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Review

Pentafluorophenylboron halides: 40 years later

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Dedicated to Professor R.D. Chambers, University of Durham, UK, in recognition of his many contributions to fluorine chemistry

Abstract

The pentafluorophenylboron halides $C_6F_5BX_2$ (X = Cl, F) and $(C_6F_5)_2BCl$ were first reported in the early 1960s. After a period of inactivity these perfluoroarylboron derivatives have been employed for the synthesis of a variety of important compounds, including monomeric iminoboranes, a highly electrophilic hydroboration reagent, strong Lewis acids (with one or two acceptor sites) that activate alkyl metallocene polymerization catalysts, and the first organoxenon(IV) compounds. These recent developments provide a cogent example of the time lag that often occurs between discovery and applications in fundamental research. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Lewis acids; Pentafluorophenylboron compounds; Boron–nitrogen compounds; Xenon–carbon compounds

1. Introduction

Pentafluorophenylboron compounds were discovered in the early 1960s. Massey, Park and Stone reported the synthesis of tris(pentafluorophenyl)borane $B(C_6F_5)_3$ and some of its Lewis base adducts [1]. In the same issue of *Proceedings of the Chemical Society* Chambers and Chivers described the preparation of pentafluorophenylboron dihalides $C_6F_5BX_2$ (X = Cl, F) [2]. Following their initial discovery these perfluorinated systems were accorded scant attention until 1991 when Marks et al. and Ewen and co-workers independently reported the use of $B(C_6F_5)_3$ as a co-catalyst, in conjunction with group 4 metallocene alkyls, for olefin polymerization [3]. In the past 10 years $B(C_6F_5)_3$ has become an industrially important reagent [4] and several related perfluorinated systems with more highly Lewis acidic centers have been investigated [5]. At the same time pentafluorophenylboron halides have been used by various groups around the world in the discovery of several important classes of compounds, viz. (a) monomeric iminoboranes, (b) a borinic acid that is an effective catalyst for the oxidation of allylic and benzylic alcohols, (c) a highly electrophilic hydroboration reagent, (d) strong Lewis acids with one or more acceptor sites, (e) the first organoxenon (IV) compounds, and (f) metal–boryl complexes. These recent developments in the chemistry of pentafluorophenylboron halides are the subject of this review.[1]

2. Pentafluorophenylboron halides

The first syntheses of $C_6F_5BX_2$ (X = Cl, F) and $(C_6F_5)_2BCl$ employed organotin methodology, i.e. the stoichiometric reaction of pentafluorophenyltin compounds $Me_xSn(C_6F_5)_{4-x}$ ($x = 2, 3$) with the appropriate boron trihalide [2,6]. Subsequently, $C_6F_5BF_2$ was obtained by fluorination of $C_6F_5BCl_2$ with SbF_3, although low temperatures are necessary to minimize C_6F_5 transfer to antimony [6,7]. Very recently Frohn and co-workers have reported a new route to $C_6F_5BF_2$ that takes advantage of the stronger Lewis acidity of BF_3 in an exchange reaction with the $[C_6F_5BF_3]^-$ anion (Scheme 1) [8]. The salt $K[C_6F_5BF_3]$ was first prepared by the reaction of $C_6F_5BF_2$ with an aqueous solution of potassium fluoride [9].

Bis(pentafluorophenyl)boron fluoride, $(C_6F_5)_2BF$, was first isolated from thermolysis of $C_6F_5BF_2$ at 95 °C [6].

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[1] This article is based on a lecture given by the author at the University of Durham (UK) on 12 July 2001 on the occasion of the retirement of Prof. R.D. Chambers.

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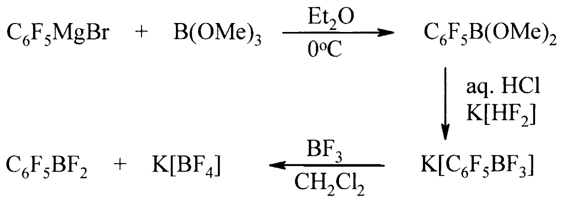


Scheme 1. Synthesis of $C_6F_5BF_2$.

