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Synthesis, Structure, and Bonding of Weakly Coordinating Anions Based on CN Adducts

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Abstract: The addition of alkali or silver salts of dicyanoamide (dca), tricyanomethanide (tcm) and tetracyanoborate (tcb) to a solution of $B(C_6F_5)_3$ in diethyl ether affords salts containing very voluminous $B(C_6F_5)_3$ adduct anions of the type $[E(CN)_n^-]\cdot[B(C_6F_5)_3]_n$: E = N (dca_*n*b with $n = 1, 2$; b = $B(C_6F_5)_3$); E = C (tcm_*n*b with $n = 1, 2, 3$), and E = B (tcb_*n*b with $n = 1, 2, 3, 4$). Salts bearing these anions such as $B[(CN)\cdot B(C_6F_5)_3]_4^-$ (= $[B(CN)_4^-]\cdot[B(C_6F_5)_3]_4$), $C[(CN)\cdot B(C_6F_5)_3]_3^-$ (= $[C(CN)_3^-]\cdot[B(C_6F_5)_3]_3$), and $N[(CN)\cdot B(C_6F_5)_3]_2^-$ (=$[N(CN)_2^-]\cdot[B(C_6F_5)_3]_2$) can be prepared in good yields. They are thermally stable up to over 200 °C and dissolve in polar organic solvents. Depending on the stoichiometry mono-, di-, tri-, or tetraadduct formation is observed. The solid state structures of dca_2b, tcm_3b and tcb_4b salts show only long cation···anion contacts and thereby weak interactions, large anion volumes and only small distortions of the dca, tcm or tcb core enwrapped between $B(C_6F_5)_3$ groups. That is why these anions can be regarded as weakly coordinating anions. On the basis of B3LYP/6-31+G(d) computations the energetics, structural trends and charge transfer of the adduct anion formation were studied. Since tcm_3b and tcb_4b are easily accessible and can also be prepared in large quantities, these anions may be utilized as a true alternative to other widely used weakly coordinating anions. Moreover, for both steric and electronic reasons it seems reasonable to expect that as counterions for cationic early transition metal catalysts such anions may show reduced ion pairing and hence increased catalytic activity.

Introduction

Weakly coordinating anions (WCA) have achieved great interest due to academic and commercial importance in olefin polymerization, ionic liquids, stabilizing highly reactive intermediates and battery technology.[1] This interest has grown over two decades of basic research on the physical and chemical properties of anions containing bulky hydrocarbon and fluorocarbon functionality.[1] WCAs such as borate-based anions (*e.g.* $[B(C_6F_5)_4]^-$),[2] carborane-based anions (*e.g.* $[CB_{11}H_6X_6]^-$ ion with X = Cl, Br),[1b,3−6] alkoxy- and aryloxymetallates (*e.g.* $[Al\{OC(CF_3)_3\}_4]^-$),[7] and teflate-based anions (*e.g.* $[M(OTeF_5)_6]^-$ with M = As, Sb, Bi, Nb)[8−10] display exceptional characteristics such as low nucleophilicity, chemical inertness, solubility, leaving group lability, and weak coordination resulting in applications throughout organic and inorganic chemistry.[1a] They are particularly useful for stabilizing highly reactive cations (*e.g.* $[CX_3]^+$ ions with X = Cl, Br, I),[11,12] stabilizing weakly bound

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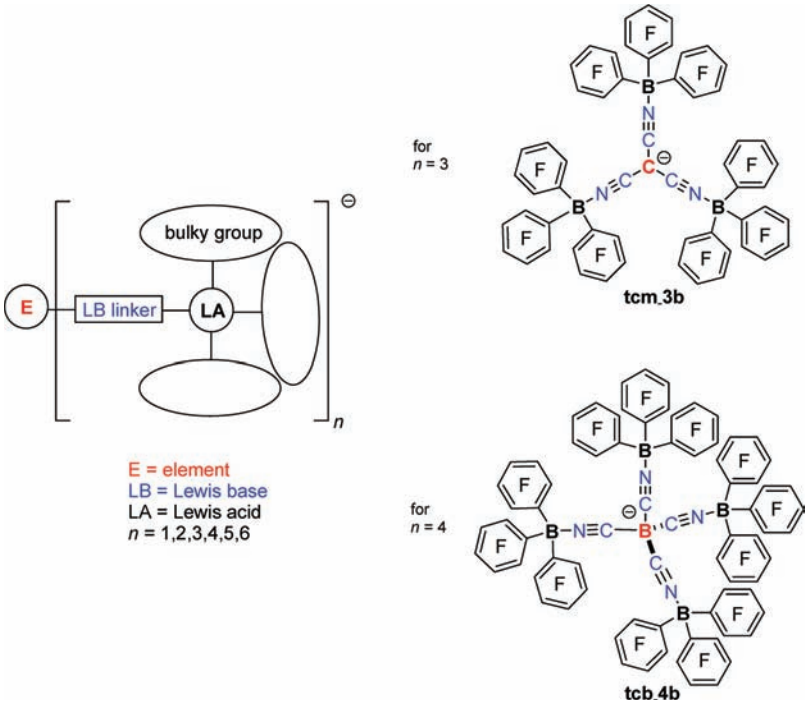

Figure 1. Concept of composing weakly coordinating anions based on Lewis acid base adducts. (Example for $n = 3$: tcm_3b = tricyanomethanide attached to three $B(C_6F_5)_3$. Example for $n = 4$: tcb_4b tetracyanoborate attached to four molecules of $B(C_6F_5)_3$.)

complexes (*e.g.* $[Ag(P_4)_2]^+$)[13−15] and as counterions for cationic Lewis acid catalysts in a wide variety of electrophilic chemistry.[16]

Almost ten years ago Bochmann and co-workers introduced an interesting simple approach to synthesize very weakly nucleophilic anions by coordinating the strong Lewis acid $B(C_6F_5)_3$ to strongly basic bridging groups Z to give WCAs of the type $[Z\{B(C_6F_5)_3\}_n]^{x-}$ (Z = CN, $Ni(CN)_4$, NH_2; $x = 1, 2$; $n = 2, 4$), a procedure also applied by workers at Dow.[16c−e,17−19] This concept can be generalized as shown in Figure 1: A WCA complex is formed (i) by attaching an element E to a Lewis base linker, and (ii) by adding a strong bulky Lewis acid with chemically robust functional groups. In such a Lewis acid/Lewis base complex the negative charge is delocalized over a large anion surface. Based on this synthetic concept, we want to report here on novel donor−acceptor complexes (with CN linker) containing anions, which can be regarded as very weakly coordinating. The synthesis, structure and charge transfer are discussed on the basis of experimentally observed and theoretically obtained data. Since ionic liquids are receiving ever-increasing attention due to their wide potential to serve as electrolytes, as reaction media, as components for solar and fuel cells, or as lubricants,[1,20−27] the BMIM (1-butyl-3-methylimidazolium) and EMIM (1-ethyl-3-methylimidazolium) salts have also been prepared and fully characterized.

Discussion

According to Grimm's hydride displacement law the hydrides of the second row, BH_4^-, CH_3^-, NH_2^-, and OH^-, can be regarded as formal pseudohalides.[28−30] However, chemically there is a significant difference in the basicity between these pseudohalides and the halides, since halides represent only very weak bases while such formal pseudohalides are strong bases. Only the successive substitution of the hydrogen atoms in BH_4^-, CH_3^- and NH_2^- by electron-withdrawing groups such as CN leads to the class of resonance-stabilized, nonlinear pseudohalides.[30] To further decrease the basicity into the range of the halides especially in case of CH_3^- and NH_2^-, which possess one lone pair localized in a p-type atomic orbital (AO), it is also important that this electron-withdrawing group is capable

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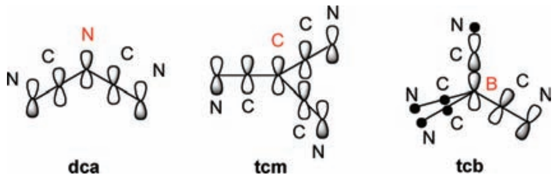

Figure 2. Delocalization of the p-type AO lone pair of the central atom into π^*(C−N) orbitals in dca and tcm. σ(B−C) → π^*(C−N) hyperconjugation in tcb (only one interaction is shown for clarity).

of delocalizing the p-type AO lone pair *e.g.* into empty π^* orbitals which is the case in resonance-stabilized pseudohalides such as dicyanoamide or tricyanomethanide (Figure 2). But also the π^*(CN) orbitals in $B(CN)_4^-$ are slightly populated according to NBO analysis[31−34] due to a small σ(B−C) → π^*(C−N) hyperconjugative effect[35] as displayed in Figure 2. Although the basicity in $B(CN)_4^-$ (tcb = tetracyanoborate), $C(CN)_3^-$ (tcm = tricyanomethanide) and $N(CN)_2^-$ (dca = dicyanamide) is strongly decreased by CN substitution, these anions cannot be regarded to be weakly coordinating as shown on numerous occasions due to the basic terminal nitrogen atom of the cyano group.[36−38] Hence, further delocalization of the anion charge (besides the introduction of steric strain) is achieved by adding a strong bulky Lewis acid such as $B(C_6F_5)_3$ resulting in the formation of the new WCAs such as $B[(CN)\cdot B(C_6F_5)_3]_4^-$ (tcb_4b) and $C[(CN)\cdot B(C_6F_5)_3]_3^-$ (tcm_3b). Salts of $N[(CN)\cdot B(C_6F_5)_3]_2^-$ (dca_2b) have already been described.[16e,39] This approach can be generalized with respect to the Lewis base linker as well as to the bulky Lewis acid (Figure 1).

Synthesis. Synthesis of $M^+B[(CN)\cdot B(C_6F_5)_3]_4^-$, $M^+C[(CN)\cdot B(C_6F_5)_3]_3^-$ and $M^+N[(CN)\cdot B(C_6F_5)_3]_2^-$ (M = alkali metal, Ag, NMe_4, EMIM, BMIM) is easily achieved by adding the corresponding MX salt (X = tcb, tcm, and dca) to a solution of $B(C_6F_5)_3$ (slight excess) in diethyl ether. Within a short period (*ca.* 30 min) the formation of a clear colorless solution can be observed. Removal of the solvent followed by washing with *n*-hexane (removal of excess $B(C_6F_5)_3$) gives the corresponding borane adduct salts in good yields. Recrystallization from diethyl ether yields pure colorless crystals. Often solvent molecules are embedded in the crystals which, however, can be removed readily by thermal treatment (50−60 °C) of the crystalline material over a period of 6−24 h. Furthermore, EMIM and BMIM salts can also be prepared by salt metathesis reaction starting from the silver salt.

Properties. Alkali, ammonium, imidazolium, and silver salts of M[X_*n*b] (X = tcb, tcm, and dca; *n* = 4, 3, 2) are neither air nor moisture sensitive. They dissolve in polar solvents such as CH_2Cl_2, diethyl ether, or thf, but slowly decompose in water under formation of the $H_2O\cdot B(C_6F_5)_3$ adduct as shown by ^{19}F and ^{11}B NMR studies.[40−42] The astonishing stability against water can be attributed mainly to kinetic hindrance by the $B(C_6F_5)_3$ groups. For comparison, it is known that for instance in $CH_3CN\cdot B(C_6F_5)_3$ the acetonitrile molecule can partially be removed by water, which has been studied by means of equilibrium titration.[40] All mentioned tcb, tcm, and dca adduct salts are easily prepared in bulk and are infinitely stable when stored in a sealed tube in the dark (silver salts).

