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Tris(perfluorotolyl)borane – a Boron Lewis Superacid

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Abstract: Tris(tetrafluoro-4-(trifluoromethyl)phenyl)borane (BToIF) was prepared by reacting boron tribromide with tetrameric $F_3CC_6F_4$ -Cu(I). The latter was generated from $F_3CC_6F_4MgBr$ and copper(I) bromide. Lewis acidities of BToIF evaluated by the Gutmann-Beckett method and calculated fluoride ion affinities are 9 and 10%, respect-tively, higher than that of tris(pentafluorophenyl)borane (BCF) and even higher than that of SbF₅. The molecular structures of BToIF and BCF were determined by gas electron diffraction, that of BToIF also by single crystal X-ray diffraction.

Tris(pentafluorophenyl)borane (BCF) is a widely used Lewis acid in synthetic chemistry. Since its first preparation in 1963^[1] it received over 20000 reaction entries in SciFinder. In contrast to the volatile and very moisture- and air-sensitive trihaloboranes BX₃ (X = F, Cl, Br), BCF was described as an ideal boron Lewis acid: it combines high Lewis acidity, thermal stability and tolerates water and oxygen.^[2] It finds applications in Lewis-acid catalysis^[3], activation of olefine polymerization pre-catalysts.^[4] BCF is also the most commonly used Lewis-acid component in frustrated Lewis pairs chemistry.^[5] One of its drawbacks is the susceptibility of its para-fluorine atom towards nucleophilic substitution.^[6] Trying to remedy that by replacing these fluorine by hydrogen atoms led to the synthesis of $B(p-C_6F_4H)_3$, but this was on the cost of Lewis acidity.^[7] A variety of perfluoroarylboranes has been synthesized^[8] and their Lewis acidities were ranked on the Gutmann-Beckett^[9] and Childs Scales.^[10] Only few boranes are more Lewis acidic than BCF: tris(3,5-(trifluoromethyl)phenyl)borane and bis((2,4,6-trifluoromethyl)phenyl)borane about 5-6% more than BCF.^[11] Tris(o-perfluorobiphenyl)borane is 14% more Lewis acidic than BCF by the Gutmann-Beckett test,^[12] but the increased steric shielding of the boron atom by the ortho-C₆F₅ groups reduces its fluoride ion affinity to less than that of BCF.^[13] Perfluoropentaphenylborole and 9-borafluorene both feature higher Lewis acidities compared to BCF - a consequence of the antiaromaticity of the borole and fluorene $4\pi\text{-systems rings.}^{[14]}$ Although unknown as a pure substance, an application of tris(pperfluorotolyl)borane (BToIF) has been recently reported.^[15] In contrast to the less Lewis acidic BCF, the adducts of BToIF with a variety of heteroaromatics like quinolines and pyridines appeared to be activated for selective trifluoromethylation by a reagent based on CF₃SiMe₃ and difluorotriphenylsilicate.^[15] More than 30 adducts were obtained using in situ generated BToIF in ether.

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This ether adduct had to be prepared each time by reacting boron trichloride with perfluorotolyl lithium, facing the dangerous thermolability of the latter above -40 °C.

Free BToIF – if it were available – promises to combine steric crowding at boron comparable to that of BCF while possessing a higher Lewis acidity. The Hammett constants of a fluorine ($\sigma_p = 0.06$) and a CF₃ group ($\sigma_p = 0.54$) in *para*-position predict the latter to act as stronger electron-withdrawing group due to its inability of π -donation.^[16] It would also protect this position against nucleophilic substitution.

