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Weakly Coordinating Anions

Trifluoromethylboranes and -Borates: New Synthetic Strategies and Applications

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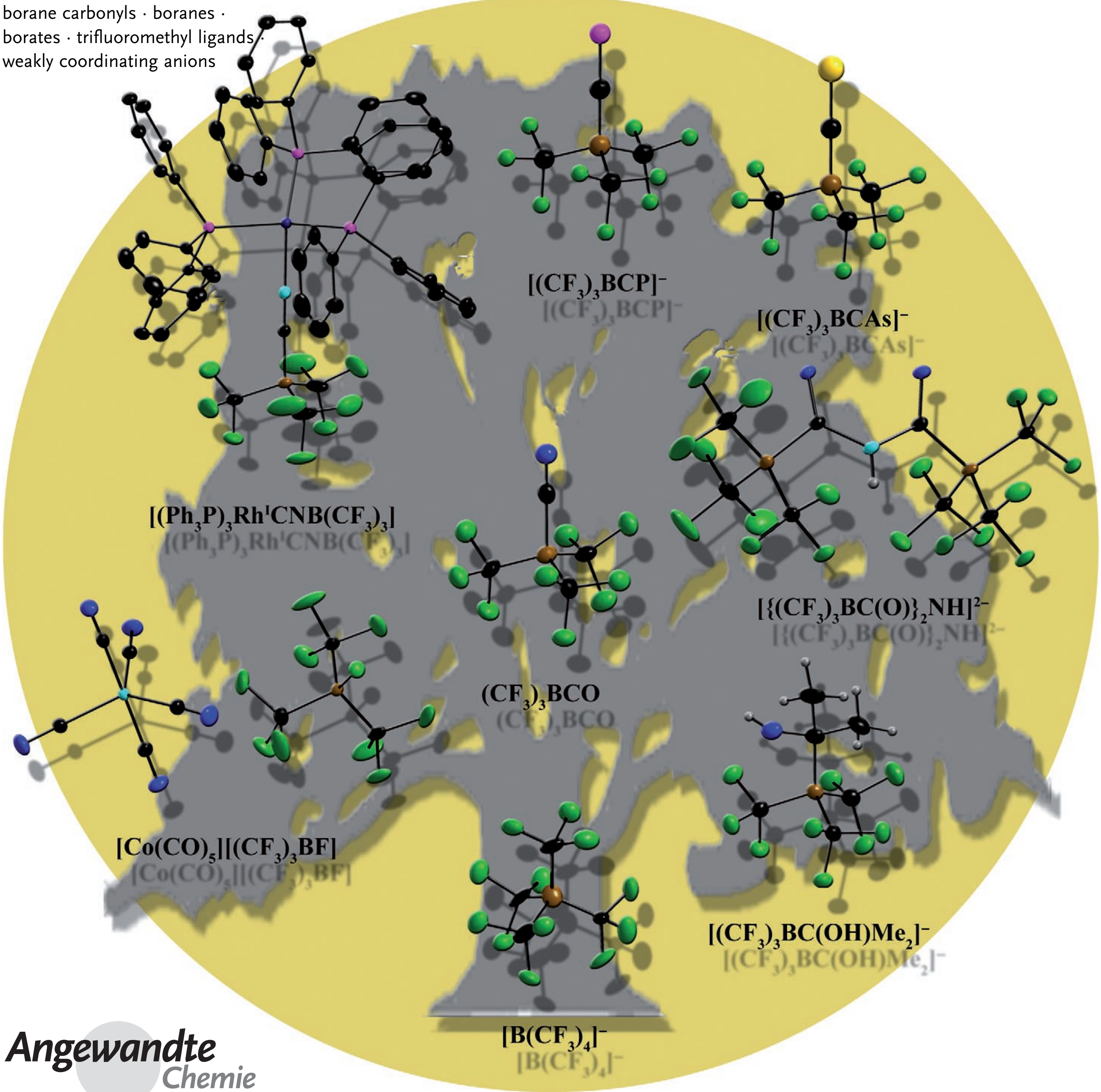

The synthesis of salts with the $[B(CF_3)_4]^-$ anion has been the starting point for new developments in the field of trifluoromethylboron chemistry. In contrast to the previous syntheses of $(CF_3)_nB$ derivatives ($n = 1$–3), achieved exclusively by CF_3 transfer, the synthesis of the $[B(CF_3)_4]^-$ anion was accomplished by fluorination of the $[B(CN)_4]^-$ anion with ClF or ClF_3 in anhydrous HF. Owing to its thermal and chemical stability, $[B(CF_3)_4]^-$ is an attractive weakly coordinating anion. However, in concentrated sulfuric acid one of the four CF_3 groups is solvolyzed to a CO ligand to yield the neutral borane carbonyl $(CF_3)_3BC{\equiv}O$. It has been shown that the borane carbonyl compound is a versatile synthetic building block, and numerous reactions have been investigated. The addition of nucleophiles to the C atom of the CO ligand is favored, and examples for new derivatives are the anions $[(CF_3)_3BC{\equiv}Pnic]^-$ (Pnic = N, P, As). Under certain conditions, ligand-exchange reactions are also observed, for example, the formation of $(CF_3)_3BN{\equiv}CH$. Finally, the borane carbonyl compound is a component of the conjugated Brønsted–Lewis superacid $HF/(CF_3)_3BCO$.

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1. Introduction

Weakly coordinating anions play a key role in electrochemical, synthetic, catalytic, and photochemical processes as well as for the stabilization of highly reactive cations.[1–5] With increasing requirements concerning their chemical, thermal, and electrochemical stabilities, new weakly coordinating anions have been developed, and their properties have been tuned according to their special demands. The largest group of new weakly coordinating anions, which have been developed since the beginning of the 1990s, carry perfluorinated alkyl or aryl substituents.[4,5] Fluorinated tetraarylborates are a well-developed and extensively investigated class of weakly coordinating anions, which are suited for the stabilization of highly reactive cations such as $[Cp^R_2ZrMe]^+$[4] or R_3Si^+.[6] However, a crucial weakness of these anions is their sensitivity towards electrophilic attack at the *ipso*-C atom of the aryl groups. A possibility to avoid this problem is the exchange of the perfluoroaryl ligands against perfluoroalkyl groups, that is, the synthesis of tetrakis(perfluoroalkyl)borates.

The simplest member of this group is the tetrakis(trifluoromethyl)borate anion $[B(CF_3)_4]^-$, which was unknown until the beginning of our investigations. In contrast, numerous trifluoromethylboron compounds with one, two, and three CF_3 groups have been described, and the results were summarized in 1995[7] and in 2000.[8] Since all known syntheses of B-CF_3 compounds are CF_3 transfer reactions, which are not appropriate for the preparation of the $[B(CF_3)_4]^-$ anion, and because no suitable starting compound is available for a direct fluorination, the development of a new synthetic route was necessary.

An elegant access to the $[B(CF_3)_4]^-$ anion was found in the fluorination of the tetracyanoborate anion,[9] which was prepared for this purpose for the first time.[10] In subsequent studies the syntheses of $[B(CN)_4]^-$[11,12] and $[B(CF_3)_4]^-$[13] have been improved. A series of reactive cations was stabilized with the $[B(CF_3)_4]^-$ ion, for example Ag^+,[9] $[Ag(CO)_n]^+$ ($n = 1$–4),[9] NO^+,[14] Ph_3C^+,[15] $[H(Et_2O)_2]^+$,[15] $[Co(CO)_5]^+$,[16,17] $[Co(CO)_2(NO)_2]^+$,[17] and $[Ru(CO)_5NO]^+$.[18] The Li salt is a very good conducting salt for lithium ion batteries,[19] and applications of the $[B(CF_3)_4]^-$ anion in the area of ionic liquids have also been investigated.[20]

The $[B(CF_3)_4]^-$ anion reacts with concentrated sulfuric acid, and the previously unknown carbonyltris(trifluoromethyl)borane $(CF_3)_3BCO$[21,22] is obtained. It is the only mononuclear borane carbonyl that is sufficiently stable for subsequent studies besides H_3BCO, the simplest borane carbonyl possible. In addition, some other B-CO compounds with B–B bonds are known.[22–26]

The syntheses and reactions of salts of the $[B(CF_3)_4]^-$ anion as well as of the borane carbonyl $(CF_3)_3BCO$ are summarized in this review. The borane carbonyl $(CF_3)_3BCO$ was established as a synthetic building block for other boranes and borates containing the unstable and inaccessible free Lewis acid $(CF_3)_3B$. Interesting examples for new compounds are salts of the first phospha- and arsaethynyl complexes of

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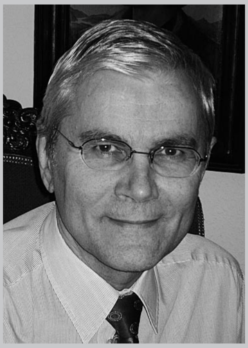
boron $[(CF_3)_3BCP]^-$ and $[(CF_3)_3BCAs]^-$.[27] Moreover, with anhydrous hydrogen fluoride, $(CF_3)_3BCO$ forms a conjugated Brønsted–Lewis superacid that contains the weakly coordinating anion $[(CF_3)_3BF]^-$.[16,28]

New aspects of CF_3 transfers onto boron as well as novel developments in the chemistry of trifluoromethyl-substituted carboranes and -borates are also discussed herein.

2. Synthetic Methods for CF_3-B Compounds

The first synthesis of compounds containing a CF_3-B group was accomplished by CF_3 transfer to BF_3 using Me_3SnCF_3. This method results in a mixture of the borate anions $[CF_3BF_3]^-$ and $[(CF_3)_2BF_2]^-$, and their ratios can be tuned by variation of the reaction conditions [Eq. (1)].[7,8,29,30]

$$\begin{aligned} &BF_3 + Me_3SnCF_3 \xrightarrow{CCl_4} [Me_3Sn][CF_3BF_3] \\ &[Me_3Sn][CF_3BF_3] + Me_3SnCF_3 \xrightarrow{CCl_4} [Me_3Sn][(CF_3)_2BF_2] + Me_3SnF \end{aligned} \qquad (1)$$



Helge Willner, born 1947 in Hamm, Germany, studied chemistry at the University of Münster and received his doctorate in 1974 with H. J. Becher. During a postdoctoral stay with A. Haas at the University of Bochum, he started with fluorine chemistry by application of matrix isolation. After a stay with L. Andrews in Charlottesville, USA, he finished his habilitation in 1981 and was appointed Professor at the University of Hannover in 1982. He worked on superacids and homoleptic transition-metal carbonyl cations as a visiting member in the group of F. Aubke, Vancouver, Canada. Since being appointed Professor at the Universities of Duisburg in 1998 and Wuppertal in 2003, he has concentrated his work on small reactive molecules and radicals, weakly coordinating anions, and coordination chemistry in superacidic media.

Maik Finze, born in 1975 in Nienburg, Germany, studied chemistry at the University of Hannover and received his diploma (2002) and PhD (2004) under the guidance of H. Willner in Duisburg and Wuppertal. While a member of the group of R. M. Waymouth at Stanford University (1999/2000), he worked in the field of zirconocene chemistry. Since December 2004 he has been a member of W. Frank's group at the Heinrich-Heine-University of Düsseldorf. His current interests are the synthesis and characterization of novel substituted carborates and carboranes as functional building blocks.

Eduard Bernhardt, born in 1965 in Karaganda, USSR, studied chemistry from 1982 until 1990 at the Institute of Fine Chemical Technology in Moscow. He obtained his PhD in 1993 from the Russian Academy of Sciences in Moscow. From 1996 until 1997 he did postdoctoral research in the group of W. Preetz in Kiel, Germany. Since 1998 he has been working in the field of cationic carbonyl complexes and weakly coordinating borate ions with H. Willner.

Recently, it was shown that one CF_3 group can be added to trimethoxyborane by using trifluoromethyltrimethylsilane [Eq. (2)].[31]

$$B(OMe)_3 + Me_3SiCF_3 + KF \xrightarrow[RT,\ 18\ h]{THF} K[CF_3B(OMe)_3] + Me_3SnF \qquad (2)$$

The synthesis of boron derivatives with more than two CF_3 groups can not be achieved by trifluoromethyl transfer when the Lewis acidity of the B atom of the intermediate $(CF_3)_2BR$ is too high. The synthesis of boron with three trifluoromethyl ligands is possible by CF_3 transfer to aminoboranes R_2NBHal_2 (R = alkyl; Hal = Cl, Br), a class of boranes with a reduced Lewis acidity at the B atom owing to the nitrogen substituent.[7,8] Suitable CF_3 transfer compounds are Ruppert's[32] [Eq. (3)] and Pawelke's reagent[33] [Eq. (4)].