Salts of tcb_4b, tcm_3b, and dca_2b are thermally stable up to over 200 °C (Table 1). The melting points of Ktcb_4b and Ktcm_3b are significantly decreased upon adduct formation although the formula weight increases considerably (ΔT_{mp}(KX − KX_*n*b, X = tcm and tcb): 77.1 °C tcm, 131.1 °C tcb), while for K[dca]/K[dca_2b] an increased melting point is found (ΔT_{mp} = −24.0°). Further decrease in the melting points is achieved by exchanging the metal cations by EMIM and BMIM cations with the smallest melting points always found for the BMIM salts: 122.3° dca_2b, 161.6° tcm_3b and 147.9° tcb_4b (Table 1). Hence, neither of these salts can be regarded as a true ionic liquid (mp < 100 °C).[43]

Spectroscopic Studies. The ^{11}B and ^{13}C data for a number of known compounds and for compounds described in this work are listed in Table 1. ^{11}B and ^{13}C NMR spectroscopy are particularly well suited to distinguish between three-coordinate borane and the four-coordinate boron found in the Lewis acid-base adducts for which the ^{11}B resonance (−11.8 dca_2b, −10.1 tcm_3b, and −8.5 ppm tcb_4b) is shifted to lower frequency with respect to free $B(C_6F_5)_3$ by more than 65 ppm (*cf.* $B(C_6F_5)_3$ in CD_2Cl_2: 59.1 ppm).[44−49] The data illustrate that when boron is directly attached to nitrogen, the $^{11}B\{^1H\}$ resonance is sharp and is observed in the range of −7 to −12 ppm. If the central four-coordinate boron atom is attached to the carbon atoms of CN group as in tcb_4b, the signal is found at −36.1 (*cf.* −38.6 in naked tcb) ppm. A shift of *ca.* 10 to 12 ppm for the *C*N resonance is observed in the ^{13}C spectra upon adduct formation (120.6/108.0 dca/dca_2b; 122.1/111.6 tcm/tcm_3b; 121.9/111.2 ppm tcb/tcb_4b). The ^{19}F NMR spectra of dca_2b, tcm_3b and tcb_4b show resonances shifted to lower frequency compared to $B(C_6F_5)_3$ but similarly broad.

The IR and Raman data of all considered $B(C_6F_5)_3$ adduct anions in Table 1 show sharp bands in the expected region 2290−2380 cm^{-1}, which can be assigned to the ν_{CN} stretching frequencies. As previously shown, the coordination of $B(C_6F_5)_3$ to a NC−R species causes a significant band shift to higher

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Table 1. Thermal Analysis[a] and Spectroscopic Data[b] of dca_2b, tcm_3b and tcb_4b Based Salts along with the Data of the Adduct Free Potassium Salts

	K[dca]	K[dca_2b]	EMIM[dca_2b]	BMIM[dca_2b]	Ag[dca]	Ag[dca_2b]
formula wt in g/mol	105.14	1129.10	1201.17	1229.22	173.91	1197.87
mp in °C						
onset	226.6	250.2	152.5	119.6	*e*	154.6
peak	228.5	252.5	153.8	122.3		155.0
dec point in °C						
onset	280.5[c]	252.5[d]	210.0	211.6	251.7	155.0[d]
Raman ν_{CN} in cm^{-1}	2212	2365	2366	2367	2212	2365
IR ν_{CN} in cm^{-1}		2286	2290	2294	2183	2291
		2369	2364	2374	2249	2363
NMR δ in ppm						
^{11}B-C_6F_5		−11.8	−11.8	−11.8	*f*	−12.0
^{13}CN	120.6	108.0	108.0	108.0		107.5

	K[tcm]	K[tcm_3b]	EMIM[tcm_3b]	BMIM[tcm_3b]	Ag[tcm]	Ag[tcm_3b]
formula wt in g/mol	129.16	1665.10	1737.17	1765.22	197.93	1733.87
mp in °C						
onset	295.7	219.8	192.5	160.5	*e*	*e*
peak	298.0	220.9	197.4	161.6		
dec point in °C						
onset	387.9	264.9	275.9	276.9	394.8	162.2
Raman ν_{CN} in cm^{-1}	2225	2353	2349	2346	2228	*h*
	2173	2297	2297	2295	2170	
IRν_{CN} in cm^{-1}	2171	2292	2290	2289	2174	2290
NMR δ in ppm						
^{11}B-C_6F_5		−10.1	−10.3	−10.1	*f*	−10.1
^{13}C-CN	6.4	14.5	14.5	14.5		14.5
^{13}CN	122.1	111.6	111.6	111.6		111.6

	K[tcb]	K[tcb_4b]	EMIM[tcb_4b]	BMIM[tcb_4b]	Ag[tcb]	Ag[tcb_4b]
formula wt in g/mol	153.98	2201.90	2273.96	2302.02	222.75	2270.67
mp in °C						
onset	410.4	*e*	174.5	140.1	*e*	180.5
peak	413.0		176.2	147.9		184.2
dec point in °C						
onset	554.3	281.9[d]	240.5	230.0	462.5	243.0
Raman ν_{CN} in cm^{-1}	2234	2323	2330	2329	2232	*h*
NMR δ in ppm						
^{11}B-C_6F_5[g]		−8.5	−7.8	−7.6	*f*	−8.5
^{11}B-CN	−38.6	−36.1	−36.1	−36.1		−36.1
^{13}CN	121.9	111.2	110.8	110.7		111.2

[a] Melting and decomposition points. [b] IR, Raman, and NMR. [c] Trimerization.[51] [d] Decomposition begins with the melting. [e] Expected mp above decomposition point. [f] Insoluble in standard organic solvents. [g] $B(C_6F_5)_3$ ^{11}B NMR (CD_2Cl_2, 96 MHz, 25 °C): $\delta = 59.1$(s). ^{19}F NMR (CD_2Cl_2, 282 MHz, 25 °C): $\delta = -128.4$ to -128.5 (m, *o*-F, 2F); -144.2 (t, *p*-F, 1F, $^3J_{FF} = 20.5$ Hz); -161.2 to -161.4 (m, *m*-F, 2F). ^{13}C NMR (CD_2Cl_2, 75 MHz, 25 °C): $\delta = 148.7$ (dm, *o*-C, 6C, $^1J_{CF} = 249.7$ Hz); 141.8 (dm, *p*-C, 3C, $^1J_{CF} = 289.0$ Hz); 138.0 (dm, *m*-C, 6C, $^1J_{CF} = 256.2$ Hz); 113.5 (br, C−B, 3C). [h] Raman laser induced decomposition.

wave numbers ($\Delta\nu$ for potassium salts: 153 dca, 128 tcm, 89 tcb cm^{-1}).[50] Hence, both IR and Raman spectroscopy are also particularly well suited to distinguish between $B(C_6F_5)_3$ adduct anions and the naked anions. The shift to higher wave numbers upon adduct formation correlates nicely with a smaller C−N distance (Table 6, see section on bonding and charge transfer) and decreases along the series dca > tcm > tcb (Table 6).

Influence of Stoichiometry. Depending on the stoichiometry, different adduct anions are formed with less than the maximum number of $B(C_6F_5)_3$ attached to the naked anion. In the case of tcb salts we have studied the influence in more detail. When a large excess of $B(C_6F_5)_3$ is used, the final product is always tcb_4b, which has been synthesized with a number of different cations. However, when an excess of tcb salt was used, we were able to observe the di- and triadducts. For instance, it was possible to isolate the potassium salt with only two $B(C_6F_5)_3$ groups attached to the tcb anion (K[tcb_2b], Figure 3, Table S1 in the Supporting Information), and the 1-ethyl-3-methylimidazolium salt with three $B(C_6F_5)_3$ groups attached to the tcb anion (EMIM[tcb_3b], Figure 4, Table S1 in the Supporting Information). Both anions have been characterized by X-ray crystallography, however, only poor data sets were obtained, which do not allow a detailed discussion of structural parameters but are good enough to prove unambiguously the existence of both anions.

X-ray crystallography. The structures of M[dca_2b] (M = Li, K, Ag), [K(18-crown-6)][tcm_3b] and M[tcb_4b] (M = K, NEt_4) have been determined. Tables 2 and 3 present the X-ray crystallographic data. Selected molecular parameters are listed in Table 4. The molecular structures of the three adduct anions are depicted as superposition of ball-and-stick and space-filling models in Figures 5, 6, and 7. ORTEP

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(50) Jacobsen, H.; Berke, H.; Doering, S.; Kehr, G.; Erker, G.; Froehlich, R.; Meyer, O. *Organometallics* **1999**, *18*, 1724.

(51) Irran, E.; Juergens, B.; Schnick, W *Chem. Eur. J.* **2001**, *7*, 5372.

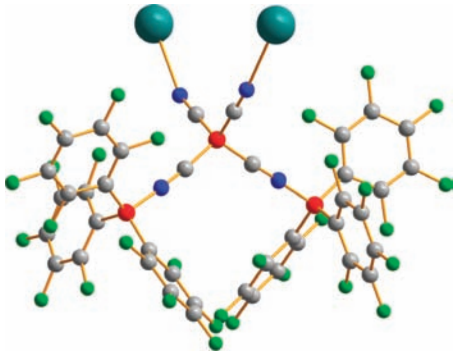

Figure 3. Molecular structure of the tcb_2b anion attached to two K^+ centers in $[K^+]$[tcb_2b]. Color code: boron, red; carbon, dark gray; nitrogen, blue; fluorine, light green; potassium, violet.

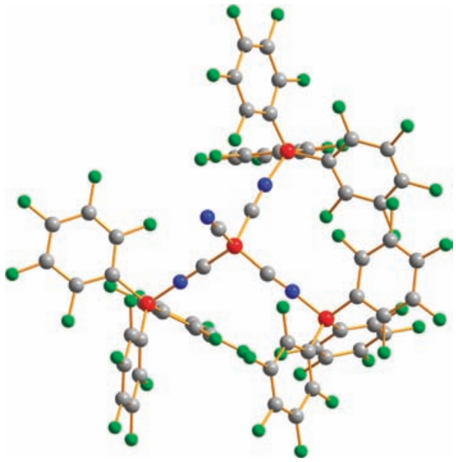

Figure 4. Molecular structure of the tcb_3b anion in [EMIM][tcb_3b]. Color code: boron, red; carbon, dark gray; nitrogen, blue; fluorine, light green.

representations of the asymmetric unit are shown in Figures S1−S5 in the Supporting Information.

(1) K[tcb_4b]. K[tcb_4b] crystallizes in the triclinic space group $P\bar{1}$ with two formula units per cell. The structure consists of separated K^+(diethyl ether)$_4$ and tcb_4b units with no significant cation···anion contacts. Only (ether)C−H···F−C(aryl) interactions are found. The crystallographic asymmetric unit contains one ion pair $[K^+$(diethyl ether)$_4]$[tcb_4b]. The K^+ ion is bonded to each oxygen atom of the four diethyl ether molecules forming a tetrahedral coordination environment around the cation with K−O distances between 2.659(2) and 2.708(2) Å. Two of the diethyl ether molecules are disordered.

The tcb anion (Figure 5) and the four $B(C_6F_5)_3$ groups are connected by means of strong B−N bonds (1.600(2), 1.601(2), 1.622(2) and 1.604(2) Å; *cf.* 1.616(3) Å in $CH_3CN\cdot B(C_6F_5)_3$).[50] The central boron atom of the $B(CN)_4$ core and the boron atoms of the four $B(C_6F_5)_3$ are tetracoordinated. The average length of the B-CN and B−C(aryl) linkages amounts to 1.593(2), and 1.632 Å, respectively (*cf.* 1.595(1) in Ktcb,[36] 1.629 Å in $CH_3CN\cdot B(C_6F_5)_3$[50]). Compared to the naked tcb anion slightly shorter C−N bonds ranging between 1.133(2) and 1.138(2) Å (*cf.* 1.142(1) Å in Ktcb) are observed. The coordination geometry around boron in the $B(CN)_4$ core is slightly distorted with the smallest angle of 107.9(1), and the largest 111.6(1)°. The same holds true for the boron center of the $B(C_6F_5)_3$ groups with average N−B−C(aryl) bonding angles of 105.2(1)° and average C(aryl)−B−C(aryl) angles of 113.2(1)° (*cf.* 104.0(2) and 114.3(2)°, respectively, in $CH_3CN\cdot B(C_6F_5)_3$[50]). In the crystal, the $(NC)_3B-C-N[B(C_6F_5)_3]$ and the $[(NC)_3B]C-N-B(C_6F_5)_3$ axes are close to linear, with average bond angles of 176.3(2) and 176.4(2)°, respectively.

