotation of the NMe_2 group. In contrast, the rotation of the NHMe group in $[(CF_3)_3BC(O)NHMe]^-$ and the NH_2 group in $[(CF_3)_3BC(O)NH_2]^-$ are frozen because neither the ^{13}C nor the ^1H NMR spectra show any broadening for the respective signals.

The ^1H chemical shifts of the carbamoyl groups (Table 4, Figure S5) are similar to $\delta(^1H)$ of related organic compounds.[53] Two different signals are found in the ^1H NMR spectrum of the $[(CF_3)_3BC(O)NH_2]^-$ anion, due to the hindered rotation of the NH_2 group. In the $^1H\{^{14}N\}$ NMR spectrum of $[(CF_3)_3BC(O)NH_2]^-$, only the signal at 6.1 ppm shows a ^3J coupling to ^{11}B (4.2 Hz). Taking the results of ^{11}B NMR spectroscopy into account, this proton is in trans position to boron. In the case of $[\{(CF_3)_3BC(O)\}_2NH]^{2-}$ and $[(CF_3)_3BC(O)NHR]^-$ (R = Me, ^{n}Pr), the $^5J(^1H,^{19}F)$ coupling (0.8−1.0 Hz) was found in the $^1H\{^{11}B\}$ NMR spectra (Lorentz−Gauss processing[54,55]). For $(CF_3)_3BC(O)PMe_3$, even the $^6J(^1H,^{19}F)$ coupling (0.3 Hz) is observed. Similar long-range, through-space couplings have been reported for $(CF_3)_3CC(O)NMe_2$.[43]

Summary and Conclusion

Reactions of the borane carbonyl $(CF_3)_3BCO$ with selected amines and phosphines were studied. The exclusive attack at the carbonyl C atom is remarkable, although ligand exchange under release of CO is thermodynamically favored, as predicted by DFT calculations. This behavior contrasts the reactions of HCN and nitriles with $(CF_3)_3BCO$ where only exchange products are obtained.[14]

Especially the syntheses of $[(CF_3)_3BC(O)NH_2]^-$ using either $(CF_3)_3BCO$ or $K[(CF_3)_3BC(O)F]$ are of interest because $[(CF_3)_3BC(O)NH_2]^-$ salts are starting materials for the syntheses of $[(CF_3)_3BCN]^-$ salts.[16] Recently, the potential of $[(CF_3)_3BCN]^-$ as a novel ligand was demonstrated by the synthesis of $(PPh_3)_3RhNCB(CF_3)_3$.[21] Furthermore, the straightforward preparation of the dimeric borate anion $[\{(CF_3)_3BC(O)\}_2NH]^{2-}$ promises to enable its application as a bidentate chelating ligand in transition metal chemistry. In the crystal structure of $K_2[\{(CF_3)_3BC(O)\}_2NH]\cdot 2MeCN$, the chelating ability of the diborate anion is already demonstrated.

The novel $(CF_3)_3B$ compounds are extensively characterized by multinuclear NMR spectroscopy and by vibrational spectroscopy, as well as their thermal properties. Noteworthy are their well-resolved, highly coupled NMR spectra, which are unusual for ^{11}B NMR spectroscopy.[14, 52]

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Supporting Information Available: A view of the unit cell of $K_2[\{(CF_3)_3BC(O)\}_2NH]\cdot 2MeCN$; plots of the ^{15}N and ^1H NMR spectra of $[(CF_3)_3BC(O)NH_2]^-$ and $[\{(CF_3)_3BC(O)\}_2NH]^{2-}$; a figure of the ^{11}B and ^{19}F NMR spectra of $(CF_3)_3BC(O)NMe_3$ and $(CF_3)_3BC(O)PMe_3$ and a plot of the ^{13}C NMR spectrum of $(CF_3)_3BC(O)PMe_3$; a table with the calculated energies, ZPCs and enthalpies; a table with the experimental (K^+ salt), as well as calculated vibrational data of the $[(CF_3)_3BC(O)NH_2]^-$ anion; and a table with NMR spectroscopic relaxation rates and line widths. This material is available free of charge via the Internet at http://pubs.acs.org.

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