More recently, $(C_6F_5)_2BF$ was generated as a co-product in the synthesis of the $[C_6F_5Xe]^+$ cation [10] (Eq. (1)).

$$[(MeCN)XeC_6F_5][(C_6F_5)_2BF_2] + AsF_5 \Big\downarrow {\scriptstyle MeCN \atop < -20^{\circ}C} \quad [C_6F_5Xe][AsF_6] + (C_6F_5)_2BF \tag{1}$$

The etherate $(C_6F_5)_2BF{\cdot}OEt_2$ is readily accessible by treatment of $BF_3{\cdot}OEt_2$ with two equivalents of C_6F_5MgBr [11]. The monofluoride has been used to prepare $(C_6F_5)_2BR$ (R = fluorenyl, indenyl) by reaction with the appropriate organolithium reagent [11]. Heating $(C_6F_5)_2BF{\cdot}OEt_2$ above 100 °C produces $(C_6F_5)_2BOEt$ as a result of ether cleavage [11].

The pentafluorophenylboron fluorides, $(C_6F_5)_{3-x}BF_x$ ($x = 1, 2$), have also been generated as by-products of the reaction of $B(C_6F_5)_3$ with $Fe(\eta^5\text{-}C_5H_5)(CO)_2Me$ to give $\{[\overline{Fe\text{-}\sigma\text{-}C_6F_4(2\text{-}C(O}Me)](\eta^5\text{-}C_5H_5)(CO)\}$ [12]. A mechanism involving the transition-metal-assisted transfer of fluorine from a C_6F_5 group to boron, with the formation of tetrafluorobenzyne, has been suggested [12].

Pentafluorophenylboron dichloride is currently prepared by the original method (Eq. (2)) [6], but the procedure for the synthesis of $(C_6F_5)_2BCl$ has been adapted by using hexanes as solvent in order to facilitate the separation of Me_2SnCl_2 by-product (Eq. (3)) [13a]. Bis(pentafluorophenyl)zinc also serves as an effective C_6F_5 transfer agent towards BCl_3, but this reaction gives rise to an inseparable mixture of $C_6F_5BCl_2$, $(C_6F_5)_2BCl$ and $(C_6F_5)_3B$ [13b].

$$Me_3SnC_6F_5 + 2BCl_3 \underset{20\,^{\circ}C}{\overset{\text{no solvent}}{\longrightarrow}} C_6F_5BCl_2 + Me_2SnCl_2 + MeBCl_2 \tag{2}$$

$$Me_2Sn(C_6F_5)_2 + BCl_3 \underset{120\,^{\circ}C/72\,h}{\overset{\text{hexanes}}{\longrightarrow}} (C_6F_5)_2BCl + Me_2SnCl_2 \tag{3}$$

The only pentafluorophenylboron halide to be structurally characterized, $(C_6F_5)_2BCl$, adopts a trigonal planar geometry. Although the C_6F_5 rings are twisted by ca. 35° out of planarity, presumably to reduce steric interactions between *ortho*-fluorine substituents, the B–C bond lengths are ca. 0.1 Å shorter than the corresponding distances in complexes containing pyramidal boron centers consistent with the presence of π–p interactions [14], a phenomenon that had been indicated by earlier ^{19}F NMR studies [6,7].

The pentafluorophenylboron bromides, $C_6F_5BBr_2$ and $(C_6F_5)_2BBr$, can be prepared from the reaction of C_6F_5HgBr and BBr_3 in toluene at reflux by using the appropriate stoichiometry [11].

3. Pentafluorophenylboron–nitrogen compounds

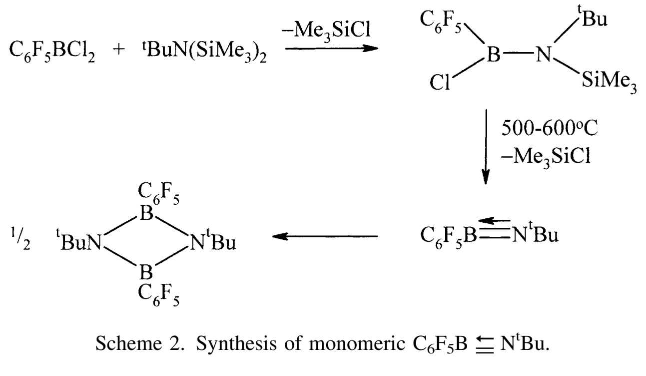
A variety of interesting pentafluorophenylboron–nitrogen compounds are available from the reactions of $C_6F_5BCl_2$ or $(C_6F_5)_2BCl$ with the appropriate nitrogen-containing reagent. For example, the borazine $(C_6F_5BNH)_3$ is obtained by passing dry NH_3 gas into a solution of $C_6F_5BCl_2$ in diethyl ether at 0 °C [7].