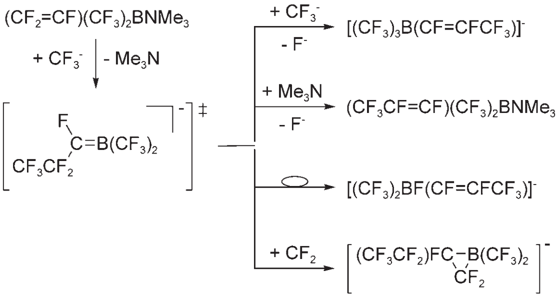
$$\begin{aligned} &Cl_2BNR_2 + 3\,P(NEt_2)_3 + 3\,CF_3Br \xrightarrow{CH_2Cl_2} \\ &[BrP(NEt_2)_3][(CF_3)_3BNR_2] + 2\,[ClP(NEt_2)_3]Br \end{aligned} \qquad (3)$$

$$\begin{aligned} &Cl_2BNR_2 + 3\,(Me_2N)_2C{=}C(NMe_2)_2 + 3\,CF_3I \xrightarrow{CH_2Cl_2} \\ &[(CF_3)_3BNR_2]^- + 3\,[(Me_2N)_2C\text{-}C(NMe_2)_2]^{2+} + 2\,Cl^- + 3\,I^- \end{aligned} \qquad (4)$$

The synthesis of $[Me_3NH][(CF_3)_3B(CF{=}CFCF_3)]$ starting from $[(CF_3)_2SiMe_3]^-$ and $(CF_2{=}CF)(CF_3)_2BNMe_3$, which is obtained from the reaction of $(CF_3)_2BNMe_2$ with CF_3CFH_2/*t*BuLi and subsequent methylation [Eq. (5)],[8,34] is another

$$\begin{aligned} &(CF_3)_2BNMe_2 + CF_3CFH_2 \xrightarrow[2.\ H_2O,\ -78\,^\circ C]{1.\ tBuLi,\ -78\,^\circ C} (CF_2{=}CF)(CF_3)_2BNHMe_2 \\ &\xrightarrow{KOH,\ Et_2O,\ MeI} (CF_2{=}CF)(CF_3)_2BNMe_3 \end{aligned} \qquad (5)$$

example for a CF_3 transfer to a donor-stabilized intermediate with two trifluoromethyl groups $[C_2F_5CF{=}B(CF_3)_2]^-$ [Eq. (6)].[35] Several side products (60 %) are formed during the reaction, because the intermediates $(CF_3)_2B(CF{=}CF_2)$ and $[C_2F_5CF{=}B(CF_3)_2]^-$ are less stable than $(CF_3)_2BNMe_2$ [Eq. (6)].[34,35]



(6)

All methods presented so far are not suitable for the synthesis of the tetrakis(trifluoromethyl)borate anion $[B(CF_3)_4]^-$.[7,8] A multistep replacement of the NH_2 ligand in $[(CF_3)_3BNH_2]^-$, which is accessible from $[(CF_3)_3BNR_2]^-$,[7,8,36] gives the $[B(CF_3)_4]^-$ anion in a mixture with other borate anions according to Equations (7) and (8). After workup, a mixture of salts containing the anions $[B(CF_3)_4]^-$ and $[(CF_3)_3BF]^-$ is obtained in a 1:1 ratio. Until now, a separation of the anions has not been achieved.[9]

$$Cs[(CF_3)_3BNH_2] + ONCF_3 \xrightarrow[Cs_2CO_3]{THF} Cs[(CF_3)_3BN{=}NCF_3] + H_2O \tag{7}$$

$$Cs[(CF_3)_3BN{=}NCF_3] \xrightarrow{h\nu} Cs[B(CF_3)_4] + N_2 \tag{8}$$

An alternative method to CF_3 transfer is the conversion of a ligand bound to boron into a trifluoromethyl group. An ideal candidate for this synthetic approach is the thermally and chemically stable tetracyanoborate anion $[B(CN)_4]^-$.[10] It is easily formed at 300°C from a mixture of $K[BF_4]/KCN/LiCl$.[12,20] In anhydrous HF the $[B(CN)_4]^-$ anion reacts with ClF or ClF_3 to produce the $[B(CF_3)_4]^-$ anion in a yield of approximately 60% and a purity of 95% [Eq. (9); aHF: anhydrous HF].[9,19] Salts of the $[B(CF_3)_4]^-$ anion have been characterized spectroscopically and structurally, and their thermal and electrochemical properties have been studied. In Figure 1 a model of the $[B(CF_3)_4]^-$ anion in the solid state is depicted. The steric shielding of the B atom and of the C atoms is obvious in the space-filling model, and it is one main reason for the stability of the anion.

$$M[B(CN)_4] + 4\,ClF_3 \xrightarrow{aHF} M[B(CF_3)_4] + 2\,Cl_2 + 2\,N_2 \tag{9}$$

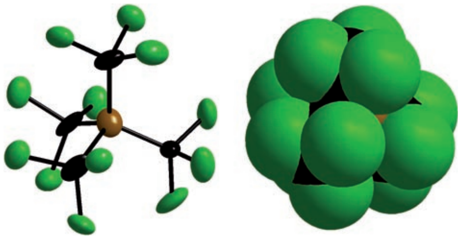


Figure 1. Ball-and-stick (left) and a space-filling model (right) of the $[B(CF_3)_4]^-$ ion in $K[B(CF_3)_4]$.[37]

An attractive alternative to the fluorination of the $[B(CN)_4]^-$ anion is the fluorination, ideally electrofluorination, of the easily accessible tetramethylborate anion $[BMe_4]^-$, but owing to the acid lability of $[BMe_4]^-$ this approach is not feasible.[38] In contrast, the conversion of B-Me groups into B-CF_3 groups was achieved in the case of the more stable boron cluster derivatives. Examples are the synthesis of $[CB_{11}(CF_3)_{12}]^-$ [Eq. (10), Figure 2],[39,40] $[1\text{-}H\text{-}2,3,4,5,6\text{-}F_5\text{-}CB_{11}(CF_3)_6]^-$, and $[1\text{-}H\text{-}CB_{11}(CF_3)_{11}]^-$ anions,[41] as well as the compounds $1,12\text{-}H_2\text{-}1,12\text{-}C_2B_{10}(CF_3)_{10}$ and $1\text{-}H\text{-}12\text{-}F\text{-}1,12\text{-}C_2B_{10}(CF_3)_{10}$ [Eq. (11)].[42]

$$\begin{aligned} &Cs[CB_{11}Me_{12}] \xrightarrow[SiO_2,\ CFCl_3]{F_2/N_2} Cs[CB_{11}C_{12}H_nF_{36-n}]\ (8 < n < 18) \\ &\xrightarrow[aHF]{K_2NiF_6} Cs[CB_{11}(CF_3)_{12}] \end{aligned} \tag{10}$$

$$\begin{aligned} &1,12\text{-}H_2\text{-}1,12\text{-}C_2B_{10}Me_{10} \xrightarrow[C_9F_{20}]{F_2/N_2} 1,12\text{-}H_2\text{-}1,12\text{-}C_2B_{10}(CF_3)_{10} \\ &+1\text{-}H\text{-}12\text{-}F\text{-}1,12\text{-}C_2B_{10}(CF_3)_{10} \end{aligned} \tag{11}$$

In contrast to the $B(CF_3)_4]^-$ anion,[9] the $[CB_{11}(CF_3)_{12}]^-$ anion is explosive.[39,40] Hence, its application as a weakly coordinating anion is difficult.

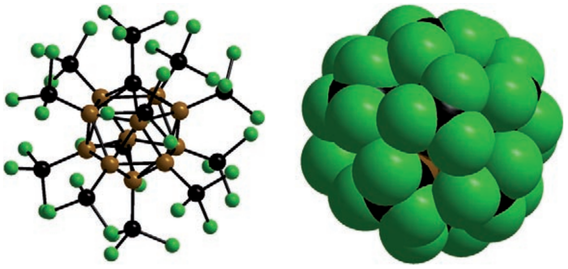


Figure 2. Calculated structure (B3LYP/6-31G*) of the $[CB_{11}(CF_3)_{12}]^-$ ion in ball-and-stick (left) and space-filling representation (right).

3. Tetrakis(trifluoromethyl)borates: Syntheses and Applications

The high chemical and electrochemical stability of the $[B(CF_3)_4]^-$ ion as well as the high thermal stability of its salts enable applications in many different fields, especially as weakly coordinating anion.[1,2,5,6] A 0.96 M solution of $Li[B(CF_3)_4]$, dissolved in a mixture of ethylene carbonate, diethyl carbonate, and dimethyl carbonate, exhibits a conductivity of 10.1 $mS\,cm^{-1}$; under comparable conditions, $Li[PF_6]$ shows a conductivity of 9.6 $mS\,cm^{-1}$ only.[19] Hence, $Li[B(CF_3)_4]$ is a promising conducting salt for lithium ion batteries. A series of ionic liquids has been prepared, and these are currently being tested for different applications.[20] Furthermore, cationic dyes have been synthesized with $[B(CF_3)_4]^-$ as the counteranion.[43] Moreover, a range of electrophilic cations has been stabilized with the $[B(CF_3)_4]^-$ anion; examples include: 1) $[Ag(CO)_n]^+$ ($n = 1$–4) from $Ag[B(CF_3)_4]$ in a CO atmosphere at different pressures,[9] 2) $[H(OEt)_2]^+$ in a metathesis reaction starting from the K^+ salt and HCl in diethyl ether [Eq. (12)],[15] 3) NO^+ by oxidation of $[C(NH_2)_3][B(CF_3)_4]$ [Eq. (13)],[14] 4) $[Co(CO)_5]^+$ [Eq. (14)],[16,17] 5) $[Co(CO)_2(NO)_2]^+$ [Eqs. (14) and (15)],[17] 6) $[Ru(CO)_5NO]^+$ [Eq. (16)],[18] and N_5^+ [Eq. (17)].[44]

$$K[B(CF_3)_4] + HCl + 2\,Et_2O \xrightarrow[-30\,^\circ C]{Et_2O} [H(OEt_2)_2][B(CF_3)_4] + KCl \tag{12}$$

$$\begin{aligned} &[C(NH_2)_3][B(CF_3)_4] + 11\,NO_2 \xrightarrow{NO_2} NO[B(CF_3)_4] + 3\,N_2 + CO_2 \\ &+6\,HNO_3 + NO \end{aligned} \tag{13}$$

$$\begin{aligned} &[Co_2(CO)_8] + 2\,NO[B(CF_3)_4] \xrightarrow[C_6H_{14}\ \text{or}\ CH_2Cl_2]{CO\ (2\ bar),\ RT} [Co(CO)_5][B(CF_3)_4] \\ &+[Co(CO)_2(NO)_2][B(CF_3)_4] + CO \end{aligned} \tag{14}$$

$$\begin{aligned} &[Co(CO)_3NO] + NO[B(CF_3)_4] \xrightarrow{CH_2Cl_2} \\ &[Co(CO)_2(NO)_2][B(CF_3)_4] + CO \end{aligned} \tag{15}$$

$$\begin{aligned} &[Ru_3(CO)_{12}] + 3\,NO[B(CF_3)_4] + 3\,CO \xrightarrow{aHF,\ CO\ (2\ bar)} \\ &3\,[Ru(CO)_5NO][B(CF_3)_4] \end{aligned} \tag{16}$$

$$N_5[SbF_6] + K[B(CF_3)_4] \xrightarrow[-64\,^\circ C]{SO_2} N_5[B(CF_3)_4] + K[SbF_6] \tag{17}$$

The trityl salt $[Ph_3C][B(CF_3)_4]$ was tested as a cocatalyst in the Ziegler–Natta polymerization of propylene. The stability of the borate anion under polymerization conditions was confirmed by NMR studies, performed on a reaction mixture of $[Ph_3C][B(CF_3)_4]$ and $[Cp_2ZrMe_2]$. Probably, the low yields of polymers were caused by the low solubility of the catalyst.[15]

In strong acidic reaction media applications of the $[B(CF_3)_4]^-$ ion are limited, as outlined in the following section.