Several attempts to obtain BToIF via reactions of perfluorotolyllithium or the respective Grignard reagent with boron trihalides remained unsuccessful in our hands. However, the synthesis of BToIF via a donor-free copper(I)-based transfer was successful. This protocol is related to a variant of the BCF synthesis via $C_6F_5Cu^{[17]}$ by Jäkle *et al.*^[18] The precursor *p*-bromoheptafluorotoluene (2) was obtained in 64% yield after distillation by bromination of neat perfluorotoluene (1) with aluminum tribromide at 130 °C along a modified procedure.^[19] (Scheme 1). The corresponding Grignard reagent was prepared and reacted with copper(I) bromide. Addition of 1,4-dioxane precipitated the magnesium salts to separate them by filtration. Removal of the solvents in vacuum yields copper compound 3 as its 1,4-dioxane adduct. The donor-free reagent was obtained by applying high vacuum while heating the yellow solid gradually from 50 to 100 °C. The heating rate in this step is crucial for obtaining pure compound 3. Heating too fast or above 110 °C leads to decomposition under formation of perfluorobitolyl and copper(0). Complete removal of 1,4-dioxane is always in conflict with minor product decomposition. In most attempts we accepted minor decomposition (diagnosed by slightly too low carbon contents). Anyhow, traces of copper or residual 1,4-dioxane do not disturb further reactions significantly, as compared to experiments employing the reagent in higher purity.



 $\begin{array}{l} \label{eq:scheme 1. Synthesis of BToIF using the donor-solvent free copper(I) transfer reagent 3. i) AlBr_3 (neat), 130 °C, 12h. ii) a) Mg, Et_2O, 50 °C; b) CuBr, 50 °C; c) 1,4-dioxane, filtration, removal of solvent d) high vacuum, 100 °C, 20h, removal of 1,4-dioxane. iii) BBr_3, CH_2Cl_2, -78 °C, 1.5h. \end{array}$

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Figure 1. Molecular structure $(P\bar{1})$ of tetramer 3b as its toluene complex. Displacement ellipsoids are displayed at 50% probability level. F(26) to F(28) are disordered. Hydrogen atoms and one non-coordinate toluene molecule are omitted for clarity. Selected bond lengths $[\hat{A}]$ and angles [deg]: Cu(1)–Cu(2) 2.488(1), Cu(1)–Cu(3) 2.601(1), Cu(1)–Cu4 2.421(1), Cu(2)–Cu(3) 2.435(1), Cu(3)–Cu4 2.485(1), Cu(1)–C(1) 1.964(2), Cu(2)–C(1) 2.139(2), Cu(2)–C(29) 2.302(2), Cu(2)–C(30) 2.354(2), centroid [C(8)–C(13)] – centroid [C(29)–C(34)] 3.672(1), centroid [C(22)–C(27)] – centroid [C(36)–C(41)] 3.717(1), Cu(4)–Cu(2) 107.8(1), Cu(1)–Cu(2)–Cu(3) 63.8(1), dihedral angle [Cu(1)–Cu(2)-Cu(3)]-Cu(3)-Cu(4)] 36.0(1).

Perfluoroaryl copper 3 was characterized by NMR spectroscopy, infrared spectroscopy and CHN elemental analysis. Mass spectra (EI, 70 eV) show perfluorobitoluene due to decomposition of 3 when heated for evaporation. Solvent-free crystals of 3 could not be obtained so far, but crystals grown from a concentrated toluene solution at -30 °C allowed determining the molecular structure of a toluene adduct **3b** by X-ray diffraction (Figure 1). The tetrameric aggregation with a butterfly-like structure is similar to that found for $[Cu(C_6F_5)]_4(\eta^2-toluene)_2$.^[20] The dihedral angle between the two Cu₃ triangles [Cu(1)Cu(2)Cu(3) and Cu(1)Cu(3)Cu(4)] measures 36.0(1)°. Copper atoms Cu(2) and Cu(4) are η^2 -coordinated by toluene with short contacts to the para-carbon atom (Cu(2)-C(29) 2.302(2) Å) and slightly longer contacts to the meta-carbon atom (Cu(2)-C(30) 2.354(2) Å). The copper atoms are bridged by perfluoroaryl groups with a copper contact of 2.601(1) Å between the non-toluene-coordinated atoms Cu(1) and Cu(3), The toluene molecules undergo intramolecular m-stacking with the adjacent perfluoroaryl groups (distance between centroids: 3.672(1) and 3.717(1) Å)) framing copper contacts of 2.435(1) (Cu(2)...Cu(3)) and 2.421(1) Å (Cu(1)…Cu(4)). These contacts are slightly shorter than those between the copper atoms Cu(1)...Cu(2) and Cu(3)...Cu(4) (2.488(1) Å, 2.485(1) Å), without additional π -stacking.