In 1966, the formation of monomeric boron imides from the reaction of $C_6F_5BCl_2$ and arylamines was claimed [15]. A subsequent reinvestigation showed that this reaction leads to the sequential formation of the aminoborane condensation products, $C_6F_5B(Cl)NHAr$, $C_6F_5B(Cl)N(Ar)B(C_6F_5)NAr$ and $C_6F_5B(NHAr)_2$ (Ar = mesityl), rather than the boron imide [16].

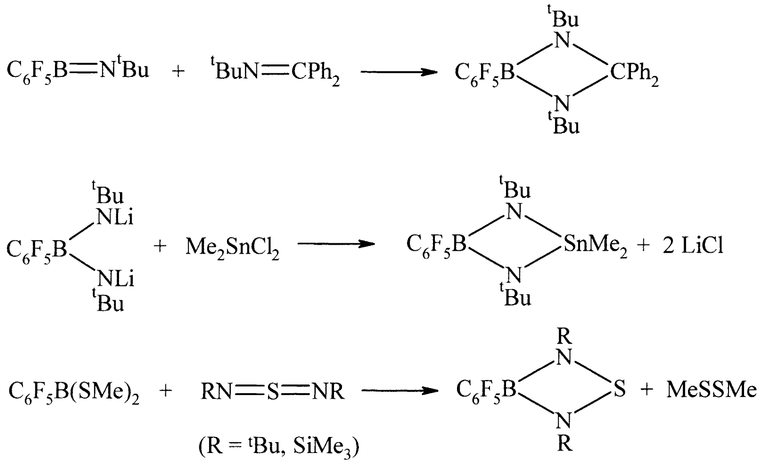
In 1979, however, Paetzold and co-workers showed that the combination of the strongly electron-withdrawing C_6F_5 group on boron and the kinetically stabilizing effect of a bulky ^tBu group attached to nitrogen does give rise to a monomeric iminoborane, which dimerizes quickly at room temperature [17]. The use of the reagent $C_6F_5BCl_2$ was the key to the synthesis of the aminoborane precursor for this iminoborane (Scheme 2). IR and NMR data indicate a BN bond order >2 in $C_6F_5B \underline{\equiv} N^tBu$.

The monomer $C_6F_5B \underline{\equiv} N^tBu$ undergoes a [2 + 2] cycloaddition reaction with the ketimine $^tBuN = CPh_2$ to give a four-membered ring that contains the pentafluorophenyl boraamidinate ligand $[C_6F_5B(N^tBu)_2]^{2-}$ [17] (Scheme 3). Some other examples of the generation of this dianionic ligand system are also shown in Scheme 3 [18].

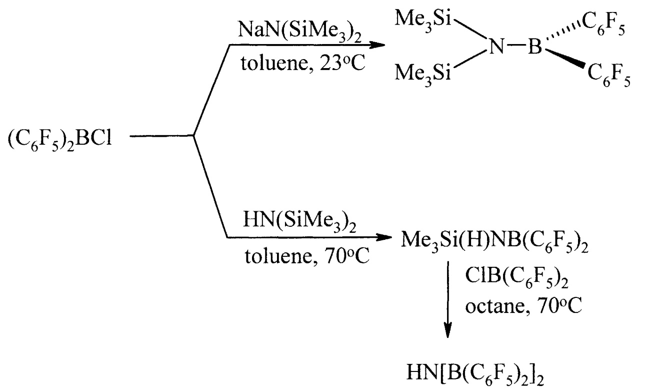
The aminoborane $(Me_3Si)_2NB(C_6F_5)_2$ is obtained from metal–halogen exchange between $(C_6F_5)_2BCl$ and $NaN(SiMe)_3$ [19], while $(Me_3Si)(H)NB(C_6F_5)_2$ or $[HN\{B(C_6F_5)_2\}_2]$ are prepared by heating a mixture of $(C_6F_5)_2$ BCl and $HN(SiMe_3)_2$ in the appropriate molar ratios (Scheme 4) [19].



Scheme 2. Synthesis of monomeric $C_6F_5B \underline{\equiv} N^tBu$.