(2) $[NEt_4]$[tcb_4b]·$1.5Et_2O$. $[NEt_4]$[tcb_4b]·$1.5Et_2O$ crystallizes in the triclinic space group $P\bar{1}$ with two formula units per cell. The structure consists of separated ions with no significant cation···anion contacts. Only (ether)C−H···F−C(aryl) interactions are found. The crystallographic asymmetric unit contains one ion pair $[NEt_4]$[tcb_4b] and 1.5 diethyl ether molecules. Since there are no significant differences in the molecular structure of the tcb_4b anion compared to that in the potassium salt, we refer to the discussion above (see also Table 4).

(3) K[tcm_3b]. Since we did not succeed in obtaining single crystals of K[tcm_3b], K[tcm_3b] was recrystallized in the presence of 18-crown-6 ether in diethyl ether. [K(18-crown-6)][tcm_3b] crystallizes in the triclinic space group $P\bar{1}$ with four formula units per cell. The asymmetric unit consists of two independent $[K(18\text{-crown-}6)]^+$ and tcm_3b units, as well as 0.46 diethyl ether molecules. No significant cation···anion contacts are found. A view along the *a* axis reveals stacked chains of $[K(18\text{-crown-}6)]^+$ and tcm_3b ions (Figure 8). Voids are partially filled with diethyl ether molecules (0.92 ether molecule per unit cell).

As depicted in Figure 6, the $C(CN)_3$ core of the tcm_3b anion is nearly trigonal planar ($\sum\angle(C_{central}) = 359.9(2)°$). As already discussed before, the $(NC)_3C-C-N[B(C_6F_5)_3]$ and the $[(NC)_3C]C-N-B(C_6F_5)_3$ axes are close to linear, with average bond angles of 177.8(3) and 175.8(3)°, respectively. The boron coordination geometry is slightly distorted tetrahedral with average C−B−C bonding angles of 109.5°. The average length of the B−CN and B−C(aryl) linkages amounts to 1.593(2) and 1.632 Å, respectively (*cf.* 1.595(1) in Ktcb,[36] 1.629 Å in $CH_3CN\cdot B(C_6F_5)_3$[50]). The C−N bonds range between 1.130(3) and 1.141(3) Å (average 1.134(4) Å), and an average C−C bond length of 1.399(4) Å is found. Interestingly, the tricyanomethanide anion in K[tcm] has also approximate D_{3h} symmetry with C−C bond distances averaging 1.39(2) Å and C−N distances averaging 1.17(1) Å.[52] The central C atom is 0.026 Å above the plane of the three N atoms.

Strong B−N donor−acceptor bonds (1.582(4), 1.602(4), 1.563(4) Å; *cf.* 1.616(3) Å in $CH_3CN\cdot B(C_6F_5)_3$[50]) between the tcm anion (Figure 6) and the three $B(C_6F_5)_3$ groups are found with an average distance of 1.582(4) Å being slightly shorter than that in tcb_4b with 1.607(2) Å.

(4) K[dca_2b]. K[dca_2b] crystallizes in the monoclinic space group $P2_1/c$ with four formula units per cell. The asymmetric unit consists of one K[dca_2b] unit with significant cation···anion contacts (Figure 9). A close inspection of the anion···cation interactions revealed ten K···F(aryl) interactions (d(K−F) < 4 Å) with seven different C_6F_5 moieties (Figure 10). The shortest K···F contact is found at 2.670(3) Å (to F3). Among these ten contacts are four bidentate and two monodentate coordination modes.

(5) K[dca_2b]. K[dca_2b] contains the bent dca_2b anion of approximate symmetry C_{2v} (average bond lengths, $C-N_{bridge}$ 1.294(6), $C-N_{term}$ 1.136(6) Å; average angles, N−C−N 174.9(5)°, C−N−C 118.8(4)°; *cf.* $[Ph_3C]^+$ $[dca\_2b]^-$, $C-N_{bridge}$ 1.282(13), $C-N_{term}$ 1.145(12) Å; average angles N−C−N 172.1(10)°, C−N−C 119.8(9)°;[16e] K[dca] average, $C-N_{bridge}$ 1.33, $C-N_{term}$ 1.13, N−C−N 170°, C−N−C 120°).[51] The average B−N

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(52) Witt, J. R. *Acta Crystallogr.* **1971**, *B27*, 1835.

Table 2. Crystallographic Details of K[dca_2b], [Ag(Et_2O)$_3$][dca_2b] and [Li(thf)$_4$][dca_2b]

	K[dca_2b]	[Ag(Et_2O)$_3$][dca_2b]	[Li(thf)$_4$][dca_2b]
chem formula	$C_{38}B_2F_{30}KN_3$	$C_{50}H_{30}AgB_2F_{30}N_3O_3$	$C_{54}H_{32}B_2F_{30}LiN_3O_4$
formula wt [g mol^{-1}]	1129.13	1420.26	1385.39
color	colorless	colorless	colorless
cryst system	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a [Å]	9.579(2)	9.313(2)	9.253(2)
b [Å]	20.267(4)	12.772(3)	13.331(3)
c [Å]	19.729(4)	23.118(5)	23.851(5)
α [deg]	90.00	78.87(3)	83.84(3)
β [deg]	101.78(3)	83.65(3)	82.06(3)
γ [deg]	90.00	88.61(3)	79.71(3)
V [Å^3]	3749(1)	2681.4(9)	2856(1)
Z	4	2	2
ρ_{calc} [g cm^{-3}]	2.000	1.759	1.611
μ [mm^{-1}]	0.331	0.527	0.167
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	200(2)	173(2)	173(2)
measd reflections	11245	61702	65491
indep reflections	5944	15577	12967
reflections with $I > 2\sigma(I)$	3012	13962	8297
R_{int}	0.0771	0.0214	0.0448
F(000)	2192	1404	1384
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0513	0.0310	0.0440
wR_2 (F^2)	0.1131	0.0853	0.1223
GOF	0.927	1.053	1.070
params	667	808	857

Table 3. Crystallographic Details of [K(18-crown-6)][tcm_3b]·0.46Et_2O, [K(Et_2O)$_4$][tcb_4b] and [N(Ete)$_4$][tcb_4b]·1.5Et_2O

	[K(18-crown-6)][tcm_3b] · 0.46Et_2O	[K(Et_2O)$_4$][tcb_4b]	[N(Et)$_4$][tcb_4b] · 1.5Et_2O
chem formula	$C_{71.82}H_{28.38}B_3F_{45}KN_3O_{6.46}$	$C_{92}H_{40}B_5F_{60}KN_4O_4$	$C_{90}H_{35}B_5F_{60}N_5O_{1.50}$
formula wt [g mol^{-1}]	1963.11	2498.43	2404.28
color	colorless	colorless	colorless
cryst system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	18.433(4)	17.9158(5)	14.916(8)
b [Å]	19.776(4)	18.8215(6)	18.504(9)
c [Å]	24.987(5)	21.0662(6)	20.187(9)
α [deg]	68.15(3)	111.374(2)	110.39(1)
β [deg]	81.19(3)	111.849(2)	105.51(1)
γ [deg]	71.50(3)	112.211(2)	106.62(2)
V [Å^3]	8011(3)	4938.0(3)	4567(4)
Z	4	2	2
ρ_{calc} [g cm^{-3}]	1.628	1.680	1.748
μ [mm^{-1}]	0.225	0.221	0.189
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173(2)	173(2)	173(2)
measd reflections	114777	129717	34742
indep reflections	28083	28210	9855
reflections with $I > 2\sigma(I)$	18592	17868	7390
R_{int}	0.0252	0.0275	0.0394
F(000)	3884	2472	2374
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0573	0.0464	0.0334
wR_2 (F^2)	0.1808	0.1292	0.0801
GOF	1.099	1.051	1.029
params	2629	1581	1550

donor−acceptor bond length is 1.560(6) Å, which is slightly longer than that found in the Ph_3C^+ salt with 1.522 Å.[16e]

(6) [Li(thf)$_4$][dca_2b]. [Li(thf)$_4$][dca_2b] crystallizes in the triclinic space group $P\bar{1}$ with two formula units per cell. The asymmetric unit consists of one [Li(thf)$_4$][dca_2b] unit with four significant cation solvent interactions. The lithium cation has a tetrahedral coordination environment formed by the four thf molecules at 1.906 Å (average). Compared to the potassium salt, similar structural features are found for the dca_2b anion (Table 4).

(7) [Ag(Et_2O)$_3$][dca_2b]. [Ag(Et_2O)$_3$][dca_2b] also crystallizes in the triclinic space group $P\bar{1}$ with two formula units per cell. The silver cation is coordinated by three oxygen atoms of the diethyl ether molecules at significantly different distances (2.266(1), 2.274(1) and 2.341(1) Å, Figure 11). The local coordination environment, however, is almost planar with O−Ag−O angles of 105.30(4), 117.00(4) and 137.45(5)° (angle sum 359.75°). These fairly different Ag−O structural parameters can be attributed to steric repulsion between the ethyl groups (Figures 11 and S4 in the Supporting Information). In agreement with our experimental observations, theoretical results by Feller and Dixon obtained for the gas phase species [Ag(DME)$_n$]$^+$ (n = 1−4, DME = dimethyl ether) show the same picture: For Ag^+, there is essentially no difference between the first and

Table 4. Selected Structural Data of dca_2b, tcm_3b, and tcb_4b Salts[a]

	$K[dca\_2b]$	$[Ag(Et_2O)_3][dca\_2b]$	$[Li(thf)_4][dca\_2b]$	$[K(18\text{-crown-6})][tcm\_3b]$	$[K(Et_2O)_x][tcb\_4b]$	$[NEt_4][tcb\_4b]$
d(C−N)	1.135(6)	1.142(2)	1.142(2)	1.133(3)	1.133(2)	1.076(3)
	1.136(6)	1.145(2)	1.144(2)	1.139(4)	1.135(2)	1.087(3)
				1.142(3)	1.137(2)	1.103(3)
					1.138(2)	1.126(3)
d(E−CN)[b]	1.290(6)	1.285(2)	1.286(2)	1.389(4)	1.590(2)	1.591(5)
	1.298(6)	1.290(2)	1.288(2)	1.397(4)	1.593(2)	1.594(5)
				1.400(4)	1.594(2)	1.602(5)
					1.596(2)	1.609(5)
d(N−B)	1.544(6)	1.556(2)	1.566(2)	1.572(4)	1.600(2)	1.604(4)
	1.575(7)	1.564(2)	1.571(2)	1.591(4)	1.601(2)	1.613(4)
				1.598(4)	1.604(2)	1.627(4)
					1.622(2)	1.629(4)
∠(E−C−N)[b]	174.8(5)	172.5(1)	172.3(2)	174.9(3)	173.8(1)	169.1(3)
	175.0(5)	174.3(1)	173.1(2)	176.9(3)	176.3(2)	175.0(3)
				178.4(3)	177.0(2)	175.1(3)
					178.0(1)	175.4(3)
∠(C−N−B)	164.4(5)	169.6(1)	171.1(2)	174.9(3)	173.1(1)	173.0(3)
	175.6(4)	172.1(1)	173.1(2)	175.9(3)	173.8(1)	174.0(3)
				175.9(3)	179.0(1)	175.6(3)
					179.1(1)	176.9(3)

[a] Distances in Å, angles in deg. [b] E = N dca, C tcm, and B tcb.