4. Reactions of Trifluoromethyl Ligands at Boron with Lewis and Brønsted Acids

Abstractions of fluoride anions from trifluoromethyl groups bonded to boron that occur under action of strong Lewis or Brønsted acids are typical reactions for this class of compounds.[7,8,21,22,28] The intermediate difluorocarbene complexes are highly reactive; hence, all attempts to isolate them have been unsuccessful so far, and their formation is claimed on the basis of the observed reaction and decomposition products.[28] A number of syntheses of difluorocarbene complexes from CF_3 complexes are known in transition-metal chemistry, and some CF_2 complexes were isolated also.[45]

A pivotal problem of the synthesis of boron compounds with trifluoromethyl substituents is the intramolecular attack of the Lewis acidic B atom onto one bonded CF_3 group, under formation of a highly reactive CF_2 complex. Examples of such acid-mediated transformations of CF_3 ligands at boron are discussed below.

So far, CF_3BF_2 is not accessible, in contrast to perfluoroalkyldifluoroboranes with longer chains R^FBF_2 ($R^F = C_nF_{2n+1}$, $n \geq 2$), which are stable at room temperature.[28,46] Synthesis of CF_3BF_2 according to procedures reported earlier could not be reproduced.[7,47] Reaction of $K[CF_3BF_3]$ with AsF_5 gives a mixture of BF_3 and $C_2F_5BF_2$.[28] The easy formation of difluorocarbene and BF_3 by intramolecular fluorine transfer from carbon to boron and dissociation of the intermediate species CF_2BF_3, followed by trapping of difluorocarbene with CF_3BF_2, explains the instability of the borane as well as the formation of $C_2F_5BF_2$. In Figure 3 the transition state of the fluorine transfer is depicted, and the activation energy is calculated to be 80.7 kJ mol^{-1}.

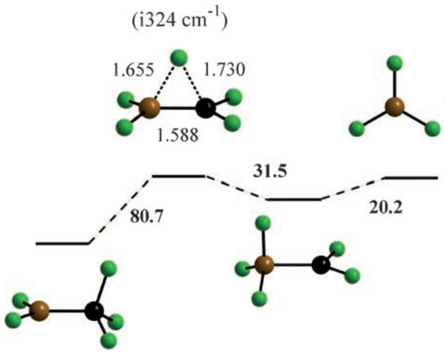


Figure 3. Calculated isomerization of CF_3BF_2 into F_3BCF_2 and dissociation of F_3BCF_2 into CF_2 and BF_3 (energy (bold type in kJ mol^{-1}) and geometry: B3LYP/6-311 + G(d); wavenumbers and zero-point corrections: B3LYP/6-311G(d)).[28]

Until now, similarly to CF_3BF_2, all attempts to obtain direct experimental evidence for the formation of $(CF_3)_3B$ have not been successful—not even by low-pressure flash pyrolysis of $(CF_3)_3BCO$ and application of the matrix-isolation technique.[28] In the product mixtures of all reactions, BF_3 and nonbranched perfluoroalkyldifluoroboranes R^FBF_2 ($R^F = C_nF_{2n+1}$, $n \geq 2$) were observed. An explanation for the formation of $C_2F_5BF_2$ and $C_3F_7BF_2$ is derived from the reaction course shown in Figure 4. The difluorocarbene

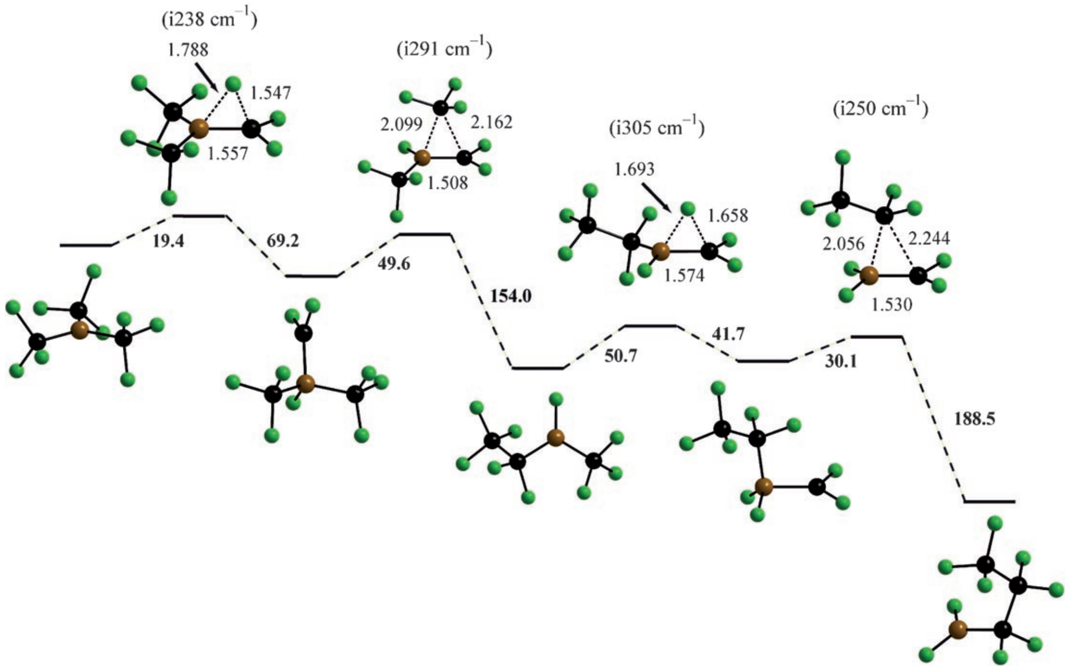
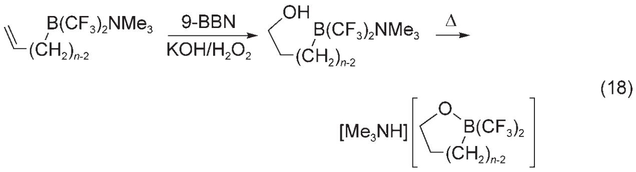


Figure 4. Calculated isomerization of $(CF_3)_3B$ to $C_3F_7BF_2$ (quantities defined as in Figure 3; energy and geometry: B3LYP/6-311 + G(d); wavenumbers and zero-point corrections: B3LYP/6-311G(d)).[28]

complexes $R^FBF_2(CF_2)$, which are formed as intermediate species, undergo reversible dissociation into CF_2 and R^FBF_2, or the perfluoroalkyl group migrates from the boron atom to the CF_2 ligand to give $R^FCF_2BF_2$. The formation of difluoroboranes with perfluoroalkyl chains with more than three C atoms is rationalized by trapping of difluorocarbene by perfluoroalkyldifluoroborane to yield difluorocarbene complexes and subsequent intramolecular perfluoroalkyl migration. $(CF_3)_2BF$ is expected to behave similarly to CF_3BF_2 and $(CF_3)_3B$, but no study has been undertaken so far.

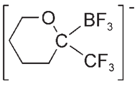
Salts of the $[B(CF_3)_4]^-$ ion react with strong Lewis acids under loss of a fluoride anion to give $(CF_3)_3BCF_2$ as an intermediate.[28] In the gas phase a mixture of BF_3 and linear perfluoroalkyldifluoroboranes R^FBF_2 ($R^F = C_nF_{2n+1}$, $n \geq 2$) is observed similar to the reaction of $(CF_3)_3B$. In addition, branched perfluoroalkyldifluoroboranes are obtained. Their formation is explained by the instability of $(C_2F_5)_2BF$, which isomerizes to $(C_2F_5)(CF_3)FCBF_2$ via a monofluorocarbene complex.

Recently, the syntheses of $[Me_3NH][cyclo\text{-}O(CH_2)_nB(CF_3)_2]$ ($n = 3, 4, 5$) by heating a suspension of $\{HO(CH_2)_n\}(CF_3)_2BNMe_3$ in nBu$_2$O at 140 °C were reported [Eq. (18)].[48]



(18)

The cyclic trifluoroborate anions **1** and **2** were identified as side products, and were partly isolated from the mixtures obtained after thermal treatment of $\{HO(CH_2)_n\}(CF_3)_2BNMe_3$ ($n = 4, 5$). Their formation indicates a reaction course[48] comparable to that found for the isomerisations of CF_3BF_2 (Figure 3), $(CF_3)_3B$ (Figure 4), and $(CF_3)_3BCF_2$. A similar consideration is reasonable for the formation of the cyclic side product **3**, which is obtained from the synthesis of $[(CF_3)_3B(CF{=}CFCF_3)]^-$ [see Eq. (6)].[35]



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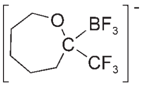

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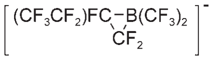


$$[(CF_3CF_2)FC(CF_2)\text{-}B(CF_3)_2]^-$$

3

The $[B(CF_3)_4]^-$ ion is not stable against concentrated sulfuric acid. Probably, in the first step the difluorocarbene complex $(CF_3)_3BCF_2$ is formed, which immediately reacts to give carbonyltris(trifluoromethyl)borane $(CF_3)_3BCO$ [Eq. (19)]. The borane carbonyl is isolated from the reaction mixture in 90% yield under reduced pressure.[21,22,49] Attempts to isolate $H_3O[B(CF_3)_4]$ at room temperature failed—under these conditions the borate anion probably reacts to form $(CF_3)_3BCO$ [Eq. (19)].[18]

$$[B(CF_3)_4]^- + H_3O^+ \xrightarrow[25\,^\circ C]{\text{conc. } H_2SO_4} (CF_3)_3BCO(g) + 3\,HF \qquad (19)$$

Previously, similar reactions of trifluoromethyl complexes of transition metals have been described.[50–53] Related reactions in organic chemistry are the hydrolyses of CF_3 groups bonded to aryl systems[54] and the reactions of perfluoroisobutene with SO_3 in the presence of Lewis acids to form derivatives of fluorosulfonic acids.[55–58] Attempts to synthesize $(CF_3)_2BF(CO)$ and $CF_3BF_2(CO)$ in an analogous manner failed. According to quantum chemical calculations, the B−CO bond energies strongly decrease from $(CF_3)_3B$, the strongest Lewis acid in the series $(CF_3)_nBF_{3-n}$, to BF_3, which explains the unsuccessful syntheses.[28] The trend in B−CO bond energies parallels the trend in fluoride ion affinity.

The wavenumber of the CO stretch of $(CF_3)_3BCO$ (2269 cm^{-1}) is the highest value observed for all borane carbonyls known so far (Table 1),[22] which reflects the strong Lewis acidity of the free borane $(CF_3)_3B$. Comparable wavenumbers have been reported for homoleptic transition-metal carbonyl cations, indicating a related bonding situation.[59–62] The thermal stabilities of the three borane carbonyl derivatives H_3BCO,[22,23,63] $(BF_2)_3BCO$,[24,26] and $(BCl_2)_3BCO$[26] are comparable to the stability of $(CF_3)_3BCO$ (Table 1). All other B-CO complexes investigated until now (except for CO complexes of boron clusters) are weak van der Waals adducts only.[22,23] Examples include the above-mentioned adduct F_3BCO[23,64] or $(C_6F_5)_3BCO$.[22,65] Thermally stable B-CO complexes of boron clusters are, for example, 1,10-$B_{10}H_8(CO)_2$,[25] 1,12-$B_{12}H_{10}(CO)_2$,[25] and 7-Me_3N-9-OC-7-$CB_{10}H_{10}$.[66]

Table 1: Properties of selected borane carbonyl derivatives.[a]

compound	T_{decomp}[b]	Ref.	D(B-C) [kJ mol^{-1}]	Ref.	r(B-C) [Å]	Ref.	$\tilde{\nu}_{CO}$ [cm^{-1}]	Ref.
F_3BCO	−200	[23]	7.6	[64]	2.89	[67]	2151	[68]
$(C_6F_5)_3BCO$	−100	[22]	(38)	[65]	(1.61)	[65]	2230	[22]
$(CF_3)_3BCO$	0	[22]	112	[22]	1.62	[22]	2269	[22]
H_3BCO	10	[22]	90	[c]	1.53	[69]	2165	[70]
$(BF_2)_3BCO$	20	[26]			1.52	[26]	2162	[24]
$(BCl_2)_3BCO$	20	[26]			1.54	[26]	2176	[26]
1,10-$B_{10}H_8(CO)_2$	200	[25]				[25]	2147	[25]
1,12-$B_{12}H_{10}(CO)_2$	400	[25]			1.54	[71]	2210	[25]

[a] Calculated values in parentheses. [b] In °C; estimated by behavior described in the literature. [c] Estimate from five experimental values according to reference [65].