Scheme 3. Synthetic routes to pentafluorophenylboraamidinate complexes.



Scheme 4. Synthesis of bis(pentafluorophenyl)aminoboranes.

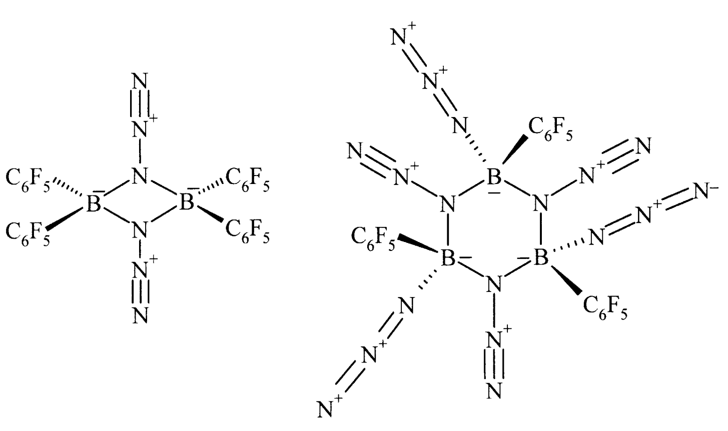
The B–N bond length of 1.400(3) Å in $(Me_3Si)_2NB(C_6F_5)_2$ is ca. 0.03 Å shorter than the mean value for B–N bonds in similar environments reflecting the strongly electron-withdrawing C_6F_5 groups. The ^{11}B NMR spectrum of $[(Me_3Si)(H)NB(C_6F_5)_2]$ in C_6D_6 exhibits two resonances at $\delta = 38.2$ and -2.8 in a 4:1 ratio. This observation is indicative of a monomer–dimer equilibrium involving three- and four-coordinate boron environments, respectively. However, variable temperature NMR data were not reported [19].

The pentafluorophenylboron azides $(C_6F_5)_2BN_3$ [20a] and $C_6F_5B(N_3)_2$ [20b] are readily obtained by the reaction of the corresponding chlorides with trimethylsilyl azide (Eqs. (4) and (5)).

$$(C_6F_5)_2BCl + Me_3SiN_3 \overset{\text{toluene}}{\underset{23\,^{\circ}C}{\rightarrow}} \tfrac{1}{2}[(C_6F_5)_2BN_3]_2 + Me_3SiCl \qquad (4)$$

$$C_6F_5BCl_2 + 2Me_3SiN_3 \overset{CH_2Cl_2}{\underset{23\,^{\circ}C}{\rightarrow}} \tfrac{1}{3}[C_6F_5B(N_3)_2]_3 + 2Me_3SiCl \qquad (5)$$

Klapötke et al. have shown that the monoazide, $(C_6F_5)_2BN_3$, which was first prepared by Paetzold et al. in 1983 [20c], has a unique dimeric structure in the solid state (Scheme 5), although ^{11}B NMR data (a single resonance at δ 43.9) indicate the formation of monomers in solution [20a]. In a similar vein Klapötke et al. have shown that the diazide $C_6F_5B(N_3)_2$ is trimeric in the solid state (Scheme 5), but monomeric in solution [$\delta(^{11}B)$ 34.6] [20b].



Scheme 5. Structural representations of pentafluorophenylboron azides.

By contrast, the halogenoboron azides $(X_2BN_3)_3$ (X = Cl, F) are trimeric in both the solid state and in solution [21]. Thus, it appears that the pentafluorophenylboron azides are weaker Lewis acids than the corresponding chloro- or fluoro-boron azides. Both $[(C_6F_5)_2BN_3]_2$ and $[C_6F_5B(N_3)_2]_3$ form monomeric adducts with one equivalent of pyridine [20]. The B_3N_3 ring in $[C_6F_5(BN_3)_2]_3$ adopts a slightly twisted boat conformation and the endocyclic B–N bond distances are ca. 0.1 Å longer than the exocyclic B–N bonds, which are typical single bonds [20b].