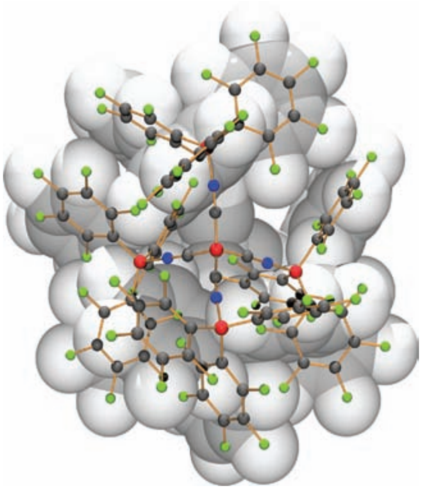

Figure 5. Molecular structure of the tcb_4b anion in $[K(Et_2O)_4][tcb\_4b]$ as superposition of ball-and-stick and space-filling models. Color code: boron, red; carbon, dark gray; nitrogen, blue; fluorine, light green.

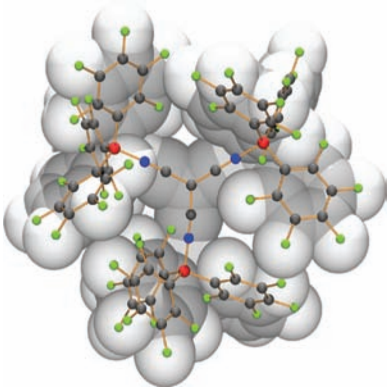

Figure 6. Molecular structure of the tcm_3b anion in [K(18-crown-6)][tcm_3b] as superposition of ball-and-stick and space-filling models. Color code: boron, red; carbon, dark gray; nitrogen, blue; fluorine, light green.

second binding energies ($[Ag(DME)]^+$:[53] ΔH_0(MP2) = 36.6 kcal/mol; $[Ag(DME)_2]^+$: ΔH_0(MP2) = 36.7 kcal/mol). The binding energy of the third DME ligand ($[Ag(DME)_3]^+$: ΔH_0(MP2) = 16.2 kcal/mol) is considerably smaller than that of the first or second. Thus two small and one long Ag−O distances (2.192 *vs* 2.284 Å) have been calculated.[53] It can be assumed that the significant asymmetry in the coordination sphere around the silver cation indicates already the transition from tricoordination to dicoordination which is the usual coordination mode of solvents found for silver salts such as $[Ag(NH_3)_2]^+$. The synthesis of $[Ag(Et_2O)_3][BF_4]$ has already been reported but without any structural data,[54] and in agreement with our observation this salt loses the ether molecules at room temperature. The WCA dca_2b seems to stabilize this unusual tricoordination. Again, the structural parameters of the dca_2b anion are very similar to those found in the potassium salt (Table 4).

Anion Size and Lattice Enthalpies. The ion volumes of dca, tcm and tcb and their adduct anions have been estimated from the average atomic volumes simply by summing the volume contributions from each atom in the molecular formula as introduced by Hofmann (Table 5).[55] It should be noted that Hofmann's approach is not always the best source of volumes. For instance the anion and cation volumes are equal since no charge considerations are made. Jenkins and Liebman's isomegethic rule can be considered as the theoretical basis of Hofmann's approach. In addition, the isomegethic rule offers another way to ion volumes.[56]

As expected the anion volumes increase along the series dca (63) < tcm (91) < tcb (116) and dca_2b (924) < tcm_3b (1382) < tcb_4b (1838 Å^3). Compared to the naked anions dca, tcm

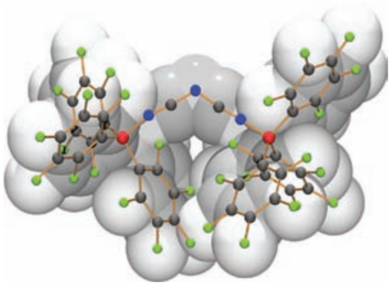

Figure 7. Molecular structure of the dca_2b anion in K[dca_2b] as superposition of ball-and-stick and space-filling models. Color code: boron, red; carbon, dark gray; nitrogen, blue; fluorine, light green.

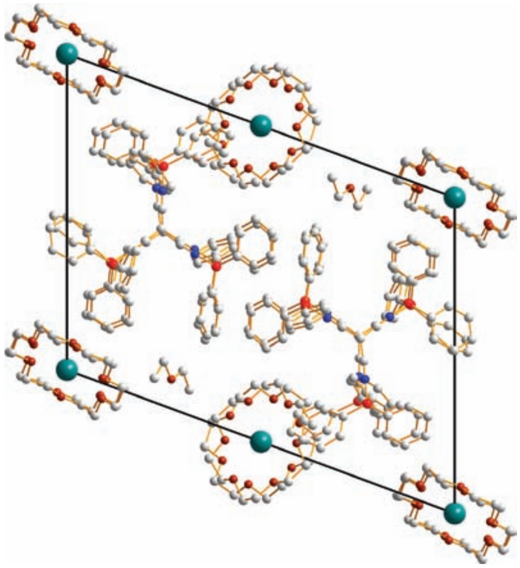

Figure 8. Stacking diagram of [K(18-crown-6)][tcm_3b]·0.46 Et_2O (view along 100). Color code: boron, red; carbon, dark gray; nitrogen, blue; oxygen, brown; potassium, violet. Fluorine and hydrogen atoms are omitted for clarity.

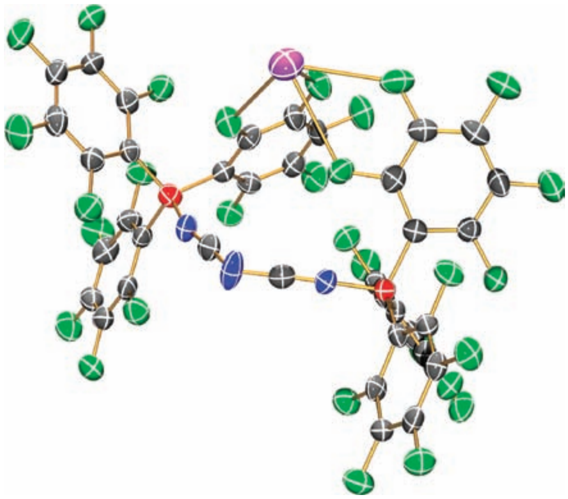

Figure 9. ORTEP drawing of the molecular structure of K[dca_2b] in the crystal. Thermal ellipsoids with 50% probability at 173 K. Color code: boron, red; carbon, dark gray; nitrogen, blue; fluorine, light green; potassium, violet.

and tcb the volume of the $B(C_6F_5)_3$ adduct anions dramatically increases with the largest increase found for tcb_4b (*cf.* $\Delta V_{\text{ion}} = V_{\text{adduct-ion}} - V_{\text{ion}} = 861$ dca_2b/dca, 1292 tcm_3b/tcm and 1722 tcb_4b/tcb). Each $B(C_6F_5)_3$ group contributes to the ion volume by about 430.5 Å^3.

Since the potassium salt Kdca_2b crystallized without solvent molecules, the experimentally determined cell volume could be used to calculate the ion volume of the dca_2b according to eq 1 for an A^+X^- salt.[57] With a cell volume of 3749.36 Å^3, $Z = 4$ and $V(K^+) = 14.4$ Å^3,[58,59] an anion volume V(dca_2b) = 922 Å^3 is calculated (V(dca_2b) ≈ V([K(dca_2b)] − $V(K^+)$)), in accord with the volume derived by Hofmann's approach (*cf.* 924 Å^3, Table 5).

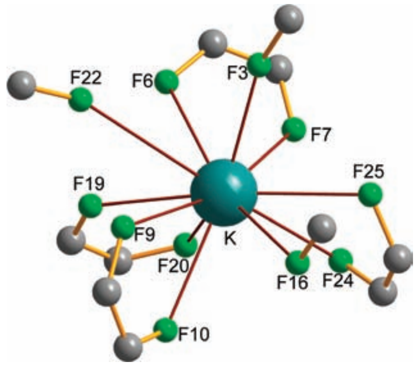

Figure 10. K···F contacts in K[dca_2b] (shown for d(K···F) < 4.0 Å): F3 2.670(3); F19 2.736(3); F20 2.835(3); F25 2.890(3); F10 2.955(3); F7 2.999(3); F16 3.097(3); F24 3.154(4); F6 3.290(3). F22 3.569(3). Carbon atoms attached to the coordinating F atoms are also displayed but not assigned for clarity reasons.

$$V_{\text{ion}}(X^-) = [V_{\text{cell}}(A^+X^-)/Z] - V_{\text{ion}}(A^+) \qquad (1)$$

Principles of volume-based thermodynamics (VBT), introduced by Jenkins, Glasser and Passmore, have been used to estimate the lattice potential energy (U_{pot}), lattice enthalpy (ΔH_L) and the standard entropy ($S°_{298}$ in J mol^{-1} K^{-1} at 298.15 K and 101 kPa) of the new A^+X^- salts (A = potassium, X = dca_2b, tcm_3b and tcb_4b) from its molecular volume (Table 5).[58,59c] As expected the smallest lattice potential energy was found for K[tcb_4b] with 299.6 kJ mol^{-1} followed by 318.3 for K[tcm_3b] and 343.4 kJ mol^{-1} for K[dca_2b]. Compared to potassium salts with the naked anions the lattice potential energy decreased by 311 (dca_2b), 287 (tcm_3b), and 272 kJ mol^{-1} (tcb_4b). The high solubility of salts with these adduct anions in common polar organic solvents such as CH_2Cl_2 or thf (in contrast to salts with the naked anion) can directly be attributed to these decreased lattice potential energies.[1a] For stability estimations it might be of interest to know the standard entropy of $B(C_6F_5)_3$ which can be derived from the volume 430.5 Å^3 and amounts to 601 J K^{-1} mol^{-1}.

Computations: Energetics of Adduct Formation, Structural Trends, and Charge Transfer. Adduct anions such as dca_2b, tcm_3b and tcb_4b are typical charge transfer complexes, and the bond between the $B(C_6F_5)_3$ and the naked anions can be regarded as a donor−acceptor bond.[62] The gas phase energies for mono-, di-, tri- and tetraadduct formation according to eq 2 have been computed at the B3LYP/6-31+G(d) level of theory (Table 6):

$$[E(CN)_n^-]\cdot[B(C_6F_5)_3]_{m(g)} + B(C_6F_5)_{3(g)} \rightarrow [E(CN)_n^-]\cdot[B(C_6F_5)_3]_{m+1(g)} \qquad (2)$$

where E = N, $n = 2$, $m = 0, 1, 2$; E = C, $n = 3$, $m = 0, 1, 2, 3$; and E = B, $n = 4$, $m = 0, 1, 2, 3, 4$.