5. HF/(CF$_3$)$_3$BCO: A Conjugated Brønsted–Lewis Superacid

In anhydrous HF, (CF$_3$)$_3$BCO behaves as a synthon for the unstable Lewis acid (CF$_3$)$_3$B, and it forms a Brønsted superacid [Eq. (20)].[16,17,28] The reaction of the borane carbonyl

$$(CF_3)_3BCO(solv) + 2\,HF(l) \xrightarrow{aHF} [H_2F][(CF_3)_3BF](solv) + CO(g) \quad (20)$$

with anhydrous HF in the presence of [Co$_2$(CO)$_8$] gives the sparingly soluble salt [Co(CO)$_5$][(CF$_3$)$_3$BF], which contains the first example of a trigonal-bipyramidal homoleptic metal carbonyl cation [Eq. (21)] (Figure 5).[16,17] In a similar fashion

$$2\,(CF_3)_3BCO + [Co_2(CO)_8] + 2\,HF \xrightarrow[CO\ (2\ bar)]{aHF} 2\,[Co(CO)_5][(CF_3)_3BF] + H_2 \quad (21)$$

[Mn$_2$(CO)$_{10}$] reacts with HF/(CF$_3$)$_3$BCO to give [Mn(CO)$_6$][(CF$_3$)$_3$BF].[72] [Ru$_3$(CO)$_{12}$] yields poorly soluble [Ru(CO)$_6$][C$_2$F$_5$BF$_3$]$_2$ as sole product in one day [Eq. (22)].[73]

$$6\,(CF_3)_3BCO + [Ru_3(CO)_{12}] + 12\,HF \xrightarrow[CO\ (0.5\ bar),\ RT]{aHF} 3\,[Ru(CO)_6][C_2F_5BF_3]_2 + 3\,H_2 + 6\,HCF_3 \quad (22)$$

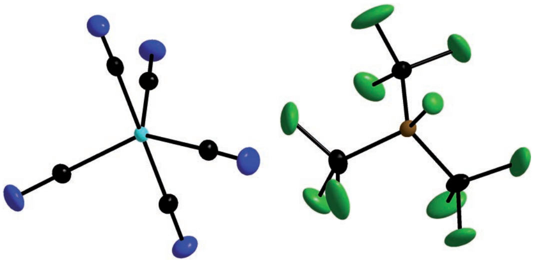


Figure 5. Structure of a formula unit of [Co(CO)$_5$][(CF$_3$)$_3$BF] in the solid state.[16,17]

The formation of the [C$_2$F$_5$BF$_3$]$^-$ ion can be explained by the slow oxidation of [Ru$_3$(CO)$_{12}$] to [Ru(CO)$_6$]$^{2+}$, enabling the transformation of [(CF$_3$)$_3$BF]$^-$ into [C$_2$F$_5$BF$_3$]$^-$. Probably, a further reason is a higher lattice energy of [Ru(CO)$_6$][C$_2$F$_5$BF$_3$]$_2$ in comparison to that of [Ru(CO)$_6$][(CF$_3$)$_3$BF]$_2$.[73] The formation of [Ru(CO)$_6$][BF$_4$]$_2$[74] in anhydrous HF in the presence of BF$_3$ is significantly slower—even after one week the reaction is incomplete, owing to the lower acidity of the system HF/BF$_3$.

The reaction of [Fe(CO)$_5$] with HF/(CF$_3$)$_3$BCO leads to the formation of [HFe(CO)$_5$][C$_2$F$_5$BF$_3$], and not [Fe(CO)$_6$][(CF$_3$)$_3$BF]$_2$ as expected [Eq. (23)].[73] Similarly, [HFe(CO)$_5$][BF$_4$] is obtained by treatment of either [Fe(CO)$_5$] or [Fe$_3$(CO)$_{12}$] with HF/BF$_3$.[73] At room temperature and under reduced pressure the tetrafluoroborate salt decomposes in a reverse reaction to [Fe(CO)$_5$], BF$_3$, and HF. The corresponding salt of the more weakly coordinating ion [C$_2$F$_5$BF$_3$]$^-$ is stable up to 66 °C.

$$(CF_3)_3BCO + [Fe(CO)_5] + 2\,HF \xrightarrow[XO\ (0.5\ bar),\ RT]{aHF} [HFe(CO)_5][C_2F_5BF_3] + CO + HCF_3 \quad (23)$$

In contrast, to other conjugated Brønsted–Lewis superacids such as HF/SbF$_5$, the system HF/(CF$_3$)$_3$BCO is nonoxidizing, thereby allowing the synthesis of oxidation-sensitive cations stabilized with the anions [(CF$_3$)$_3$BF]$^-$ or [C$_2$F$_5$BF$_3$]$^-$.

6. Carbonyltris(trifluoromethyl)borane: A Synthon for the Unstable Free Lewis Acid (CF$_3$)$_3$B

The carbonyltris(trifluoromethyl)borane is an ideal starting material for the synthesis of boranes and borate ions with one or more (CF$_3$)$_3$B groups. Its attractiveness as a reagent is especially due to the possibility to prepare derivatives of (CF$_3$)$_3$B having a fourth ligand that is bonded through a C atom to boron. Until now, there was no synthetic access to this class of compounds known. Suitable starting materials and tuning of the reaction conditions enabled the syntheses of species of the type (CF$_3$)$_3$BX by ligand-exchange reactions with X = F, Cl, O, S, Se, Te, and N.

Nucleophiles either add to the C atom of the carbonyl ligand of (CF$_3$)$_3$BCO or they displace the CO ligand in an S$_N$2 reaction. A survey on the addition reactions with nucleophiles of Group 14 to Group 17 that have been investigated so far is given in Scheme 1 a, and in Scheme 1 b the ligand-exchange reactions are summarized. Addition to the electrophilic C atom is favored; hence, ligand exchange is observed only when no stable addition product is formed.

In principle, the three related borane carbonyls H$_3$BCO,[23,63] (BF$_2$)$_3$BCO,[24,26] and (BCl$_2$)$_3$BCO[26] are suited for an investigation of their chemistry because of their thermal stabilities. But only in the case of H$_3$BCO have reactions with nucleophiles been studied.[63,75–78] Similar to the reactions of (CF$_3$)$_3$BCO, nucleophiles react with H$_3$BCO either under addition or ligand exchange. In many cases the hydridic H atoms react with the primarily formed products; thus, the synthesis of H$_3$B complexes is much more limited compared to the preparation of derivatives of (CF$_3$)$_3$B.

Carbonyl ligands bonded to boron clusters can only undergo addition reactions with nucleophiles[25,66,79] because ligand-exchange reactions are excluded. Owing to the cluster geometry, a backside attack (S$_N$2) to the B atom is impossible, and the strong bond of the CO ligand to the electrophilic B atom precludes a mild dissociative mechanism (S$_N$1) in general.

6.1. Halogenoacyltris(trifluoromethyl)borates

Alkali-metal salts of the [(CF$_3$)$_3$BC(O)F]$^-$ ion are synthesized from (CF$_3$)$_3$BCO and the corresponding fluoride salt in liquid SO$_2$ (Scheme 1 a).[80,81] Long reaction times must be avoided because the [(CF$_3$)$_3$BC(O)F]$^-$ ion slowly reacts with SO$_2$F$^-$ under exchange of fluorine against oxygen. In the first step the [(CF$_3$)$_3$BCO$_2$]$^{2-}$ ion is formed, which subsequently reacts with [(CF$_3$)$_3$BC(O)F]$^-$ to give [{(CF$_3$)$_3$BC(O)}$_2$O]$^{2-}$ and F$^-$. All attempts to prepare the higher halogenoacyltris(trifluoromethyl)borates in SO$_2$ have been unsuccessful, and the

Scheme 1. Reactions of nucleophiles with $(CF_3)_3BCO$. a) Additions to the C atom of the CO ligand; b) exchange reactions with the CO ligand.

product mixtures obtained indicate that the $[\{(CF_3)_3BC(O)\}_2O]^{2-}$ ion is the main product. Owing to the increased reactivity of $[(CF_3)_3BC(O)Hal]^-$ (Hal = Cl, Br, I) compared to $[(CF_3)_3BC(O)F]^-$, the reactions with the corresponding halogenosulfinate ions to give $[\{(CF_3)_3BC(O)\}_2O]^{2-}$ proceed faster.[81]

In dichloromethane the halogenide ions Cl^-, Br^-, and I^- add to the C atom of the carbonyl ligand of $(CF_3)_3BCO$ in the presence of the weakly coordinating cations $[Et_4N]^+$, $[nBu_4N]^+$, and $[Ph_4P]^+$ (Scheme 1 a).[81] An alternative synthetic approach is halogenide exchange in $[nBu_4N][(CF_3)_3BC(O)F]$ using trimethylsilylhalogenides [Eq. (24)].

$$[nBu_4N][(CF_3)_3BC(O)F] + Me_3SiHal \xrightarrow{CH_2Cl_2} [nBu_4N][(CF_3)_3BC(O)Hal] + Me_3SiF \qquad (24)$$

The analogous exchange reactions with $K[(CF_3)_3BC(O)F]$ in acetonitrile solution give $[(CF_3)_3BC(O)Hal]^-$ as primary products. In a second step the corresponding potassium halogenide precipitates from the solution, and $(CF_3)_3BNCMe$ is formed under release of CO as the final product [Eq. (25)].[81]

$$K[(CF_3)_3BC(O)F] \xrightarrow[-Me_3SiF]{+Me_3SiHal} K[(CF_3)_3BC(O)Hal] \xrightarrow[-KHal]{} (CF_3)_3BCO \xrightarrow[-CO]{+MeCN} (CF_3)_3BNCMe \qquad (25)$$

The reaction rate for the formation of the borane carbonyl from $K[(CF_3)_3BC(O)Hal]$ [see Eq. (25)] increases in the order $Cl^- < Br^- < I^-$. This is a general trend in reactivity observed for the halogenoacylborate anions. The thermal stabilities of the corresponding tetrabutylammonium salts parallel the reactivities: $[nBu_4N][(CF_3)_3BC(O)F]$ melts at 145 °C and decomposes at 180 °C; $[nBu_4N][(CF_3)_3BC(O)Cl]$ melts at 133 °C and decomposition begins at 166 °C; $[nBu_4N][(CF_3)_3BC(O)Br]$ as well as $[nBu_4N][(CF_3)_3BC(O)I]$ melt under decomposition at 100 and 60 °C, respectively.[81]

During all reactions described above, no $[(CF_3)_3BHal]^-$ (Hal = F, Cl, Br, I) is formed—salts of these anions are formed as intermediates during thermal decomposition of the halogenoacylborates.[81] Except for the $[(CF_3)_3BI]^-$ ion all anions of the series have been prepared previously from $[(CF_3)_3BNH_2]^-$ salts.[7,8,36] $(CF_3)_3BCO$ reacts with nitrosyl chloride under release of CO to give $NO[(CF_3)_3BCl]$ (Scheme 1 b).[81]

The synthetic entries to $(CF_3)_3BC$ derivatives, starting from the borane carbonyl and a nucleophile (Scheme 1 a), are limited owing to the high reactivity of $(CF_3)_3BCO$ and the restricted number of suitable solvents. In many cases the halogenoacyltris(trifluoromethyl)borates provide a better alternative, because they tolerate a larger number of more reactive solvents, for example, tetrahydrofuran, owing to their reduced reactivity. In addition, in some cases the reactions proceed with higher selectivity. Their salts are nonvolatile, stable under an inert atmosphere at room temperature, and easier to handle. In contrast, the borane carbonyl has a half-life of 45 min at 28 °C. The reactions of salts of $[(CF_3)_3BC(O)F]^-$ and $[(CF_3)_3BC(O)Cl]^-$ investigated are summarized in Scheme 2. A comparison of the reactions of $(CF_3)_3BCO$ (Scheme 1) to those of the halogenoacylborate ions shows that some reactions are similar; for example, upon addition of water, $[(CF_3)_3BC(O)OH]^-$ is obtained in all cases. Other syntheses give different results; the most striking example are the reactions with $K[X(SiMe_3)_2]$ (X = P, As). With $(CF_3)_3BCO$ a complex reaction mixture is formed, reaction with $[(CF_3)_3BC(O)Cl]^-$ gives the phospha- and arsaethynyl complexes $[(CF_3)_3BCX]^-$,[27] and with $[(CF_3)_3BC(O)F]^-$ the dianions $[(CF_3)_3BC(OSiMe_3)XC(O)B(CF_3)_3]^{2-}$ are obtained.[73]

The reactivities of $[(CF_3)_3BC(O)Cl]^-$ and $[(CF_3)_3BC(O)Br]^-$ are very similar, but a small difference is found for the reactions with tributyltin hydride. With the chlorine derivative the aldehyde $[(CF_3)_3BC(O)H]^-$ is formed quantitatively (Scheme 2), and with the bromoacylborate anion a complex reaction course is observed. This complexity is due to the reaction of $[(CF_3)_3BC(O)H]^-$ with $[(CF_3)_3BC(O)Br]^-$, which has not reacted with nBu_3SnH.