4. Pentafluorophenylboronic and bis(pentafluorophenyl)borinic acids

Hydrolysis of $C_6F_5BCl_2$ in aqueous acetone at −78 °C produces high yields of the boronic acid $C_6F_5B(OH)_2$ [6]. In a similar manner the borinic acid $(C_6F_5)_2BOH$ is obtained as an air-stable white solid by the hydrolysis of $(C_6F_5)_2BF$ [6] or, preferably, $(C_6F_5)_2BCl$ with aqueous 2N HCl [22]. Yamamoto and co-workers have shown that the strong Lewis acid $(C_6F_5)_2BOH$ is a highly effective catalyst for the oxidation of allylic or benzylic alcohols to the corresponding aldehydes [22a] and for aldol condensation [22b].

5. Bis(pentafluorophenyl)borane

The electrophilic borane $(C_6F_5)_2BH$ is generated readily by the reaction of $(C_6F_5)_2BCl$ with dimethylchlorosilane (Eq. (9)) [23]. In the solid state the bis(pentafluorophenyl)-borane is dimeric [13] (Scheme 6), although detectable amounts of monomer are evident in dilute solution in aromatic solvents at ambient temperature on the basis of ^{11}B NMR data. This dissociation apparently contributes to the high activity of $[(C_6F_5)_2BH]_2$, compared to other commonly used hydroboration reagents, toward olefin and alkyne substrates [4,24].

Bis(pentafluorophenyl)boranc has also been used in B–C bond forming reactions with iridium hydride complexes (Eq. (6)) [25].

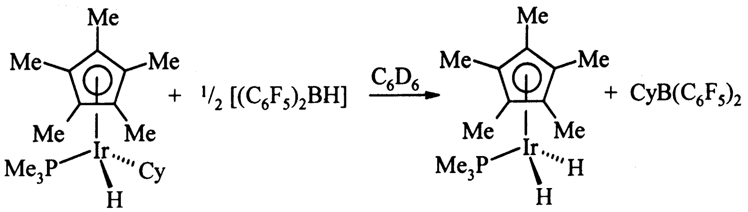
6. Highly acidic and bifunctional Lewis acids

The effectiveness of $B(C_6F_5)_3$ as a co-catalyst, in conjunction with alkylmetallocenes, for olefin polymerization [4] has prompted several groups to design perfluorinated boranes that are even stronger Lewis acids than $B(C_6F_5)_3$. The pentafluorophenylboron dihalides, $C_6F_5BCl_2$ and $(C_6F_5)_2BCl$, are key reagents for the synthesis of both monofunctional and bifunctional boranes as indicated in Schemes 7–9.[2]

The borane **A** is prepared by lithium-chlorine exchange utilizing $ClB(C_6F_5)_2$ [26] while the synthesis of **B** employs organotin methodology [27] similar to that used in the original preparation of pentafluorophenylboron chlorides [6]. Both **A** and **B** have been structurally characterized. The borafluorene ring in **B** is planar and the C_6F_5 group is tilted out of this plane by ca. 53°, thus, limiting the π–π interaction with the boron atom [27]. In **A** the two C_6F_5 groups attached to boron appear to engage in a weak intramolecular π–π stacking interaction [26]. Both **A** and **B** were shown to activate metallocene catalysts at least as efficiently as $B(C_6F_5)_3$.

Bifunctional Lewis acids are attracting interest in view of their applications in anion and molecular recognition and as catalysts for organic reactions, as well as activators for olefin polymerization. The first bifunctional borane incorporating $B(C_6F_5)_2$ groups, $^tBuCH_2CH[B(C_6F_5)_2]_2$, was reported by Marks and co-workers [28]. Hydroboration has also been used to generate bifunctional Lewis acids in which the acceptor sites are separated by an unsaturated carbon center [29] (Scheme 8).

Other bifunctional Lewis acids have been created by applying organotin methodology to the reagent 1,2-$C_6F_4(SnMe_3)_2$, (**C**) first prepared >30 years ago [30]. The dialuminum system **D** was obtained by Gabbai and co-workers from the reaction of **C** with dimethylaluminum chloride [31] (Scheme 9). Surprisingly this reaction involves cleavage of a methyl group from aluminum to give tetramethyltin so that the intended bifunctional Lewis acid 1,2-$C_6F_4(AlMe_2)_2$ is not formed. Similarly the reaction of **C** with $ClB(C_6F_5)_2$ was found by Piers et al. to generate 1,2-$C_6F_4(SnClMe_2)_2$ and $MeB(C_6F_5)_2$ [32]. However, Marks and co-workers have prepared the *para*-substituted system 1,4-$C_6F_4[B(C_6F_5)_2]_2$ from the reaction of 1,4-$C_6F_4(SnMe_3)_2$ and six equivalents of $ClB(C_6F_5)_2$ at elevated temperatures



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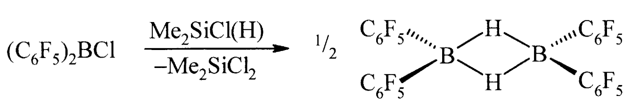

Scheme 6. Synthesis and structure of bis(pentafluorophenyl)borane.