All adduct formation steps represent exothermic reactions. The energy release upon adduct formation is always largest when the first $B(C_6F_5)_3$ group is attached and decreases along

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Table 5. Ionic Volumes, Atomic Distances for Ions Discussed in This Study and Thermodynamic Data Derived from Volume-Based Thermodynamics (VBT)[57,59c] for the Potassium Salts

	dca	tcm	tcb	dca_2b	tcm_3b	tcb_4b
V_{ion} in Å^3	63 (87)[e]	91 (113)[e]	116 (137)[e]	924 (901)[e]	1382 (1359)[e]	1838 (1766)[e]
d_{ld}(F···F)[a] in Å				15.607(5)	16.007(6)	16.411(3)
$U_{pot}(K^+X^-)$ in kJ mol^{-1}[b]	654.3	600.5	566.43	343.4	313.7	294.8
$S°_{298}(K^+X^-,s)$ in J K^{-1} mol^{-1}[c]	120.3	158.3	192.34	1291.2	1914.1	2534.3
$\Delta H_L(K^+X^-)$ in kJ mol^{-1}[d]	659.3 (656.3)	605.5 (602.8)	571.4 (569.08)	348.4 (347.8)	318.7 (318.3)	299.8 (299.6)

[a] d_{ld} = largest distance between two fluorine atoms in the adduct anion. [b] $U_{pot} = 2\{[117.3/(V_m^{1/3})] + 51.9 \text{ kJ mol}^{-1}\}$. [c] $S°_{298} = 1360V_m + 15 \text{ J K}^{-1} \text{ mol}^{-1}$. [d] The lattice enthalpy can also be calculated by means of Bartlett's relationship (value in parentheses):[60] $\Delta H_L = [232.8/(V_m^{1/3})] + 110 \text{ kJ mol}^{-1}$. [e] Values in parentheses correspond to scaled Hoffmann volumes. Markedly, Hoffmann's method does not take charge into account; however, cations of the same summary formula are always smaller than anions. Krossing *et al.* found that $V_{Hoffmann}$ correlates linearly with the experimental cation volumes according to $V_{exp} = 0.964V_{Hoffmann} - 7$ Å^3 and for the anion according to $0.946V_{Hoffmann} + 27$ Å^3.[61]

the series −198.5 dca_1b, −150.3 tcm_1b and −110.6 tcb_1b kJ/mol. For double (dca_2b, tcm_2b and tcb_2b) and triple adduct formation (tcm_3b and tcb_3b) a significantly smaller energy release is found (Table 6, values in parentheses), but even when the fourth $B(C_6F_5)_3$ group is added to the last free cyano group in tcb_3b a significant energy gain of −36.2 kJ/mol is estimated. It should be noted that B3LYP computations give complexation energies which are intrinsically too small due to an improper treatment of dispersion energy.[63] This means that these B3LYP values only represent lower limits. For the anion tcb_4b, there is a chance that, upon introduction of this anion, the strong Lewis acid $B(C_6F_6)_3$ may concomitantly be introduced as a result of the weaker complexation enthalpy tcb_4b → tcb_3b + $B(C_6F_5)_3$ (36.2 kJ/mol). Hence in more basic conditions, e.g. especially with bases that are preferable for $B(C_6F_5)_3$, tcb_4b may also serve as a source of $B(C_6F_5)_3$.

(1) Structure. In agreement with the experimental data (X-ray), the E−C−N moiety remains essentially linear (E = N, C, B in dca, tcm and tcb), and the local symmetry of the dca core (C_{2v}) in dca_2b, tcm core (D_{3h}) in tcm_3b and tcb core (T_d) in tcb_4b is also nearly maintained. The donor−acceptor CN−$B(C_6F_5)_3$ bond increases along dca_2b < tcm_3b < tcb_4b (1.558, 1.581, and 1.596 Å respectively), which is in accord with experimental data (Table 4). With increasing number of $B(C_6F_5)_3$ molecules attached, the N−B bond lengths slightly increase (for instance tcb_1b 1.576, tcb_2b 1.585, tcb_3b 1.591 and tcb_4b: 1.596 Å), while the C−N bond lengths slightly decrease (for instance $d_{uncoordinated}/d_{coordinated}$: tcb 1.164/−, tcb_1b 1.163/1.153, tcb_2b 1.162/1.151, tcb_3b 1.161/1.150 and tcb_4b −/1.149 Å). Thus successive coordination of the cyano groups to the Lewis acid $B(C_6F_5)_3$ always leads to a measurable strengthening of the cyano triple bonds as displayed by short C−N distance and a considerable shift of the ν_{CN} to higher wave numbers (Table 1). Although the reduction of the C−N bond length along the series dca > dca_1b > dca_2b, tcm > tcm_1b > tcm_2b > tcm_3b, and tcb > tcb_1b > tcb_2b > tcb_3b > tcb_4b, respectively, may seem small, it is clearly noticeable. This bond contraction Δd_{CN} (anion − anion_adduct) is compatible for experiment and theory and is about 0.01 Å. The origin of this contraction has been studied by several groups indicating that electrostatic interactions dominate the bonding in such donor−acceptor complexes.[50] However, orbital interactions provide additional stabilization (σ donation and π back donation).[50] The orbital mainly responsible for the σ donation is assumed to possess some C−N antibonding character; hence upon adduct formation electron density is removed from this orbital and consequently strengthen and shorten the bond.

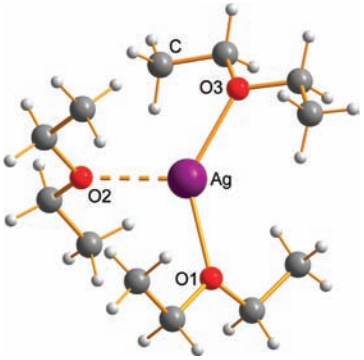

Figure 11. Coordination sphere around the Ag^+ ion in $[Ag(Et_2O)_3]$[dca_2b]. Distances in Å, angles in deg: Ag−O1 2.266(1), Ag−O2 2.341(1), Ag−O3 2.274(1); O1−Ag−O2 105.30(4), O1−Ag−O3 137.45(5), O2−Ag−O3 117.00(4).

(2) Charge Transfer. According to NBO analysis (NBO = natural orbital analysis),[31] the charge transfer is between 0.33 and 0.42 *e* per $B(C_6F_5)_3$ group attached to dca, tcm or tcb (Table 6) and therefore increases almost linearly with an increasing number of $B(C_6F_5)_3$ groups attached to the anions. Interestingly, for tcm_3b (1.22 *e*), tcb_3b (1.18 *e*) and tcb_4b (1.51 *e*) more than one electron (total charge transfer $\sum Q_{CT}$) is transferred to the attached $B(C_6F_5)_3$ groups, that is the tcm and the tcb cores of these anions are now positively charged in contrast to the singly negatively charged naked anions.

According to this fairly large charge transfer, the anion charge is strongly delocalized over 73 (dca_2b), 109 (tcm_3b) and 145 atoms (tcb_4b) and hence such voluminous anion adducts can be considered weakly coordinating anions.

Summary. In summary the formation of donor−acceptor adducts of tris(pentafluorophenyl)borane with strongly coordi-

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(58) Radii for K^+ are found in the range 1.33 (Goldschmidt) to 1.51 Å (Shannon) resulting in $V(K^+)$ = 9.85 (Goldschmidt) and 14.4 Å^3 (Shannon). Recently, Jenkins and Glasser published internally consistent ion volumes, which is 27.7 Å^3 for K^+.

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Table 6. Computed Structural Parameters, Reaction Energies and Total Charge Transfer

product/species	abbreviation	d(C≡N) in Å	d(N−B) in Å	$\Delta E_{(eq1-4)}$ in kJ/mol[a]	$\sum Q_{ct}$ in e[b]
$[N(CN)_2^-]$	dca	1.181			
$[N(CN)_2^-]\cdot[B(C_6F_5)_3]_1$	dca_1b	1.174	1.535	−198.5	0.50
$[N(CN)_2^-]\cdot[B(C_6F_5)_3]_2$	dca_2b	1.164	1.558	−323.2 (−124.7)	0.92(0.42)
$[C(CN)_3^-]$	tcm	1.173			
$[C(CN)_3^-]\cdot[B(C_6F_5)_3]_1$	tcm_1b	1.167	1.551	−150.3	0.47
$[C(CN)_3^-]\cdot[B(C_6F_5)_3]_2$	tcm_2b	1.160	1.570	−247.1 (−96.8)	0.86 (0.39)
$[C(CN)_3^-]\cdot[B(C_6F_5)_3]_2$	tcm_3b	1.156	1.581	−319.6 (−72.5)	1.22 (0.36)
$[B(CN)_4^-]$	tcb	1.164			
$[B(CN)_4^-]\cdot[B(C_6F_5)_3]_1$	tcb_1b	1.153	1.576	−110.6	0.43
$[B(CN)_4^-]\cdot[B(C_6F_5)_3]_2$	tcb_2b	1.151	1.585	−191.2 (−80.6)	0.83 (0.39)
$[B(CN)_4^-]\cdot[B(C_6F_5)_3]_3$	tcb_3b	1.150	1.591	−252.6 (−61.4)	1.18 (0.36)
$[B(CN)_4^-]\cdot[B(C_6F_5)_3]_4$	tcb_4b	1.149	1.596	−288.8 (−36.2)	1.51(0.33)

[a] Values in parentheses correspond to the reaction eq(m) − eq(m − 1) of the mth step. [b] Values in parentheses correspond to $\sum Q_{ct}(m) - \sum Q_{ct}(m-1) = q_{ct}$ of the mth step.

nating anions such as dicyanoamide, tricyanomethanide and tetracyanoborate is a synthetically facile route to the bulky very weakly coordinating anions $[N(CN\cdot B(C_6F_5)_3)_2]^-$ (dca_2b), $[C(CN\cdot B(C_6F_5)_3)_3]^-$ (tcm_3b), and $[B(CN\cdot B(C_6F_5)_3)_4]^-$ (tcb_4b), which were isolated as stable alkali and silver salts. EMIM and BMIM salts have also been prepared but with melting points between 120 °C and 200 °C, such that these salts cannot be considered as true ionic liquids.[43] All studied salts with adduct anions of the type dca_2b, tcm_3b and tcb_4b are thermally stable up to over 200 °C.

As expected the volumes of the these adduct anions increase along the series dca_2b (924 Å^3) < tcm_3b (1382 Å^3) < tcb_4b (1838 Å^3) with a contribution of each $B(C_6F_5)_3$ group of about 430.5 Å^3. Computations display an exothermic formation of these adduct anions, relatively small lattice potential energies and a fairly large charge transfer per $B(C_6F_5)_3$ group slightly decreasing with an increasing number of $B(C_6F_5)_3$ groups attached.

These new anions may be utilized as a true alternative to other widely used weakly coordinating anions since they are similarly easily accessible. Moreover, both for steric and electronic reasons it seems reasonable to expect that if used as counterions for cationic early transition metal catalysts such anions may show reduced ion pairing and hence increased catalytic activity.[16]

Computational Details. Our goal was to compare the structures and energetics of differently substituted adduct anions of the type $[E(CN)_n^-]\cdot[B(C_6F_5)_3]_n$: E = N dca_$n$b with n = 1, 2; E = C tcm_nb with n = 1, 2, 3; E = B tcb_nb with n = 1, 2, 3, 4. Structural data of all considered species were calculated by using the hybrid density functional theory (B3LYP) with the program package Gaussian03.[64] Three different types of basis sets were used for the adduct free anions: (i) a 6-31+G(d), (ii) an aug-cc-pVDZ, and (iii) a 6-311+G(2df) basis. Moreover, trial MP2 calculations were carried out for methanide anions only. Further details are presented in the Supporting Information. If not otherwise stated, all discussed computational data refer to the B3LYP/6-31+G(d) level of theory. Comparison of these data sets using different basis sets exhibits differences in bond lengths no larger than 0.01−0.02 Å. The bond angles in all these molecules are also rather independent of the choice of basis sets.[65]

The reaction energies of the adduct formation were estimated using the total energies without any thermal corrections. Due to the large size of the adduct anions it was impossible to obtain frequency data. Thus thermal corrections have not been carried out.

NBO analyses[31] were carried out to investigate the charge transfer at the B3LYP level utilizing the optimized B3LYP geometry. Details of the NBO analyses are summarized in Table 6.

It should be emphasized that the computation was carried out for single, isolated (gas-phase) anions. There may well be significant differences among gas-phase, solution, and solid-state results and derived conclusions.

Experimental Section

General Information. All manipulations were carried out under oxygen- and moisture-free conditions under Argon using standard Schlenk or drybox techniques.