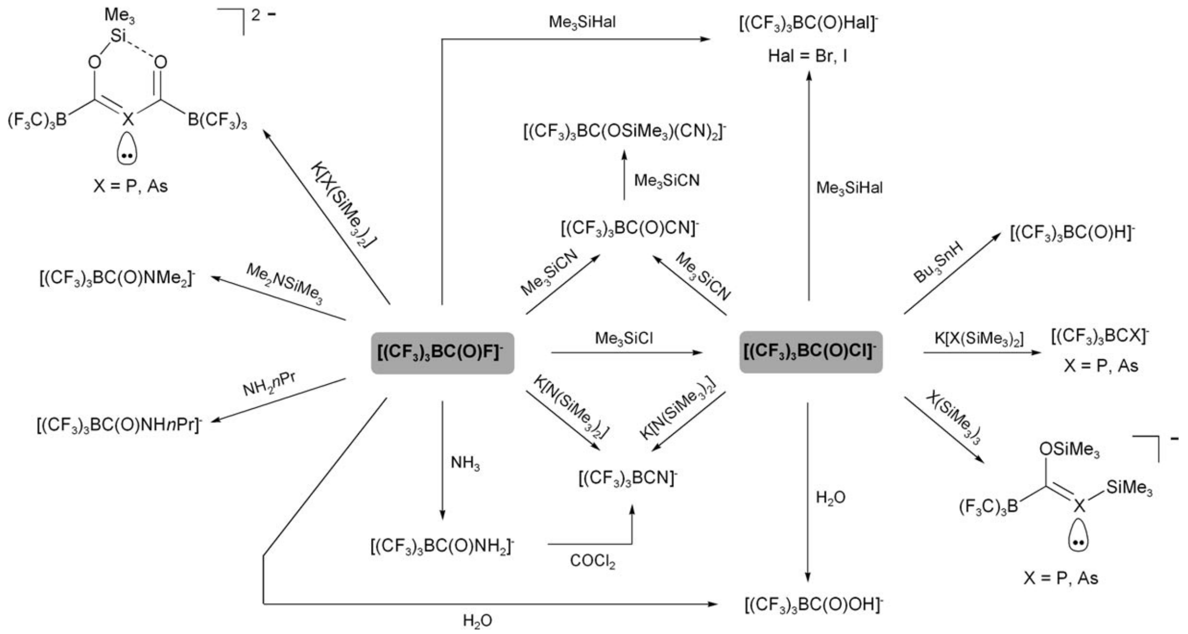
So far, no other halogenoacyl complexes of mononuclear boranes or borates are known; the synthesis of $[H_3BC(O)Cl]^-$ from H_3BCO and chloride was unsuccessful.[77] Hence, a comparison of the chemistry is not possible. However, the reactions described for $[(CF_3)_3BC(O)Hal]^-$ (Hal = F, Cl, Br) are similar to reactions of chloro and fluoroacyl substituents of B atoms of *o*-, *m*-, and *p*-carboranes[82–84] as well as acid chlorides in organic chemistry.[85]

6.2. $(CF_3)_3BXMe_2$ (X = O, S, Se, Te)—Reactions of $(CF_3)_3BCO$ with Chalcogen Bases

Water and alcohols reversibly add to the C atom of the carbonyl ligand of $(CF_3)_3BCO$ [Scheme 1 a, Eq. (26)].[22]

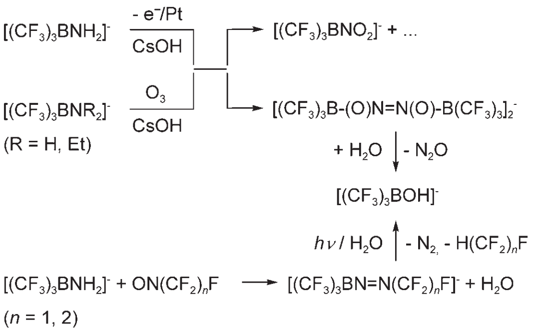
$$(CF_3)_3BCO + ROH \rightleftharpoons (CF_3)_3BC(OH)OR \underset{-ROH}{\overset{+ROH}{\rightleftarrows}} [ROH_2][(CF_3)_3BC(O)OR] \quad (26)$$

After addition of bases, thermally stable salts of the ions $[(CF_3)_3BC(O)OH]^-$, $[(CF_3)_3BCO_2]^{2-}$, and $[(CF_3)_3BC(O)OR]^-$ are obtained. The pK_a values for the loss of the two protons of $(CF_3)_3BC(OH)_2$ in water are < 1.5 and 7.0, respectively.[22] These pK_a values are comparable to those reported for the loss of the first two protons (4.2) and the second two protons (9.0) of $1,12\text{-}B_{12}H_{10}\{C(OH)_2\}_2$.[71] No ligand-exchange products, for example, $(CF_3)_3BOH_2$ or $[(CF_3)_3BOH]^-$, have been found in the reaction mixtures after addition of water. The $[(CF_3)_3BOH]^-$ ion was prepared by oxidation starting either from $[(CF_3)_3BNH_2]^-$ and



Scheme 2. Reactions of the borate ions $[(CF_3)_3BC(O)Hal]^-$ (Hal = F, Cl) with nucleophiles.

$[(CF_3)_3BNEt_2]^-$,[86] or photochemically from $[(CF_3)_3BN{=}N(CF_2)_nF]^-$ in water [Eq. (27)].[8] Furthermore, it was identified as a side product in the reactions of salts of $[(CF_3)_3BNO_2]^-$ with $Et_3N{\cdot}HF$ at 230 °C[8] and in the synthesis of $[(CF_3)_3BH]^-$ salts.[87]



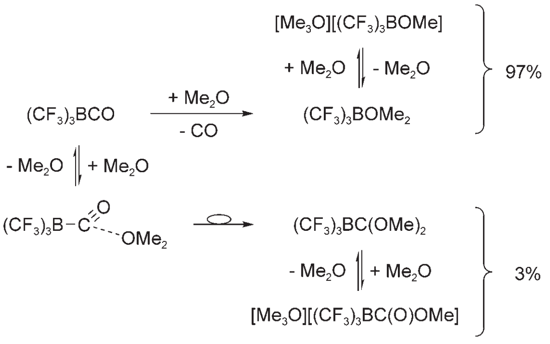
(27)

Recently, an almost quantitative synthesis of $[Me_3NH][(C_2F_5)_3BOH]$ using $(C_2F_5)_3BNMe_3$ and water as reagents was described [Eq. (28)].[88] This synthesis is not feasible for the

$$(C_2F_5)_3BNMe_3 + H_2O \xrightarrow{200\,^\circ C} [Me_3NH][C_2F_5)_3BOH] \qquad (28)$$

preparation of $[Me_3NH][(CF_3)_3BOH]$ owing to the reduced stability of CF_3 ligands in comparison to C_2F_5 groups attached to boron[28] and because of the stronger B−N bond in $(CF_3)_3BNMe_3$.[89]

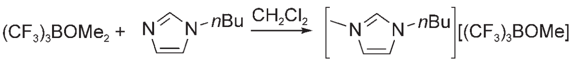
The reaction of dimethyl ether with $(CF_3)_3BCO$ proceeds under ligand exchange. $(CF_3)_3BOMe_2$ is obtained in a yield of 97 % and is contaminated by small amounts of side products (3 %) that are formed by addition reactions. Hence, this reaction is an efficient synthetic entry into $(CF_3)_3B$-O derivatives. The ions $[(CF_3)_3BOMe]^-$, $[(CF_3)_3BC(O)OMe]^-$, and $[Me_3O]^+$ were identified in traces (<1 %) by NMR spectroscopy [Eq. (29)].[43,73]



(29)

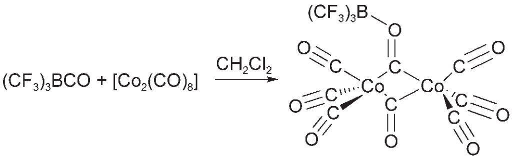
In diethyl ether solution a stepwise exchange of the methyl groups in $(CF_3)_3BOMe_2$ against ethyl groups occurs. Since the adduct $(CF_3)_3BOMe_2$ is a reactive methylating reagent, it can be applied for the preparation of salts of the $[(CF_3)_3BOMe]^-$ ion. Two representative syntheses giving ionic liquids are presented in Equations (30) and (31).[43,73]

$$(CF_3)_3BOMe_2 + nBu_3P \xrightarrow{CH_2Cl_2} [nBu_3MeP][(CF_3)_3BOMe] \qquad (30)$$



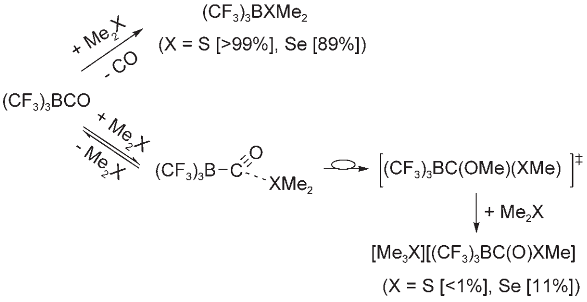
(31)

The reaction of Et_2O with $(CF_3)_3BCO$ was also investigated. Owing to the higher steric demand of the ethyl groups, the reaction course is dominated by attack at the C atom of the CO ligand, and only 20 % of the borane carbonyl groups undergo ligand-exchange reactions.[13] Only one further example for a reaction of an oxygen base with $(CF_3)_3BCO$ under ligand exchange was reported so far (Scheme 1 b). In hexane or dichloromethane, $(CF_3)_3BCO$ selectively reacts with one of the two bridging CO ligands of $[Co_2(CO)_8]$ to give $[Co_2(CO)_7CO{-}B(CF_3)_3]$ [Eq. (32)].[17] $[Co(CO)_5][(CF_3)_3BF]$ is obtained from the corresponding reaction in anhydrous HF as described in Section 5 [Eq. (19)].[16,17]



(32)

Comparable to the reactions of dimethyl ether, the higher homologues Me_2S and Me_2Se react with the borane carbonyl in a ligand-exchange reaction to produce $(CF_3)_3BSMe_2$ and $(CF_3)_3BSeMe_2$. A subsequent reaction with Me_2S and Me_2Se to give $[Me_3S][(CF_3)_3BSMe]$ and $[Me_3Se][(CF_3)_3BSeMe]$, respectively, was not observed. $[Me_3S][(CF_3)_3BC(O)SMe]$ and $[Me_3Se][(CF_3)_3BC(O)SeMe]$ were identified as side products, respectively [Eq. (33)].[73]



(33)

In the complex reaction mixture of Me_2Te and $(CF_3)_3BCO$, the products $[Me_3Te][(CF_3)_3BC(O)TeMe]$ and $(CF_3)_3BTeMe_2$ were identified by NMR spectroscopy. $(CF_3)_3BTeMe_2$ reacts slowly with Me_2Te to give $[Me_3Te][(CF_3)_3BTeMe]$.[73]

6.3. Cyano- and Isocyanotris(trifluoromethyl)borates

6.3.1. Synthesis and Reactions of $(CF_3)_3BNCH$

Hydrogen cyanide reacts with $(CF_3)_3BCO$ under release of CO and formation of the molecular borane complex $(CF_3)_3BNCH$ [Eq. (34)][90] similar to the reactions with nitriles