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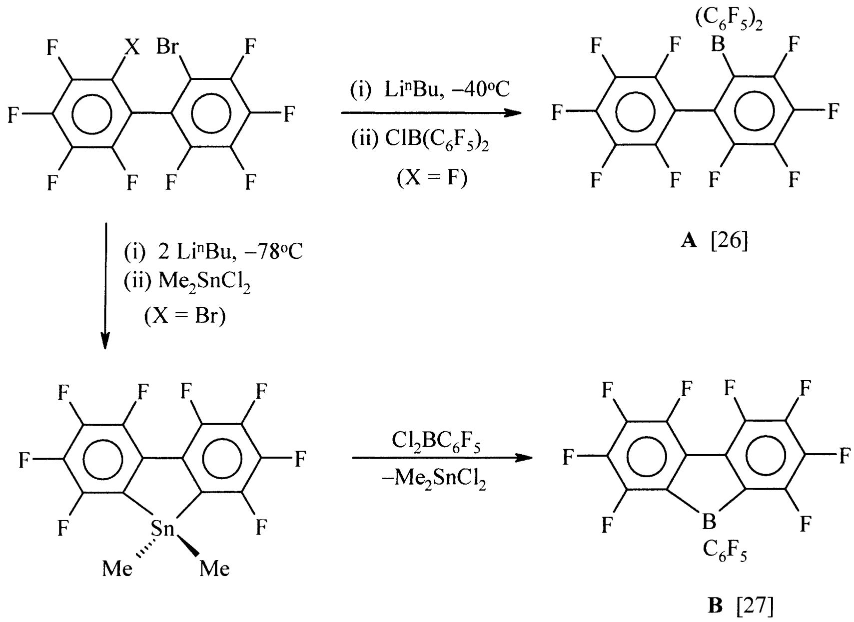
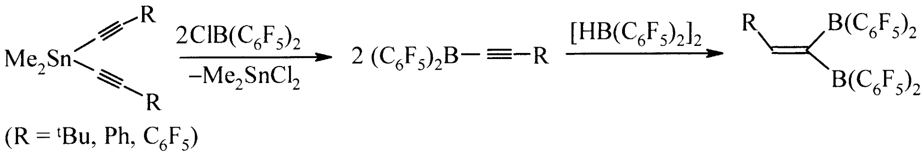
[2] For reviews of highly Lewis acidic bifunctional boranes, see [5].



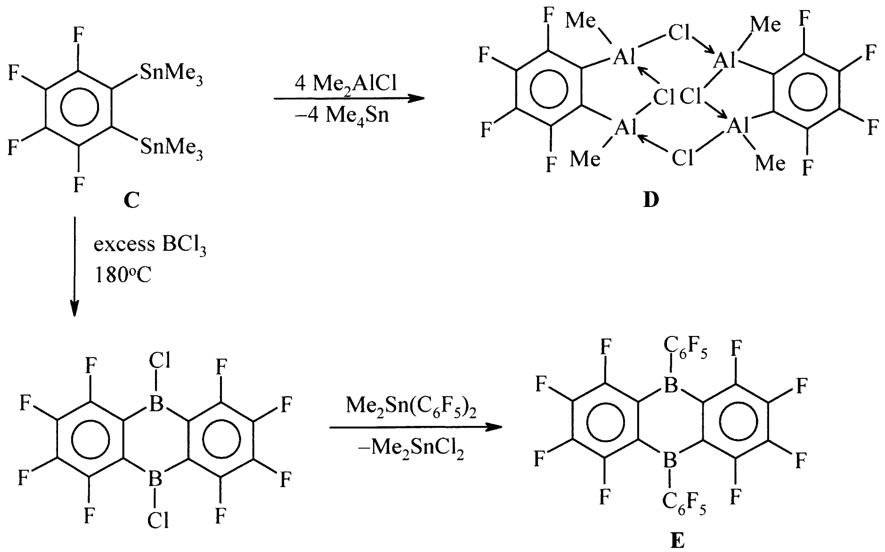
Scheme 7. Monofunctional perfluorinated boranes.