Dichloromethane was purified according to a literature procedure,[66] dried over CaH_2 and freshly distilled prior to use. Diethyl ether was dried over Na/benzophenone and freshly distilled prior to use. n-Hexane was dried over Na/benzophenone/tetraglyme and freshly distilled prior to use. $B(C_6F_5)_3$ was prepared by a modified literature procedure originally developed by Massey *et al.*[67] K[tcm] and K[tcb] were prepared according to modified literature procedures.[68,69] K[dca] (99% Merck), [EMIM]Cl (99% Fluka) and [BMIM]Cl (99.99% Merck) were used as received.

NMR. $^{19}F\{^1H\}$, ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker spectrometers AVANCE 250, 300, or 500. The ^1H and ^{13}C NMR chemical shifts were referenced to the solvent signals (^{13}C δ_{CD2Cl2} = 54.0; ^1H δ_{CDHCl2} = 5.31). The ^{19}F and ^{11}B chemical shifts are referred (δ = 0) to $CFCl_3$ and $B(OH)_3$ (δ = 0), respectively.

IR. Nicolet 6700 FT-IR spectrometer with a Smart Endurance ATR device or Nicolet 380 FT-IR with Smart Orbit ATR module.

Raman. Bruker VERTEX 70 FT-IR with RAM II FT-Raman module, equipped with a Nd:YAG laser (1064 nm).

MS. Finnigan MAT 95-XP from Thermo Electron.

CHN analyses. Analysator Flash EA 1112 from Thermo Quest.

DSC. Thermoanalytical measurements were performed with a DSC 823e from Mettler-Toledo instrument. Two point calibrations with In (mp 156.6 °C) and Zn (mp 419.6 °C) were carried out.

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(64) All calculations were performed using the Gaussian program package: Frisch, M. J.; et al. *Gaussian 03, Revision E.01*; Gaussian, Inc.: Wallingford, CT, 2004.

(65) For a more thorough discussion on the basis set dependence of molecular geometries, see: Klapötke, T. M.; Schulz, A. *Ab initio Methods in Main Group Chemistry*; with an invited chapter by R. D. Harcourt about VB Theor;, John Wiley & Sons: New York, 1998.

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About 2−6 mg of the solid samples were weighed and contained in sealed aluminum crucibles. They were studied in the temperature range of 20 °C to 600 °C with a heating rate of 5 °C/min; throughout this process the furnace was flushed with dry nitrogen. For the evaluation of the output the Star^e software was employed.

X-ray Structure Determination. X-ray quality crystals of all samples were selected in Fomblin 1800 oil (Alfa Aesar) at ambient temperatures. All measurements were carried out at 173(2) K (except from K[dca_2b] at 200(2) K). The data were collected on a Bruker-Nonius Apex X8 CCD diffractometer (Nonius Kappa CCD diffractometer, K[dca_2b]), using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (*SHELXS-97*)[70] and refined by full-matrix least squares procedures (*SHELXL-97*).[71] Semiempirical absorption corrections were applied except for K[dca_2b] (SADABS).[72] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in the refinement at calculated positions using riding models.

General Synthetic Procedure. For the synthesis of $M^+B[(CN)\cdot B(C_6F_5)_3]_4^-$, $M^+C[(CN)\cdot B(C_6F_5)_3]_3^-$ and $M^+N[(CN)\cdot B(C_6F_5)_3]_2^-$ (M = alkali metal, Ag, NMe_4, EMIM, BMIM) salts: To a solution of $B(C_6F_5)_3$ (3−5-fold excess) in diethyl ether was added the cyanide salt. After stirring for 30 min a colorless solution was observed. Removal of the solvent led to a white solid, which was washed three times with 20 mL of *n*-hexane (removal of the $B(C_6F_5)_3$ excess), and dried in vacuo. The products were obtained as colorless powders. Recrystallization from diethyl ether yields pure colorless crystals. Included solvents molecules can be removed by thermal treatment at 50−60 °C in vacuo.

$KN[(CN)B(C_6F_5)_3]_2$, K[dca_2b]. $B(C_6F_5)_3$ (1.530 g, 3 mmol, 3 equiv) in 60 mL of diethyl ether and K[dca] (0.105 g, 1 mmol, 1 equiv) give the product Kdca_2b. Yield of K[dca_2b]: 0.68 g (60%), mp 252.5 °C (DSC). $C_{38}B_2F_{30}KN_3$ (1129.10): calcd N 3.72, C 40.42; found N 3.02, C 40.12. ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C): $\delta = 147.7$ (dm, *o*-C, 2C, $^1J_{CF} = 240.7$ Hz); 139.4 (dm, *p*-C, 1C, $^1J_{CF} = 249.6$ Hz); 136.7 (dm, *m*-C, 2C, $^1J_{CF} = 245.6$ Hz); 117.5 (br, C−B, 1C); 107.5 (br, CN, 1C). ^{11}B NMR ($CDCl_3$, 96 MHz, 25 °C): $\delta = -11.99$ (s). ^{19}F NMR ($CDCl_3$, 282 MHz, 25 °C): $\delta = -135.1$ to -135.2 (m, *o*-F, 2F); −159.5 (t, *p*-F, 1F, $^3J_{FF} = 20.3$ Hz); −165.5 to −165.6 (m, *m*-F, 2F). IR (ATR, cm^{-1}): $\nu = 2982$ (w), 2516 (w), 2369 (w), 2285 (s), 1645 (s), 1515 (s), 1462 (vs), 1455 (vs), 1377 (w), 1282 (s), 1097 (s), 975 (vs), 874 (s), 865 (w), 797 (s), 772 (w), 762 (s), 750 (s), 737 (w), 728 (w), 705 (s), 680 (s), 672 (s), 632 (w), 619 (w), 607 (w), 576 (w). Raman (1500 mW, 50 scans, 25 °C, cm^{-1}): $\nu = 2360$ (10) 1650 (2), 1520 (2), 1302 (1), 700 (1), 580 (3), 490 (3), 449 (4), 396 (4). MS *m/z* (%): 167 (12), 361 (30), 512 (45) $[B(C_6F_5)_3]^-$, 578 (100) $[NC{-}N{-}CN\ B(C_6F_5)_3]^-$, 1090 (20) $[M - H]^-$. HRMS (ESI): calcd for $C_{38}{}^{11}B_2F_{30}N_3$ ($[M - H]^-$) 1089.98048, found 1089.9818.

$AgN[(CN)B(C_6F_5)_3]_2$, Ag[dca_2b]. $B(C_6F_5)_3$ (1.530 g, 3 mmol, 3 equiv) in 60 mL of diethyl ether and Ag[dca] (0.173 g, 1 mmol, 1 equiv) give the product Ag[dca_2b]. Yield of Ag[dca_2b]: 0.86 g (72%), mp 155.0 °C (DSC). $C_{38}AgB_2F_{30}N_3$ (1197.80): calcd N 3.51, C 38.10; found N 3.48, C 37.07. ^{13}C NMR (CD_2Cl_2, 75 MHz, 25 °C): $\delta = 147.3$ (dm, *o*-C, 6C, $^1J_{CF} = 240.9$ Hz); 139.0 (dm, *p*-C, 3C, $^1J_{CF} = 248.9$ Hz); 136.3 (dm, *m*-C, 6C, $^1J_{CF} = 248.7$ Hz); 116.9 (br, C−B, 3C); 107.5 (br, CN, 1C). ^{11}B NMR (CD_2Cl_2, 96 MHz, 25 °C): $\delta = -12.0$ (s). ^{19}F NMR (CD_2Cl_2, 282 MHz, 25 °C): $\delta = -135.1$ to -135.2 (m, *o*-F, 2F); −159.5 (t, *p*-F, 1F, $^3J_{FF} = 20.3$ Hz); −165.5 to −165.6 (m, *m*-F, 2F). IR (ATR, cm^{-1}): $\nu = 2985$ (w), 2890 (w), 2363 (w), 2291 (s), 1645 (s), 1515 (s), 1449 (vs),1382 (s), 1282 (s), 1086 (s), 1068 (s), 971 (vs), 931 (w), 867 (w), 839 (w), 795 (s), 771 (s), 739 (w), 729 (w), 698 (w) 678 (s), 619 (w), 576 (w). Raman (1500 mW, 50 scans, 25 °C, cm^{-1}): $\nu = 2365$ (10) 1647 (2), 1520 (2), 1302 (1), 703 (1), 580 (4), 492 (4), 448 (4), 395 (4). MS *m/z* (%): 167 (12), 361 (40), 512 (68) $[B(C_6F_5)_3]^-$, 578 (100) $[NC{-}N{-}CN\ B(C_6F_5)_3]^-$, 1059 (18), 1090 (5) $[M - H]^-$. HRMS (ESI): calcd for $C_{38}{}^{11}B_2F_{30}N_3$ ($[M - H]^-$) 1089.98048, found 1089.98152.

$[EMIM]N[(CN)B(C_6F_5)_3]_2$, EMIM[dca_2b]. $B(C_6F_5)_3$ (2.56 g, 5 mmol, 3 equiv) in 60 mL of diethyl ether and EMIM[dca] (0.177 g, 1 mmol, 1 equiv) give the product EMIM[dca_2b]. Yield of EMIM[dca_2b]: 0.72 g (60%), mp 153.8 °C (DSC). $C_{44}H_{11}B_2F_{30}N_5$ (1201.17): calcd N 5.83, C 44.00; found N 5.17, C 44.75. ^{1}H NMR (CD_2Cl_2, 300 MHz, 25 °C): $\delta = 8.15$ (s, N−CH−N, 1H); 7.35−7.34 (m, MeNCH, 1H); 7.32 - 7.30 (m, EtNCH, 1H); 4.24 (q, CH_2, 2H, $^3J_{CH3CH2} = 7.4$ Hz); 3.95 (s, NCH_3, 3H); 1.59 (t, CH_3, 3H, $^3J_{CH3CH2} = 7.3$ Hz). ^{11}B NMR ($CDCl_3$, 96 MHz, 25 °C): $\delta = -12.03$ (s). ^{19}F NMR ($CDCl_3$, 282 MHz, 25 °C): $\delta = -135.1$ to -135.3 (m, *o*-F, 2F); −159.4 (t, *p*-F, 1F, $^3J_{FF} = 21.4$ Hz); −165.4 to −165.6 (m, *m*-F, 2F). ^{13}C NMR ($CDCl_3$, 63 MHz, 25 °C): $\delta = 148.7$ (dm, *o*-C, 2C, $^1J_{CF} = 243.6$ Hz); 140.4 (dm, *p*-C, 1C, $^1J_{CF} = 248.8$ Hz); 137.6 (dm, *m*-C, 2C, $^1J_{CF} = 246.4$ Hz); 134.2 (br, NCHN, 1C); 124.8 (s, MeNCH, 1C); 123.3 (s, EtNCH, 1C); 118.5 (br, C−B, 1C); 109.5 (br, CN, 1C); 46.6 (s, $N{-}CH_2$, 1C); 37.3 (s, $N{-}CH_3$, 1C); 15.4 (s, $NCH_2{-}\mathit{C}H_3$, 1C). IR (ATR, cm^{-1}): $\nu = 2363$ (w), 2290 (s), 1646 (s), 1600(w), 1569 (w), 1516 (s), 1453 (vs),1379 (s), 1282 (s), 1164 (w), 1096 (s), 970 (vs), 863 (w), 835 (w), 795 (w), 771 (s), 742 (w), 730 (w), 698 (w) 680 (s), 619 (w), 576 (w). Raman (1500 mW, 50 scans, 25 °C, cm^{-1}): $\nu = 2368$ (10) 1648 (3), 1384 (2), 580 (2), 485 (3), 446 (2), 390 (2).