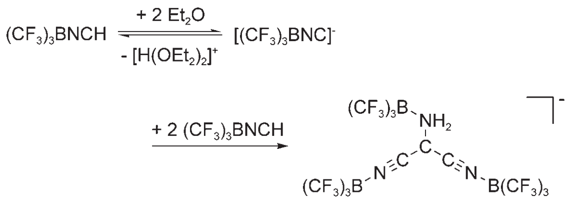
$$(CF_3)_3BCO + HCN \xrightarrow[-80\,^{\circ}C \to RT]{CH_2Cl_2} (CF_3)_3BNCH + CO \qquad (34)$$

like CH_3CN[21,22] or *t*BuCN[73] (Scheme 1b). $(CF_3)_3BNCH$ is a colorless, thermally stable solid (up to 167 °C). Proton exchange with deuterated benzene and toluene to $(CF_3)_3BNCD$ is observed.[73] Related reactions of $(CF_3)_3BNCH$ take place with Me_3SiPh to yield $(CF_3)_3BNCSiMe_3$, and with Me_3SnPh or Me_4Sn to yield $(CF_3)_3BNCSnMe_3$ [Eq. (35) and (36)].[73]

$$(CF_3)_3BNCH + Me_3XPh \rightarrow (CF_3)_3BNCXMe_3 + C_6H_6 \qquad (35)$$

$$(CF_3)_3BNCH + Me_4Sn \rightarrow (CF_3)_3BNCSnMe_3 + CH_4 \qquad (36)$$

Under basic conditions, for example, in a solution of ethers or amines, the HCN complex decomposes. The $[(CF_3)_3BNC]^-$ ion, which is formed in small quantities from $(CF_3)_3BNCH$ by deprotonation in diethyl ether, subsequently reacts with two molecules of $(CF_3)_3BNCH$ to give the $[(CF_3)_3BNH_2C\{CNB(CF_3)_3\}_2]^-$ ion [Eq. (37)],[73] from which the dianion $[(CF_3)_3BNH_2CH\{C(O)NHB(CF_3)_3\}_2]^{2-}$ is formed by hydrolysis [Eq. (38)].[73]



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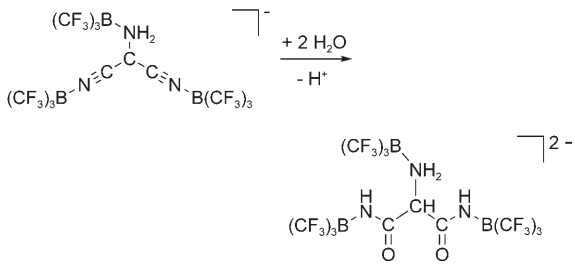


(38)

Attempted deprotonation reactions of $(CF_3)_3BNCH$ using either water or aqueous KOH failed, and complex mixtures were isolated. The anions $[(CF_3)_3BNH_2CH\{C(O)NHB(CF_3)_3\}_2]^{2-}$ and $[(CF_3)_3BNHC(O)H]^-$ were identified as products by NMR spectroscopy.[73] Colorless crystals of the molecular compound $(CF_3)_3BNH_2CH\{C(O)NH_2\}$-*cyclo*-$\{CNHB(CF_3)_2CF_2O\}$ (Figure 6) were obtained from a solution of $(CF_3)_3BNCH$ in dichloromethane with traces of water. A possible mechanism for the formation of the neutral species is shown in Equation (39).[73] Of special interest is the last step of the reaction sequence, the formation of the oxazaborole cycle, because trapping of the difluorocarbene ligand attached to boron by an O atom is similar to one crucial step postulated for the formation of $(CF_3)_3BCO$ from $[B(CF_3)_4]^-$ in concentrated sulfuric acid with $(CF_3)_3BCF_2$ as an intermediate.[22]

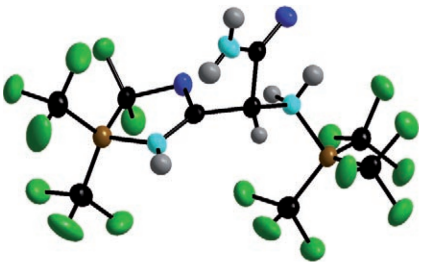
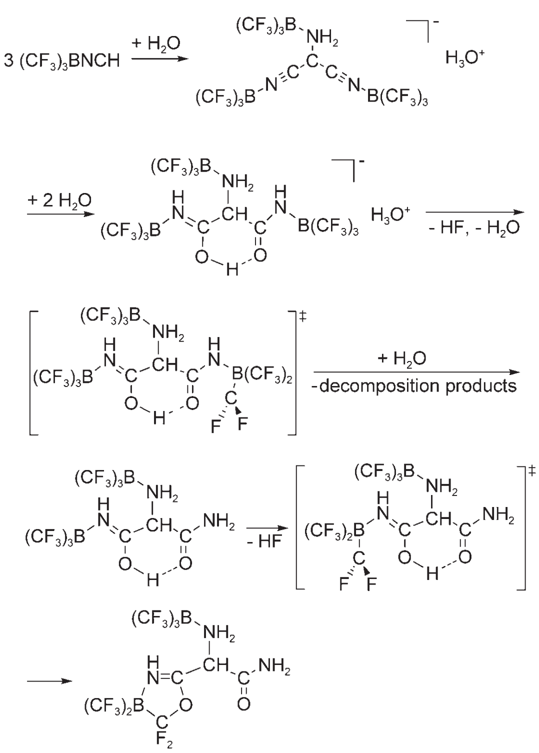


Figure 6. Structure of a molecule of $(CF_3)_3BNH_2CH\{C(O)NH_2\}$-*cyclo*-$\{CNHB(CF_3)_2CF_2O\}$ in the solid state.[73]



(39)

Successful deprotonation of $(CF_3)_3BNCH$ is achieved in toluene using $Li[N(SiMe_3)_2]$ as base [Eq. (40)].[90] Since

$$(CF_3)_3BNCH(solv) + Li[N(SiMe_3)_2](solv) \xrightarrow[-20\,^{\circ}C \to RT]{toluene} Li[(CF_3)_3BNC](s) + HN(SiMe_3)_2(solv) \qquad (40)$$

$Li[(CF_3)_3BNC]$ precipitates from the reaction mixture, a subsequent reaction with the starting material $(CF_3)_3BNCH$ is avoided.

6.3.2. *[$(CF_3)_3BNC]^-$ and [$(CF_3)_3BCN]^-$*

In neutral and basic media the [$(CF_3)_3BNC]^-$ ion is stable. Under acidic conditions, decomposition takes place, and the main product of the acidic hydrolysis of K[$(CF_3)_3BNC$] is K[$(CF_3)_3BNHC(O)H$] (Scheme 3).[90] All attempts to convert K[$(CF_3)_3BNHC(O)H$], which can be synthesized from K-[$(CF_3)_3BNH_2$] and HC(O)OEt also,[91] into K[$(CF_3)_3BNC$] have been unsuccessful so far.[90]

Solid K[$(CF_3)_3BNC$] isomerizes at 150 °C and at higher temperatures to K[$(CF_3)_3BCN$] (Scheme 3). On a preparative scale the reaction is performed at 220 °C, and isomerization is complete in a few minutes.[90] Until now, comparable reactions of CN groups bonded to boron have been reported for [$H_nB(NC)_{4-n}]^-$ ($n = 1, 2$)[92] and some isocyano derivatives of carboranes,[84] for example, for o-$C_2B_{10}H_{11}$-3-NC.[93] The isomerization enthalpy of (-34 ± 4) kJ mol^{-1} derived from DSC measurements is in good agreement with the theoretical value of -36.1 kJ mol^{-1} from density functional calculations. The reaction is of first order, and the activation energy was estimated to be (180 ± 20) kJ mol^{-1} from experimental data. This value compares well to a theoretical value of 155.7 kJ mol^{-1} calculated on the basis of an intramolecular transition state.[90] In contrast to the behavior of the [$(CF_3)_3BNC]^-$ ion and similar to the [$B(CN)_4]^-$ ion,[10] the [$(CF_3)_3BCN]^-$ ion is stable in concentrated hydrochloric acid. K[$(CF_3)_3BCN$] melts at 365 °C and decomposes in an exothermic reaction at 370 °C (DSC measurements). The cyanoborate is thermally more stable than K[$B(CF_3)_4$], which decomposes at 320 °C[9] but less stable than K[$B(CN)_4$], which is stable up to 510 °C.[12]

Three alternative syntheses for salts of the [$(CF_3)_3BCN]^-$ ion have been developed so far: dehydration of [$(CF_3)_3BC(O)NH_2]^-$ salts using phosgene in the presence of Et_3N (Scheme 1 a) and reactions of $(CF_3)_3BCO$ or of [$(CF_3)_3BC(O)Hal]^-$ salts (Hal = F, Cl) with K[$N(SiMe_3)_2$] (Scheme 1 a and 2). However, yields of isolated products from these syntheses are lower than those of the sequence starting with the reaction of $(CF_3)_3BCO$ with HCN to give $(CF_3)_3BNCH$, followed by deprotonation to give the isocyanoborate ion and subsequent isomerization.[90] In addition, the [$(CF_3)_3BCN]^-$ ion was identified as an intermediate in the fluorination reaction of [$B(CN)_4]^-$ to form [$B(CF_3)_4]^-$.[9] Other intermediate species that were identified by NMR spectroscopy are salts of the anions [$(CF_3)_2B(CN)_2]^-$ and [$CF_3B(CN)_3]^-$ as well as salts of the anions [$CF_3BF_2(CN)]^-$, [$(CF_3)_2BF(CN)]^-$, and [$CF_3BF(CN)_2]^-$ as side products.[9]

The highest wavenumbers of all known cyano- and isocyanoboranes and -borates are found for K[$(CF_3)_3BCN$] and K[$(CF_3)_3BNC$] (Figure 7). This property is due to the strong Lewis acidity of $(CF_3)_3B$ and in analogy to the high value of $\tilde{\nu}$(CO) in the isoelectronic borane carbonyl $(CF_3)_3BCO$ (Table 1). The lower value of the wavenumber of the CN stretch in the isocyanoborate ion is in agreement with a longer CN triple bond and a smaller $^1J(^{13}C,^{15}N)$ coupling constant.[90]

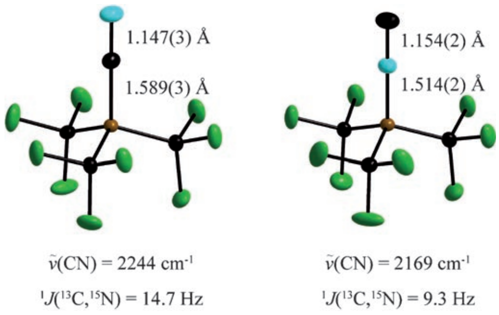
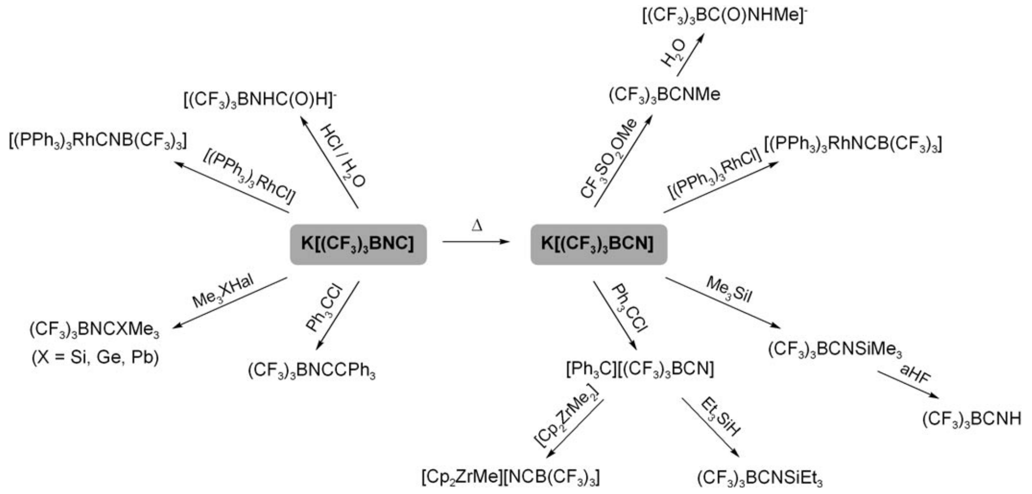


Figure 7. Models of the anions [$(CF_3)_3BCN]^-$ (left) and [$(CF_3)_3BNC]^-$ (right) in the solid state with selected bond parameters and spectroscopic data.[90]

6.3.3. *Main-Group Derivatives and Transition-Metal Complexes of [$(CF_3)_3BNC]^-$ and [$(CF_3)_3BCN]^-$*

The potassium salts of [$(CF_3)_3BCN]^-$ and [$(CF_3)_3BNC]^-$ serve as starting materials for the syntheses of a variety of derivatives with transition metals as well as Lewis acids of main-group elements (Scheme 3).