Scheme 8. An alkenyl diborane.

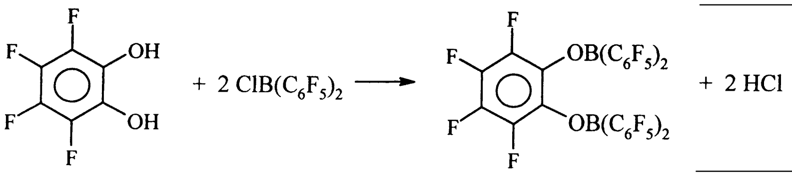
[33]. Marks and co-workers have also shown that the bis(trimethylstannyl) reagent **C** reacts with an excess of BCl_3 to generate a diboraanthracene with B–Cl bonds, which is converted to the perfluorinated system **E** by treatment with $Me_2Sn(C_6F_5)_2$ [34]. The diboraanthracene **E** was shown to be a stronger Lewis acid than $B(C_6F_5)_3$ by competitive equilibration studies with acetonitrile as the Lewis base. Dimethylmetallocenes activated by this new Lewis acid exhibit significantly higher polymerization activities than those based on $B(C_6F_5)_3$.

Catechol-based bifunctional Lewis acids, including a perfluorinated system (Eq. (7)) have been reported by Green



Scheme 9. Bifunctional boron and aluminum Lewis acids.

and co-workers [35]. However, O(pπ) → B(pπ) interactions result in weaker acceptor sites than those in the analogous systems with carbon-based linkages between the boryl units.



(7)

7. Pentafluorophenylxenon compounds

The successful synthesis of the first compounds containing a xenon-carbon bond involved the use of $B(C_6F_5)_3$ as a C_6F_5 transfer agent [36,37]. Thus, the salt $[C_6F_5Xe][C_6F_5BF_3]$ was obtained by reaction of XeF_2 with $B(C_6F_5)_3$ in dichloromethane [37]. More recently Frohn and co-workers have made the first organoxenon(IV)compound by treating xenon tetrafluoride with $C_6F_5BF_2$ in dichloromethane (Eq. (8)) [38] (for a review of the chemistry of xenon–carbon compounds, see [39]) The success of the reagent $C_6F_5BF_2$ in this transformation is attributed to the fact that this relatively weak Lewis acid (compared to BF_3) does not abstract fluoride ion from XeF_4 as well as the stability of the $[BF_4]^-$ anion towards oxidation. The thermally unstable $[C_6F_5XeF_2]^+$ cation, which exhibits a characteristic 1:2:1 triplet in the ^{25}Xe NMR spectrum [38], has also been observed in the $XeF_6/C_6F_5BF_2$ reaction system [40].

$$C_6F_5BF_2 + XeF_4 \xrightarrow[-55\,°C]{CH_2Cl_2} [C_6F_5XeF_2][BF_4] \qquad (8)$$

8. Pentafluorophenyliodine compounds

Frohn and co-workers have also used $C_6F_5BF_2$ as a C_6F_5 transfer agent for the preparation of iodonium compounds (Eq. (9)) [41]. The anion–cation interactions in the solid-state structure of $[(C_6F_5)_2I][BF_4]$ give rise to a polymeric zigzag chain.

$$C_6F_5IF_2 + C_6F_5BF_2 \xrightarrow[20\,°C]{CH_2Cl_2} [(C_6F_5)_2I][BF_4] \qquad (9)$$

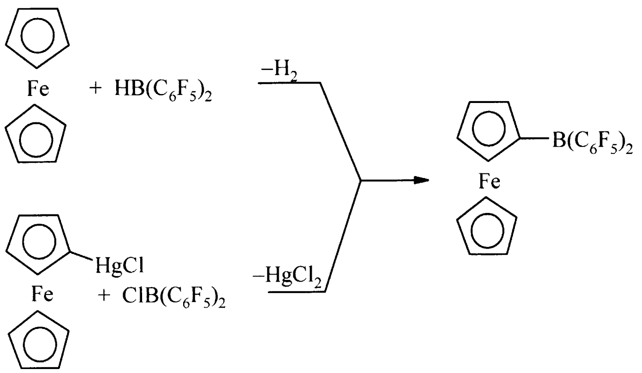
9. Bis(pentafluorophenyl)boryl complexes