$[BMIM]N[(CN)B(C_6F_5)_3]_2$, BMIM[dca_2b]. $B(C_6F_5)_3$ (2.56 g, 5 mmol, 3 equiv) in 60 mL of diethyl ether and BMIM[dca] (0.205 g, 1 mmol, 1 equiv) give the product BMIM[dca_2b]. Yield of BMIM[dca_2b]: 0.74 g (60%), mp 122.3 °C (DSC). $C_{46}H_{15}B_2F_{30}N_5$ (1229.22): calcd N 5.70, C 44.95; found N 5.25, C 44.94. ^{1}H NMR (CD_2Cl_2, 300 MHz, 25 °C): $\delta = 8.14$ (s, N−CH−N, 1H); 7.33−7.30 (m, CH−CH, 2H); 4.16 (t, $N{-}CH_2$, 2H, $^3J_{CH3CH2} = 7.5$ Hz); 3.95 (s, $N{-}CH_3$, 3H); 1.92−1.82 (m, $N{-}CH_2{-}\mathit{CH}_2$, 2H); 1.43−1.31 (m, $\mathit{CH}_2{-}CH_3$, 2H); 0.97 (t, $CH_2{-}\mathit{CH}_3$, 3H, $^3J_{CH3CH2} = 7.3$ Hz). ^{11}B NMR ($CDCl_3$, 96 MHz, 25 °C): $\delta = -12.07$ (s). ^{19}F NMR ($CDCl_3$, 282 MHz, 25 °C): $\delta = -135.1$ to -135.2 (m, *o*-F, 2F); −159.4 (t, *p*-F, 1F, $^3J_{FF} = 20.0$ Hz); −165.4 to −165.6 (m, *m*-F, 2F). ^{13}C NMR ($CDCl_3$, 63 MHz, 25 °C): $\delta = 148.4$ (dm, *o*-C, 2C, $^1J_{CF} = 242.5$ Hz); 140.1 (dm, *p*-C, 1C, $^1J_{CF} = 246.5$ Hz); 137.4 (dm, *m*-C, 2C, $^1J_{CF} = 242.4$ Hz); 134.4 (br, NCHN, 1C); 124.7 (s, MeNCH, 1C); 123.6 (s, EtNCH, 1C); 118.5 (br, C−B, 1C); 109.0 (br, CN, 1C); 51.2 (s, $N{-}CH_2$, 1C); 37.4 (s, $N{-}CH_3$, 1C); 32.4 (s, $N{-}CH_2{-}\mathit{C}H_2{-}CH_2{-}CH_3$, 1C); 30.0 (s, $N{-}CH_2{-}CH_2{-}\mathit{C}H_2{-}CH_3$, 1C), 13.4 (s, $N{-}CH_2{-}CH_2{-}CH_2{-}\mathit{C}H_3$, 1C). IR (ATR, cm^{-1}): $\nu = 2973$ (w), 2374 (w), 2294 (s), 1646 (s), 1515 (s), 1452 (vs),1380 (s), 1280 (s), 1160 (w), 1099 (s), 973 (vs), 873 (w), 829 (w), 797 (w), 772 (s), 742 (w), 729 (w), 698 (w) 678 (s), 621 (w), 576 (w). Raman (1500 mW, 50 scans, 25 °C, cm^{-1}): $\nu = 2364$ (10) 1645 (2), 1025 (2), 580 (3), 490 (3), 447 (3), 390 (2).

$KC[(CN)B(C_6F_5)_3]_3$, K[tcm_3b]. $B(C_6F_5)_3$ (2.048 g, 4 mmol, 4 equiv) in 60 mL of diethyl ether and K[tcm] (0.129 g, 1 mmol, 1 equiv) give the product K[tcm_3b]. Yield of K[tcm_3b]: 1.17 g (70%), mp 220.9 °C (DSC). $C_{58}B_3F_{45}KN_3$ (1165.10): calcd N 2.52, C 41.84; found N 2.14, C 42.22. ^{13}C NMR (CD_2Cl_2, 75 MHz, 25 °C): $\delta = 148.5$ (dm, *o*-C, 18C, $^1J_{CF} = 242.0$ Hz); 140.9 (dm, *p*-C, 9C, $^1J_{CF} = 241.7$ Hz); 137.6 (dm, *m*-C, 18C, $^1J_{CF} = 243.1$ Hz); 115.5 (br, C−B, 9C); 111.6 (s, CN, 3C); 14.5 (s, $\mathit{C}(CN)_3$, 1C). ^{11}B NMR (CD_2Cl_2, 96 MHz, 25 °C): $\delta = -10.1$ (s). ^{19}F NMR (CD_2Cl_2, 282 MHz, 25 °C): $\delta = -135.1$ to -135.2 (m, *o*-F, 2F); −157.7 (t, *p*-F, 1F, $^3J_{FF} = 20.4$ Hz); −164.5 to −164.8 (m, *m*-F, 2F). IR (ATR, cm^{-1}): $\nu = 2980$ (w), 2292 (s), 1647 (w), 1518 (s), 1456 (vs), 1383 (w), 1286 (w), 1101 (s), 970 (vs), 860 (w), 796 (w), 773 (s), 740 (w), 730 (w), 702 (w), 680 (s), 639 (w), 619 (w), 593 (w), 574

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(w). Raman (1500 mW, 100 scans, 25 °C, cm^{-1}): ν = 2353 (8), 2297 (10), 1650 (5), 833 (2), 577 (3), 492 (4), 449 (3), 393 (3).

AgC[(CN)B(C_6F_5)$_3$]$_3$, Ag[tcm_3b]. $B(C_6F_5)_3$ (2.048 g, 4 mmol, 4 equiv) in 60 mL of diethyl ether and Ag[tcm] (0.198 g, 1 mmol, 1 equiv) give the product Ag[tcm_3b]. Yield of Ag[tcm_3b]: 1.04 g (60%), dec 162.2 °C (DSC). $C_{58}B_3F_{45}AgN_3$ (1733.87): calcd N 2.42, C 40.18; found N 3.56, C 40.09. ^{11}B NMR (CD_2Cl_2, 96 MHz, 25 °C): $\delta = -9.7$ (s). ^{19}F NMR (CD_2Cl_2, 282 MHz, 25 °C): $\delta = -135.1$ to -135.2 (m, *o*-F, 2F); -157.7 (t, *p*-F, 1F, $^3J_{FF} = 20.4$ Hz); -164.6−164.8 (m, *m*-F, 2F). ^{13}C NMR (CD_2Cl_2, 75 MHz, 25 °C): $\delta = 148.6$ (dm, *o*-C, 18C, $^1J_{CF} = 242.6$ Hz); 140.9 (dm, *p*-C, 9C, $^1J_{CF} = 250.0$ Hz); 137.8 (dm, *m*-C, 18C, $^1J_{CF} = 239.1$ Hz); 115.9 (br, C−B, 9C); 111.8 (s, CN, 3C); 14.0 (s, *C*(CN)$_3$, 1C). IR (ATR, cm^{-1}): ν = 2278 (s), 1647 (w), 1518 (s), 1456 (vs), 1383 (w), 1286 (w), 1101 (s), 970 (vs), 860 (w), 796 (w), 773 (s), 740 (w), 730 (w), 702 (w), 680 (s), 639 (w), 619 (w), 593 (w), 574 (w). Raman (dec).

[EMIM]C[(CN)B(C_6F_5)$_3$]$_3$, EMIM[tcm_3b]. $B(C_6F_5)_3$ (2.048 g, 4 mmol, 4 equiv) in 60 mL of diethyl ether and EMIM[tcm] (0.201 g, 1 mmol, 1 equiv) give the product EMIM[tcm_3b]. Yield of EMIM[tcm_3b]: 1.18 g (68%), mp 197.4 °C (DSC). $C_{64}H_{11}B_3F_{45}N_5$ (1737.17): calcd N 4.03, C 44.25, H 0.64; found N 3.75 %, C 44.46, H 0.68. ^{1}H NMR (CD_2Cl_2, 300 MHz, 25 °C): δ = 8.13 (s, N−CH−N, 1H); 7.33−7.32 (m, CH−CH, 1H); 7.30−7.29 (m, CH−CH, 1H); 4.22 (q, CH_2, 2H, $^3J_{CH3CH2} = 7.3$ Hz); 3.93 (s, NCH_3, 3H); 1.57 (t, CH_3, 3H, $^3J_{CH3CH2} = 7.3$ Hz). ^{13}C NMR (CD_2Cl_2, 75 MHz, 25 °C): $\delta = 148.4$ (dm, *o*-C, 18C, $^1J_{CF} = 243.5$ Hz); 140.9 (dm, *p*-C, 9C, $^1J_{CF} = 237.4$ Hz); 137.9 (dm, *m*-C, 18C, $^1J_{CF} = 241.3$ Hz), 133.9 (br, N−CH−N, 1C); 124.6 (s, MeNCH, 1C), 123.1 (s, EtNCH, 1C); 115.6 (br, C−B, 9C); 111.6 (s, CN, 3C); 46.5 (s, N−CH_2, 1C); 37.2 (s, N−CH_3, 1C); 15.3 (s, CH_2−*C*H_3, 1C); 14.5 (s, *C*(CN)$_3$, 1C). ^{11}B NMR (CD_2Cl_2, 96 MHz, 25 °C): $\delta = -10.3$ (s). ^{19}F NMR (CD_2Cl_2, 282 MHz, 25 °C): $\delta = -135.1$ to -135.2 (m, *o*-F, 2F); -157.7 (t, *p*-F, 1F, $^3J_{FF} = 20.0$ Hz); -164.7 to -164.8 (m, *m*-F, 2F). IR (ATR, cm^{-1}): ν = 2290 (s), 1648 (w), 1519 (s), 1456 (vs), 1384 (w), 1286 (w), 1165 (w), 1103 (s), 972 (vs), 861 (w), 829 (w), 796 (w), 773 (s), 739 (w), 702 (w), 680 (s), 639 (w), 619 (w), 593 (w), 574 (w). Raman (1500 mW, 500 scans, 25 °C, cm^{-1}): ν = 2349 (8), 2297 (10), 1649 (5), 830 (2), 577 (5),510 (2), 491 (4), 448 (3).

[BMIM]C[(CN)B(C_6F_5)$_3$]$_3$, BMIM[tcm_3b]. $B(C_6F_5)_3$ (2.048 g, 4 mmol, 4 equiv) in 60 mL of diethyl ether and BMIM[tcm] (0.229 g, 1 mmol, 1 equiv) give the product BMIM[tcm_3b]. Yield of BMIM[tcm_3b]: 1.06 g (60%), mp 161.6 °C (DSC). $C_{66}H_{15}B_3F_{45}N_5$ (1765.22): calcd N 3.97, C 44.91, H 0.86; found N 3.93, C 45.13, H 0.92. ^{1}H NMR (CD_2Cl_2, 300 MHz, 25 °C): δ = 8.12 (s, N−CH−N, 1H); 7.30−7.27 (m, CH−CH, 2H); 4.13 (t, N−CH_2, 2H, $^3J_{CH3CH2} = 7.4$ Hz); 3.92 (s, N−CH_3, 3H); 1.90−1.80 (m, N−CH_2−C*H*$_2$, 2H); 1.40−1.28 (m, C*H*$_2$−CH_3, 2H); 0.93 (t, CH_2−C*H*$_3$, 3H, $^3J_{CH3CH2} = 7.4$ Hz). ^{13}C NMR (CD_2Cl_2, 75 MHz, 25 °C): $\delta = 148.5$ (dm, *o*-C, 18C, $^1J_{CF} = 244.6$ Hz); 140.3 (dm, *p*-C, 9C, $^1J_{CF} = 242.5$ Hz); 137.4 (dm, *m*-C, 18C, $^1J_{CF} = 233.8$ Hz); 134.2 (br, NCHN, 1C); 124.6 (s, MeNCH, 1C); 123.4 (s, EtNCH, 1C); 115.5 (br, C−B, 9C); 111.6 (s, CN, 3C); 51.0 (s, N−CH_2, 1C); 37.2 (s, N−CH_3, 1C); 32.1 (s, NCH_2−*C*H_2−CH_2−CH_3, 1C); 19.8 (s, NCH_2−CH_2-*C*H_2−CH_3, 1C), 13.3 (s, NCH_2−CH_2−CH_2−*C*H_3, 1C); 14.5 (s, *C*(CN)$_3$, 1C). ^{11}B NMR (CD_2Cl_2, 96 MHz, 25 °C): $\delta = -10.1$ (s). ^{19}F NMR (CD_2Cl_2, 282 MHz, 25 °C): $\delta = -135.1$ to -135.2 (m, *o*-F, 2F); -157.7 (t, *p*-F, 1F, $^3J_{FF} = 20.3$ Hz); -164.7 to -164.8 (m, *m*-F, 2F). IR (cm^{-1}): ν = 3174 (w), 2970 (w), 2289 (s), 1647 (w), 1596 (w), 1567 (w), 1518 (s), 1456 (vs), 1384 (s), 1285 (s), 1163 (w),1102 (s), 971 (vs), 861 (w), 829 (w), 796 (w), 773 (w), 739 (w), 701 (w), 680 (s), 639 (w), 621 (w), 593 (w), 574 (w). Raman (1500 mW, 300 scans, 25 °C, cm^{-1}): ν = 2346 (8), 2295 (10), 1649 (5), 830 (2), 577 (5),510 (2), 490 (4), 448 (3).