Scheme 3. Reactions of the isoelectronic borates K[$(CF_3)_3BNC$] and K[$(CF_3)_3BCN$].

The $[(CF_3)_3BCN]^-$ ion reacts with methyl triflate to produce $(CF_3)_3BCNMe$. Its isomer $(CF_3)_3BNCMe$ is obtained in a ligand-exchange reaction of acetonitrile and $(CF_3)_3BCO$[22,49] (Section 6.3.1., Scheme 1 b) or by dehydration of $(CF_3)_3BNH_2C(O)Me$ using P_4O_{10}.[7] In contrast to the Me^+ ion, which forms covalent bonds to both borate ions,[73] the reaction of the trityl cation with the isocyanoborate ion gives the molecule $(CF_3)_3BNCCPh_3$ while $K[(CF_3)_3BCN]$ reacts with Ph_3CCl to give the salt $[Ph_3C][(CF_3)_3BCN]$ (Scheme 3).[15] $(CF_3)_3BNCSiMe_3$ and $(CF_3)_3BCNSiMe_3$ are both molecules, similar to $(CF_3)_3BNCH$ and $(CF_3)_3BCNH$ in that they are not salts. Protonation of $[(CF_3)_3BCN]^-$ was achieved by reaction of $(CF_3)_3BCNSiMe_3$ with anhydrous HF (Scheme 3); the reaction of $K[(CF_3)_3BCN]$ with HCl in Et_2O yields $(CF_3)_3BCNH{\cdot}OEt_2$.[73,94]

$(CF_3)_3BNCCMe_3$ is synthesized from $(CF_3)_3BCO$ and pivaloyl nitrile. Preparation of the homologous Si compound by ligand exchange using Me_3SiCN is not possible; however, its preparation is achieved by a metathesis reaction of $K[(CF)_3BNC]$ and Me_3SiHal (Hal = Cl, I). Similarly, the other homologues with Ge, Sn, and Pb are accessible.[73] Other alternatives are the reactions of $(CF_3)_3BNCH$ with Me_3XPh (X = Si, Sn) or Me_4Sn [Eqs. (35) and (36)].

In the series of adducts $(CF_3)_3BNCXMe_3$ (X = C, Si, Ge, Sn, Pb) the strengths of coordination of Me_3X^+ to the isocyano group decreases from X = C to Pb. Hence, decreasing wavenumbers of the CN stretch ($2336\,cm^{-1}$ C, $2286\,cm^{-1}$ Si, $2275\,cm^{-1}$ Ge, $2255\,cm^{-1}$ Sn, $2219\,cm^{-1}$ Pb) and decreasing $^1J(^{13}C,^{15}N)$ coupling constants in the same order (31.2 Hz Si, 27.4 Hz Ge, 22.3 Hz Sn, 16.1 Hz Pb) are observed.[73]

ClCN and BrCN react with $(CF_3)_3BCO$ to produce $(CF_3)_3BNCCl$ and $(CF_3)_3BNCBr$, analogous to the reactions of nitriles. In contrast, FCN does not react with $(CF_3)_3BCO$ at all, and with ICN a complex reaction mixture is obtained.[95] Only one of the two cyano groups of dicyan reacts with the borane carbonyl to give $(CF_3)_3BNCCN$. Formation of $(CF_3)_3BNCCNB(CF_3)_3$ is not observed.[95]

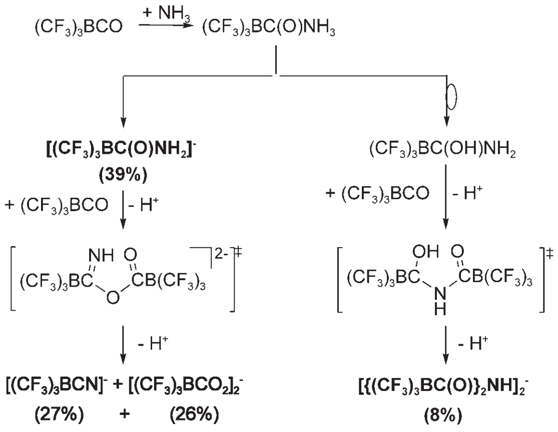
The $[(CF_3)_3BCN]^-$ ion as well as the $[B(CN)_4]^-$ ion react with $(CF_3)_3BCO$ under release of CO to give the anions $[(CF_3)_3BCNB(CF_3)_3]^-$ and $[B\{CNB(CF_3)_3\}_4]^-$, respectively (Scheme 1 b).[13,22,73] During the reaction of $(CF_3)_3BCO$ with $K[B(CN)_4]$ in SO_2 all three possible intermediate borate ions $[B\{CNB(CF_3)_3\}_{4-n}(CN)_n]^-$ ($n = 1$–3) were characterized by NMR spectroscopy.[13] Poorly soluble yellow $[Ph_3C][B\{CNB(CF_3)_3\}_3CN]$ precipitates from a reaction mixture of $[Ph_3C][B(CN)_4]$[15] with the borane carbonyl in dichloromethane.[18] Both borate ions $[(CF_3)_3BCNB(CF_3)_3]^-$ and $[B\{CNB(CF_3)_3\}_4]^-$ are potential weakly coordinating anions, but two of the four bridging CN groups of $[B\{CNB(CF_3)_3\}_4]^-$ hydrolyze upon contact with water.[13]

A similar method to that used for the preparation of $K[B\{CNB(CF_3)_3\}_4]$ in liquid SO_2 can also be applied for reactions with homoleptic cyano metalates. Examples are the syntheses of the square-planar complexes $[Au^{III}\{CNB(CF_3)_3\}_4]^-$ and $[Pt^{II}\{CNB(CF_3)_3\}_4]^{2-}$ as well as the octahedral complex $[Pt^{IV}\{CNB(CF_3)_3\}_6]^{2-}$ (Scheme 1 b).[73]

The first examples for transition-metal complexes of both borate ions are the Rh^I complexes $[(PPh_3)_3Rh^INCB(CF_3)_3]$ and $[(PPh_3)_3Rh^ICNB(CF_3)_3]$, which are obtained by reacting the K^+ salts with $[(PPh_3)_3RhCl]$ (Scheme 3).[96] The properties of $[(CF_3)_3BCN]^-$ and $[(CF_3)_3BNC]^-$ as ligands in the Rh^I complexes were studied in detail and compared to the respective behaviors of $[Ph_3BCN]^-$ and $[Ph_3BNC]^-$.[96] The wavenumbers of the CN stretches in both complexes are shifted to lower values, compared to the respective noncoordinated anions, owing to π back-donation. All previously discussed derivatives exhibit $\tilde{\nu}(CN)$ shifts at higher wavenumbers.[73,96]

6.4. Reactions of $(CF_3)_3BCO$ with NH_3, Amines, and Phosphanes

$(CF_3)_3BCO$ reacts with ammonia under attack at the C atom similarly to the reaction with water. A ligand-exchange reaction under release of CO is not observed (Scheme 1 a). In Equation (41) the reactions in liquid ammonia are summarized.[22,97]



(41)

The reaction of $K[(CF_3)_3BC(O)F]$ with liquid NH_3 proceeds to $K[(CF_3)_3BC(O)NH_2]$ without formation of any side products (Scheme 2).[81,97] Using the fluoroacylborate ion as a starting species allowed the synthesis of a number of other carbamoyl complexes of $(CF_3)_3B$. While $[NH_4]_2[\{(CF_3)_3BC(O)\}_2NH]$ is only a side product of the reaction of liquid ammonia with $(CF_3)_3BCO$, it is formed in quantitative yield by slow addition of gaseous ammonia to a solution of $(CF_3)_3BCO$ in Et_2O.[97] The structural similarity between the $[\{(CF_3)_3BC(O)\}_2NH]^{2-}$ ion and the acetylacetonate anion promises a comparably rich coordination chemistry.

Addition of Me_3N and Me_3P to $(CF_3)_3BCO$ leads to the formation of the internal salts $(CF_3)_3BC(O)NMe_3$ and $(CF_3)_3BC(O)PMe_3$, respectively; no ligand exchange giving either $(CF_3)_3BNMe_3$[98] or $(CF_3)_3BPMe_3$ takes place. The phosphane adduct is thermally stable up to 142 °C while the solvated compound $(CF_3)_3BC(O)NMe_3$ slowly decomposes at room temperature. Neither $(CF_3)_3BNMe_3$[98] nor $(CF_3)_3BPMe_3$ was identified as a decomposition product.[97]

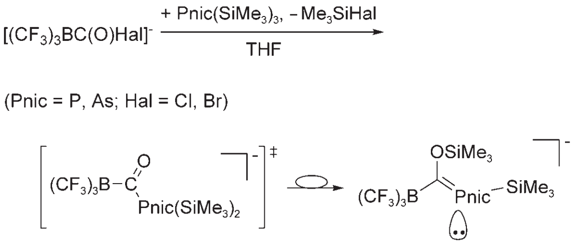
6.5. Pnicogeneethynyltris(trifluoromethyl)borates

The syntheses of phospha- and arsaethynyltris(trifluoromethyl)borates with the isoelectronic anions $[(CF_3)_3BCP]^-$

and $[(CF_3)_3BCAs]^-$ are performed by reacting $[Ph_4P][(CF_3)_3BC(O)Hal]$ (Hal = Cl, Br) with $K[Pnic(SiMe_3)_2]$ (Pnic = P, As) [Eq. (42)].[27] These reactions resemble the

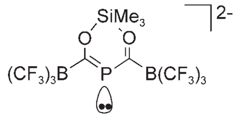
$$\begin{aligned}&[Ph_4P][(CF_3)_3BC(O)Hal] + K[Pnic(SiMe_3)_2] \xrightarrow[-15\,^\circ C \to RT]{THF,\ Pnic(SiMe_3)_3} \\ &[Ph_4P][(CF_3)_3BCPnic] + KHal + O(SiMe_3)_2\end{aligned} \tag{42}$$

syntheses of $[(CF_3)_3BCN]^-$ salts using $K[N(SiMe_3)_2]$ and $M[(CF_3)_3BC(O)Hal]$ (Hal = F, Cl) or $(CF_3)_3BCO$ (Scheme 2 and 1 a, Section 6.3.2.)[90] and the syntheses of transition-metal cyano complexes by treating the respective CO complexes with $[N(SiMe_3)_2]^-$ salts.[99,100] Probable intermediate species are phospha- and arsaalkenes, which are accessible by reaction of haloacylborate ions and $Pnic(SiMe_3)_3$ [Eq. (43)].[73] Only the *Z* isomer is formed owing to the large steric demand of the $(CF_3)_3B$ group. The acyl derivatives $[(CF_3)_3BC(O)Pnic(SiMe_3)_2]^-$ were not observed under the reaction conditions [Eq. (43)].[73]



(43)

In contrast to $M[(CF_3)_3BC(O)Hal]$ (Hal = Cl, Br), the reaction of $M[(CF_3)_3BC(O)F]$ with $Pnic(SiMe_3)_3$ and $K[Pnic(SiMe_3)_2]/Pnic(SiMe_3)_3$ produces the dimeric species **4** and **5**



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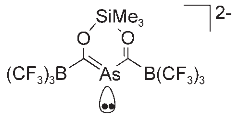


5

(Scheme 2; in this scheme, X is used instead of Pnic), which are structurally similar to the $[\{(CF_3)_3BC(O)\}_2NH]^{2-}$ ion.[73]

The potassium salts of $[(CF_3)_3BCPnic]^-$ (Pnic = P, As) were obtained by metathesis reactions of the $[Ph_4P]^+$ salts with $K[BPh_4]$ [Eq. (44)].[73]

$$\begin{aligned}&[Ph_4P][(CF_3)_3BCPnic] + K[BPh_4] \xrightarrow{CH_3CN} \\ &K[(CF_3)_3BCPnic] + [Ph_4P][BPh_4]\downarrow\end{aligned} \tag{44}$$