Transition-metal boryl complexes $L_nM\text{-}BX_2$ are of current interest in view of their role in functionalizing C–H bonds in alkanes and arenes [42]. The combination of strong B–C bonds and high Lewis acidity of the boron center make the $B(C_6F_5)_2$ group a suitable probe for the investigation of metal–boron π interactions in such complexes. The first transition–metal complex containing the $B(C_6F_5)_2$ ligand was reported recently [43]. The iron complex $CpFe(CO)_2B(C_6F_5)_2$ was obtained in 42% yield by metal–halogen exchange (Eq. (10)).

$$CpFe(CO)_2Na + ClB(C_6F_5)_2 \xrightarrow[20\,°C]{toluene} CpFe(CO)_2B(C_6F_5)_2 + NaCl \qquad (10)$$

The Fe–B distance in $CpFe(CO)_2B(C_6F_5)_2$ is ca. 0.07 Å shorter than that in the non-fluorinated analogue $CpFe(CO)_2B(C_6H_5)_2$ reflecting an enhanced π-contribution to the B–C bond, although this is not sufficient to prevent free rotation about this bond even at −110 °C. A Mulliken analysis of the Fe–B bonding interaction with an additional sub-division of the bonding density into α and π contributions corroborate this conclusion and, in addition, reveal a significantly enhanced electrostation contribution to the Fe–B bond compared to that in the hydrocarbon analogue $CpFe(CO)_2B(C_6H_5)_2$ [43].

Bis(pentafluorophenyl)boryl ferrocene $FcB(C_6F_5)_2$ (Fc = ferrocenyl) has been prepared by borylation of ferrocene with $B(C_6F_5)_2H$ or via transmetallation between FcHgCl and $B(C_6F_5)_2Cl$ [44] (Scheme 10). The acidity of the boron center in $FcB(C_6F_5)_2$ is reduced by a significant intramolecular iron–boron interaction.



Scheme 10. Synthetic routes to bis(pentafluorophenyl)boryl ferrocene.

10. Pentafluorophenylaluminum halides

In contrast to the explosive tendencies of $Al(C_6F_5)_3$ [45,46], the pentafluorophenylaluminum halides $C_6F_5AlBr_2$ and $(C_6F_5)_2AlBr$ are thermally stable up to 180 °C [47]. These aluminum derivatives are prepared by successive replacement of the bromide in $AlBr_3$ by a C_6F_5 group using methylpentafluorophenylmercury (Eq. (11) and (12)).

$$MeHgC_6F_5 + AlBr_3 \rightarrow MeHgBr + C_6F_5AlBr_2 \qquad (11)$$

$$MeHgC_6F_5 + C_6F_5AlBr_2 \rightarrow MeHgBr + (C_6F_5)_2AlBr \qquad (12)$$

An intriguing feature of the reactivity of $C_6F_5AlBr_2$ is the insertion reaction with propene [48]. It has been proposed that this reaction involves the initial formation of an alkene–Al π-complex followed by insertion of the alkene into the Al–C_6F_5 bond [48]. In this connection it is interesting to note that it has recently been demonstrated that $Al(C_6F_5)_3$ forms 1:1 complexes with benzene or toluene in which the arene is η^1-coordinated to Al [49]. The X-ray structural parameters for these complexes indicate that a π-complex involving an sp^2 carbon is the primary contributor to the Al–arene bonding. ^1H NMR studies show that η^1-coordination is maintained in solution and that the arene ligand is displaced by THF, but not by OEt_2 [49].

11. Conclusion

In a discussion of the discovery of new compounds, notably $B(C_6F_5)_3$, Stone has opined "... the usefulness of a particular molecule is often hidden for many years after its discovery..." [50]. This brief account of recent applications of pentafluorophenylboron halides provides a persuasive illustration of that tenet. Forty years after their discovery[3] these reagents are employed by groups in the USA, Canada, Germany and the UK in projects ranging from the synthesis of organoxenon(IV) compounds to the construction of highly acidic, bifunctional Lewis acids that are effective as components of alkene polymerization catalysts. By a remarkable coincidence one of the leading practitioners in this development is Professor Warren Piers, a colleague of the author at the University of Calgary.

Acknowledgements

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