KB[(CN)B(C_6F_5)$_3$]$_4$, K[tcb_4b]. $B(C_6F_5)_3$ (2.56 g, 5 mmol, 5 equiv) in 60 mL of diethyl ether and K[tcb] (0.154 g, 1 mmol, 1 equiv) give the product K[tcb_4b]. Yield of K[tcb_4b]: 1.65 g (75%), dec 281.9 °C (DSC). $C_{76}B_5F_{60}KN_4$ (2201.90): calcd N 2.54, C 41.46; found N 2.56, C 41.03. ^{13}C NMR (CD_2Cl_2, 75 MHz, 25 °C): $\delta = 150.1$ (dm, *o*-C, 6C, $^1J_{CF} = 242.0$ Hz); 142.9 (dm, *p*-C, 3C, $^1J_{CF} = 242.7$ Hz); 139.5 (dm, *m*-C, 6C, $^1J_{CF} = 248.2$ Hz); 113.8 (br, C−B, 3C); 111.2 (q, CN, 1C, $^1J_{C^{11}B} = 81.8$ Hz). ^{11}B NMR (CD_2Cl_2, 96 MHz, 25 °C): $\delta = -8.5$ (br, CN *B*, 4B); -36.1 (s, *B*(CN)$_4$, 1B). ^{19}F NMR (CD_2Cl_2, 282 MHz, 25 °C): $\delta = -133.1$ to -133.2 (m, *o*-F, 2F); -154.5 (t, *p*-F, 1F, $^3J_{FF} = 20.2$ Hz); -162.2 to -162.4 (m, *m*-F, 2F). IR (ATR, cm^{-1}): ν = 2987 (w), 1646 (s), 1517 (s), 1456 (vs), 1383 (s), 1287 (s), 1099 (s), 970 (vs), 868 (w), 833 (w), 798 (w), 773 (s), 746 (w), 740 (w), 729 (w), 680 (s), 621 (w), 577 (w). Raman (1500 mW, 100 scans, 25 °C, cm^{-1}): ν = 2323 (10), 1648 (6), 1388 (3), 802 (1), 584 (6), 487 (6), 446 (7), 390 (5).

AgB[(CN)B(C_6F_5)$_3$]$_4$, Ag[tcb_4b]. $B(C_6F_5)_3$ (2.56 g, 5 mmol, 5 equiv) in 60 mL of diethyl ether and Ag[tcb] (0.223 g, 1 mmol, 1 equiv) give the product Ag[tcb_4b]. Yield of Agtcb_4b: 1.36 g (60%), mp 184.2 °C (DSC). $C_{76}B_5F_{60}AgN_4$ (2270.67): calcd N 2.47, C 40.20; found N 2.34, C 40.35. ^{11}B NMR (CD_2Cl_2, 96 MHz, 25 °C): $\delta = -7.5$ (br, CN *B*, 4B); -36.2 (s, *B*(CN)$_4$, 1B). ^{19}F NMR (CD_2Cl_2, 282 MHz, 25 °C): $\delta = -135.1$ to -135.2 (m, *o*-F, 2F); -156.7 (t, *p*-F, 1F, $^3J_{FF} = 20.1$ Hz); -164.3 to -164.5 (m, *m*-F, 2F). ^{13}C NMR (CD_2Cl_2, 63 MHz, 25 °C): $\delta = 148.3$ (dm, *o*-C, 6C, $^1J_{CF} = 246.5$ Hz); 141.2 (dm, *p*-C, 3C, $^1J_{CF} = 246.0$ Hz); 137.6 (dm, *m*-C, 6C, $^1J_{CF} = 248.0$ Hz); 114.2 (br, C−B, 3C); 111.0 (q, CN, 1C, $^1J_{C^{11}B} = 81.6$ Hz). IR (ATR, cm^{-1}): ν = 1646 (s), 1517 (s), 1463 (vs), 1382 (s), 1288 (s), 1230 (w), 1179 (w), 1102 (s), 973 (vs), 886 (w), 861 (w), 797 (w), 774 (s), 740 (w), 682 (s), 626 (w), 577 (w). Raman (dec).

[EMIM]B[(CN)B(C_6F_5)$_3$]$_4$, EMIM[tcb_4b]. $B(C_6F_5)_3$ (2.56 g, 5 mmol, 5 equiv) in 60 mL of diethyl ether and EMIM[tcb] (0.226 g, 1 mmol, 1 equiv) give the product EMIM[tcb_4b]. Yield of EMIM[tcb_4b]: 1.66 g (73%), mp 176.2 °C (DSC). $C_{82}H_{11}B_5F_{60}N_6$ (2273.96): calcd N 3.70, C 43.31, H 0.49; found N 3.33 %, C 42.62, H 0.40. ^{1}H NMR (CD_2Cl_2, 300 MHz, 25 °C): δ = 8.13 (s, N−CH−N, 1H); 7.33−7.32 (m, MeNCH, 1H); 7.30−7.28 (m, EtNCH, 1H); 4.21 (q, CH_2, 2H, $^3J_{CH3CH2} = 7.4$ Hz); 3.93 (s, NCH_3, 3H); 1.57 (t, CH_3, 3H, $^3J_{CH3CH2} = 7.3$ Hz). ^{13}C NMR (CD_2Cl_2, 75 MHz, 25 °C): $\delta = 148.3$ (dm, *o*-C, 2C, $^1J_{CF} = 242.9$ Hz); 141.2 (dm, *p*-C, 1C, $^1J_{CF} = 246.4$ Hz); 137.8 (dm, *m*-C, 2C, $^1J_{CF} = 246.4$ Hz); 134.0 (br, NCHN, 1C); 124.6 (s, MeNCH, 1C); 123.1 (s, EtNCH, 1C); 113.7 (br, C−B, 1C); 110.8 (q, CN, 1C, $^1J_{C^{11}B} = 81.8$ Hz); 46.4 (s, N−CH_2, 1C); 37.2 (s, N−CH_3, 1C); 15.2 (s, NCH_2−*C*H_3, 1C). ^{11}B NMR (CD_2Cl_2, 96 MHz, 25 °C): $\delta = -7.8$ (br, CN *B*, 4B). -36.1 (s, *B*(CN)$_4$, 1B). ^{19}F NMR (CD_2Cl_2, 282 MHz, 25 °C): $\delta = -135.1$ to -135.2 (m, *o*-F, 2F); -156.2 (t, *p*-F, 1F, $^3J_{FF} = 20.0$ Hz); -164.1 to -164.3 (m, *m*-F, 2F). IR (ATR, cm^{-1}): ν = 3148 (w), 1648 (s), 1519 (s), 1456 (vs), 1384 (s), 1288 (s), 1164 (s), 1101 (s), 974 (vs), 864 (w), 827 (w), 797 (w), 774 (s), 740 (w), 729 (w), 681 (s), 648 (w) 621 (w), 578 (w). Raman (1500 mW, 700 scans, 25 °C, cm^{-1}): ν = 2330 (10), 1649 (3), 1393 (2), 807 (2), 585 (5), 488 (4), 447 (4), 391 (3).

[BMIM]B[(CN)B(C_6F_5)$_3$]$_4$, BMIM[tcb_4b]. $B(C_6F_5)_3$ (2.56 g, 5 mmol, 5 equiv) in 60 mL of diethyl ether and BMIM[tcb] (0.254 g, 1 mmol, 1 equiv) give the product BMIM[tcb_4b]. Yield of BMIM[tcb_4b]: 1.50 g (65%), mp 147.9 °C (DSC). $C_{84}H_{15}B_5F_{60}N_6$ (2302.02): calcd N 3.65, C 43.83, H 0.66; found N 3.22, C 44.01, H 0.72. ^{1}H NMR (CD_2Cl_2, 300 MHz, 25 °C): δ = 8.12 (s, N−CH−N, 1H); 7.30−7.29 (m, CH−CH, 2H); 4.14 (t, N-CH_2, 2H, $^3J_{CH3CH2} = 7.4$ Hz); 3.92 (s, N−CH_3, 3H); 1.91−1.81 (m, N−CH_2−C*H*$_2$, 2H); 1.41−1.29 (m, C*H*$_2$−CH_3, 2H); 0.94 (t, CH_2−C*H*$_3$, 3H, $^3J_{CH3CH2} = 7.4$ Hz). ^{13}C NMR (CD_2Cl_2, 75 MHz, 25 °C): $\delta = 148.3$ (dm, *o*-C, 2C, $^1J_{CF} = 242.3$ Hz); 141.2 (dm, *p*-C, 1C, $^1J_{CF} = 240.0$ Hz); 137.7 (dm, *m*-C, 2C, $^1J_{CF} = 239.0$ Hz); 134.2 (br, NCHN, 1C); 124.6 (s, MeNCH, 1C); 123.4 (s, EtNCH, 1C); 113.8 (br, C−B, 1C); 110.7 (q, CN, 1C, $^1J_{C^{11}B} = 82.4$ Hz); 51.1 (s, N−CH_2, 1C); 37.2 (s, N−CH_3, 1C); 32.2 (s, N−CH_2−*C*H_2−CH_2−CH_3, 1C); 19.8 (s, N−CH_2−CH_2−*C*H_2−CH_3, 1C); 13.2 (s, N−CH_2−CH_2−CH_2−*C*H_3, 1C). ^{11}B NMR (CD_2Cl_2, 96 MHz, 25 °C): $\delta = -7.6$ (br, CN *B*, 4B); -36.1 (s, $B(CN)_4$, 1B). ^{19}F NMR (CD_2Cl_2, 282 MHz, 25 °C): $\delta = -135.1$ to -135.2 (m, *o*-F, 2F); -156.2 (t, *p*-F, 1F, $^3J_{FF} = 20.0$ Hz); -164.1 to -164.3 (m, *m*-F, 2F). IR (ATR, cm^{-1}): $\nu = 3174$ (w), 1647 (w), 1602 (w), 1568 (w), 1518 (s), 1456 (vs), 1384 (s), 1289 (s), 1163 (w),1101 (s), 971 (vs), 863 (w), 831 (w), 796 (w), 774 (w), 740 (w), 701 (w), 682 (s), 621 (w), 577 (w). Raman (1500 mW, 450 scans, 25 °C, cm^{-1}): $\nu = 2329$ (10), 1648 (4), 1390 (2), 806 (2), 585 (5), 488 (4), 446 (4), 391 (3).

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Supporting Information Available: Additional material concerning X-ray elucidation, VBT theory and computations, utilized programs, derived ion volumes.[64] Complete ref 64. This material is available free of charge via the Internet at http://pubs.acs.org.

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