The $[(CF_3)_3BCP]^-$ and $[(CF_3)_3BCAs]^-$ ions are the first examples of phospha- and arsaethynyl complexes of boron.[27,101,102] Until now, the $[(CF_3)_3BCAs]^-$ ion and tri(*tert*-butylphenyl)arsaalkyne are the only cyarsido species known that are stable at room temperature.[27,103–105] $K[(CF_3)_3BCP]$ decomposes at temperatures higher than 145 °C, and $K[(CF_3)_3BCAs]$ is stable up to 95 °C.[73] Both $[Ph_4P]^+$ salts melt at 125 °C and decompose at 290 °C ($[Ph_4P][(CF_3)_3BCP]$) and 173 °C ($[Ph_4P][(CF_3)_3BCAs]$), respectively.[27] The unforeseeable high thermal stability of salts of the anions $[(CF_3)_3BCP]^-$ and $[(CF_3)_3BCAs]^-$ is rationalized by the steric hindrance of the $(CF_3)_3B$ group and the overall negative charge. A stabilization resulting from π back-donation as discussed, for example, for the complex $[RuH(CP)(dppe)_2]$[106] is not possible in the case of the borate ions.[27,100]

The anions are stable in wet $[D_3]$acetonitrile for days. Attempted metathesis reactions of $[Ph_4P][(CF_3)_3BCP]$ and $K[BPh_4]$ in wet solvents lead to the addition of two molecules of water to the triple bond, resulting in $[(CF_3)_3BCH_2P(O)(OH)H]^-$ [Eq. (45)].[27] This reaction indicates a negative charge at the C atom of the CP ligand similar to other phophaalkynes[107] but in contrast to the charge distribution in the CN ligand of the $[(CF_3)_3BCN]^-$ ion.

$$[(CF_3)_3BCP]^- + 2\,H_2O \rightarrow [(CF_3)_3BCH_2P(O)(OH)H]^- \tag{45}$$

The spectroscopic trends and bonding parameters in $[(CF_3)_3BCN]^-$, $[(CF_3)_3BCP]^-$, and $[(CF_3)_3BCAs]^-$ are comparable to related series; representative parameters are decreasing wavenumbers of $\tilde{\nu}$(CPnic) and increasing triple-bond lengths (Table 2). An assignment of the ^{31}P NMR signal of $[(CF_3)_3BCP]^-$ based on a comparison with chemical shifts $\delta(^{31}P)$ of ^{31}P nuclei of other phosphaalkynes is not possible because of the unspecific large range of frequencies.[27,102,108] An unambiguous assignment of the signal in the ^{31}P NMR spectrum is possible because of the observation of coupling to the ^{19}F nuclei and to the ^{11}B nucleus (Figure 8).[27]

The force constants of the triple bonds of the three isoelectronic borate ions were estimated from the respective wavenumbers of $\tilde{\nu}$(CPnic): $f_{CN} = 19.2$, $f_{CP} = 11.1$, and $f_{CAs} = 10.8\ N\,cm^{-1}$. The bond strength strongly decreases from CN^- to CP^-; in contrast, the decrease from the cyaphido to the cyarsido ligand is small. The reduced coupling constants $^1K(^{13}C,^{15}N)$ and $^1K(^{13}C,^{31}P)$ are in agreement with the trend found for the force constants.[73]

6.6. Ketone and Alcohol Derivatives of $(CF_3)_3BCO$

Alkyl lithium and Grignard compounds add to the C atom of the CO ligand of $(CF_3)_3BCO$. Similar reactions have been observed with the haloacyltris(trifluoromethyl)borate ions as well as with the $[(CF_3)_3BC(O)OMe]^-$ ion. The success of these reactions strongly depends on the steric demand of the carbanion; hence, the reaction of $(CF_3)_3BCO$ with *t*BuLi gives a complex mixture, and even the $[(CF_3)_3BC(O)H]^-$ ion was identified.[13,73] One equivalent of *n*BuLi reacts with the borane carbonyl to give the $[(CF_3)_3BC(O)nBu]^-$ ion. A second addition of Bu^- does not occur; instead, the $[(CF_3)_3BCH(OH)nBu]^-$ ion is formed. The sterically less demanding MeLi reacts to give $[(CF_3)_3BC(O)Me]^-$ at low temperature; at room temperature a second methyl anion is slowly added, and the $[(CF_3)_3BC(OH)Me_2]^-$ ion is obtained as the final product.[73]

Similar syntheses are the reactions of Me_3SiCN with $[(CF_3)_3BC(O)Hal]^-$ (Hal = F, Cl) to give $[(CF_3)_3BC(O)CN]^-$ and subsequently $[(CF_3)_3BC(OSiMe_3)(CN)_2]^-$ (Scheme 2) as

Table 2: Comparison of characteristic properties of C≡Pnic derivatives $[(CF_3)_3BCPnic]^-$ (Pnic = N, P, As).

Cmpd	$\tilde{\nu}_{CPnic}$ [cm^{-1}]	r(C≡Pnic) [Å]	$^1J(^{13}C,^nX)$[a] [Hz]	$^1K(^{13}C,^nX)$[a,b] [N Å^{-2} m^{-3}]	$\delta(^nX)$[a] [ppm]	$\delta(^{13}C)$ [ppm]	$\delta(^{11}B)$ [ppm]	Ref.
$K[(CF_3)_3BCN]$	2244	1.147(3)	14.7	4.8×10^{20}	−103.3	127.5	−22.3	[90]
$K[(CF_3)_3BCP]$	1476	1.563(10)[c]	27.6	2.3×10^{20}	39.6	202.3	−19.8	[27,73]
$K[(CF_3)_3BCAs]$	1332	1.675(12)[c]				233.9	−17.3	[27,73]
MeCN	2268	1.157	17.5	5.7×10^{20}	−135.5	119.6		[109–113]
MeCP	1559	1.5438(4)	49.0	4.0×10^{20}	−61	179.1		[114–117]
MeCAs	n.o.	1.661(1)				196.4		[118]
Me_3SiCN	2198	1.844(7)	11.6	3.8×10^{20}	−77.7	127.0		[109,119–122]
Me_3SiCP	1572	n.o.	14	1.1×10^{20}	96.0	212.5		[114,115]
$[RuH(CN)(dppe)_2]$	2078	n.o.	n.o.		n.o.	n.o.		[123]
$[RuH(CP)(dppe)_2]$	1229	1.573(2)	90	7.4×10^{20}	165.0	287.1		[106]
*t*BuCP	1533	1.548(1)	38.5	3.1×10^{20}	−69.2	184.8		[124,125]
Mes*CAs[d]	n.o.	1.657(7)				191.9		[103,105]

[a] $^nX = {}^{14}N, {}^{15}N, {}^{31}P$. [b] $^nK(X,Y) = 4\pi^2\,^nJ(X,Y)\,(h\gamma_X\gamma_Y)^{-1}$. [c] $[Ph_4P]^+$ salts. [d] Mes* = 2,4,6-tri-*tert*-butylphenyl. n.o. = not observed.

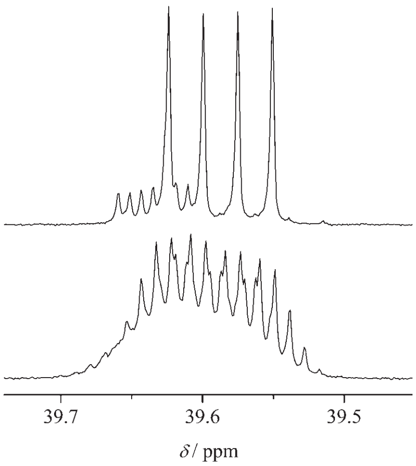
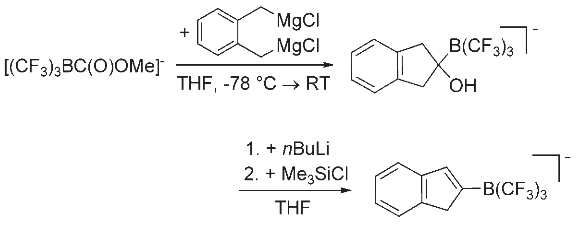


Figure 8. $^{31}P\{^{19}F\}$ NMR spectrum (top) and ^{31}P NMR spectrum (bottom) of $[(CF_3)_3BCP]^-$.[27]

well as the reaction of Me_3SiCN with $[(CF_3)_3BC(O)Me]^-$ to give $[(CF_3)_3BC(OSiMe_3)(CN)Me]^-$. The synthesis of $[(CF_3)_3BC(OSiMe_3)Me_2]^-$ starting from $[(CF_3)_3BC(O)Me_2]^{2-}$ and Me_3SiCl is not possible, and salts of the $[(CF_3)_3BCMe{=}CH_2]^-$ anion are isolated instead.[73]

Additions of carbanions to the C atom of the CO ligand are of general interest, because they allow the incorporation of the $(CF_3)_3BC$ group into ligands, polymers, as well as organic molecules. A first example is the synthesis of an indene with a $(CF_3)_3B$ substituent in the 2-position[126] [Eq. (46)].[18]

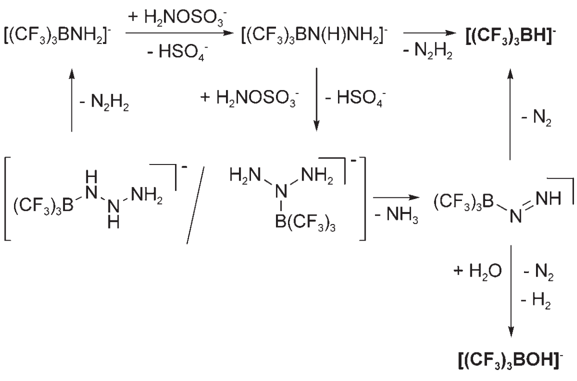


(46)

6.7. $[(CF_3)_3BC(O)H]^-$ and $[(CF_3)_3BH]^-$

A quantitative synthesis of the $[(CF_3)_3BC(O)H]^-$ ion, which was identified as a side product in the reaction of $(CF_3)_3BCO$ with *t*BuLi, is achieved by treatment of $[nBu_4N][(CF_3)_3BC(O)Cl]$ with nBu_3SnH in CH_2Cl_2 (Scheme 2).[18] The other haloacyltris(trifluoromethyl)borate ions are not suitable as starting materials since they either do not react or many impurities are formed. Attempted syntheses of the $[(CF_3)_3BC(O)H]^-$ ion by reaction of $Na[BH_4]$, $Li[AlH_4]$, or $Li[HAl(OtBu)_3]$ with the borane carbonyl or one of the haloacyl derivatives have been unsuccessful.[18]

The $[(CF_3)_3BH]^-$ ion was not identified as a side product in one of the reaction mixtures mentioned above. Its preparation by photolysis of $[(CF_3)_3BC(O)H]^-$ or $[(CF_3)_3BC(O)OH]^-$ was without success,[18] and a series of reactions using $(CF_3)_3BN$ derivatives as reagents failed also.[87] Recently, a synthesis starting from $[(CF_3)_3BNH_2]^-$ and H_2NOSO_3H was reported which gives pure salts of the $[(CF_3)_3BH]^-$ ion as minor products [Eq. (47)].[87]



(47)

7. Summary and Outlook

The synthesis of salts with the tetrakis(trifluoromethyl)borate ion[9] by fluorination of the tetracyanoborate ion marks the beginning of new developments in the field of trifluoromethylboron chemistry. Particularly, the carbonyltris(trifluoromethyl)borane,[21,22] which is obtained by solvolysis of the $[B(CF_3)_4]^-$ ion in concentrated H_2SO_4, is a valuable starting material for boranes and borates containing the $(CF_3)_3BC$ fragment, a group of compounds previously inaccessible,[7,8] and also for novel species of the type $(CF_3)_3BX$ (X = F, Cl, O, S, Se, Te, N).

Further developments in the field of CF_3B compounds are promising, because first applications for tetrakis(trifluoromethyl)borates have been developed in the area of lithium ion batteries,[19] ionic liquids,[20] and especially as a weakly coordinating anion.[9,14,15,17,44] In addition, some of its derivatives are weakly coordinating anions also[15,16] or they are attractive ligands for coordination chemistry.[96,97]

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