Treatment of three equivalents of the perfluorotolyl transfer reagent **3** with BBr₃ in dichloromethane at -78 °C afforded tris(*p*perfluorotolyl)borane (BToIF). After removal of the solvent, BToIF can directly be sublimed from the remaining copper salts. It was obtained as a colorless solid in 80% yield and characterized by NMR spectroscopy, mass spectrometry, CHN elemental analysis and single crystal X-ray diffraction.

The relative Lewis acidity determined by Gutmann and Beckett's method^[9,10] (details: ESI, Table S1) shows BToIF to be 8–9% more Lewis acidic than BCF. The fluoride ion affinities^[13] (FIA) of BToIF (499 kJ/mol) and BCF (450 kJ/mol), calculated at the (RI)BP86/SV(P) level of theory, reveal BToIF to be 10% more Lewis acidic than BCF. Comparison of the absolute FIA value

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with that of SbF_5 (493 kJ/mol) characterizes BTolF as a Lewis superacid. $^{\left[21\right] }$

Attempts to prepare bis(2,3,5,6-tetrafluoro-4-trifluoromethyl)borane, HB(*p*-C₆F₄CF₃)₂, by employing the standard protocol^[22] of (C₆F₅)₂BH synthesis, i.e. treatment of BToIF with triethylsilane, were not successful. Instead, unselective reactions and formation of fluorotriethylsilane were detected by NMR spectroscopy $[\delta(^{19}\text{F}) = 175.0 \text{ ppm} (\text{sept, }^{3}J_{\text{F,H}} = 6.3 \text{ Hz}), \text{ lit.}^{[23]}$. It is probably formed by fluoride abstraction from a CF₃ group by an intermediately formed triethylsilyl cation.

There is still no experimental structure for BCF, but crystals of BToIF for X-ray diffraction experiments were grown from a concentrated solution in *n*-hexane at -30° C. The molecules of BToIF (Figure 2) lie on twofold axes of rotation passing through B(1), C(8), C(11) and C(12). This leads to disorder of the fluorine atoms bonded to C(12).



Figure 2. Molecular structure (*C*2/*c*) of tris(*p*-perfluorotolyl)borane. Displacement ellipsoids are displayed at the 50% probability level except F(10)-F(14), which are disordered about the C_2 axis. Selected bond lengths [Å] and angles [deg]: B(1)–C(1): 1.567(2), B(1)–C(8) 1.562(4), C(2)–C(1)–B(1)–C(1') 32.5(1), C(9)–C(8)–B(1)–C(1) 46.2(1).

We determined now structures of the free molecules of BToIF and BCF in the gas phase by electron diffraction using the diffractometer at Bielefeld University^[24,25] (details see ESI). Models of D_3 and C_3 symmetry were used for refinement of BCF and BToIF, respectively. The refined structures (r_{h1} -type, see ESI and [27]) resulted in R_f factors of 1.8 % for both, BToIF and BCF. Figure 3 shows radial distribution curves and illustrations of the structures.

BToIF and BCF have planar BC3 units. The three perfluoroaryl groups are tilted out of this plane and are arranged in a propeller-like manner. The free electron pairs of the para-fluorine atom of the aromatic system are in conjugation with boron in BCF, but the para-CF₃ group in BToIF cannot. Consequently, the πelectron density and thus its interaction with the vacant boron porbital is less in BToIF than in BCF. This makes the perfluorotolyl groups more flexible regarding their rotation. It also results in lower vibrational frequencies corresponding to the their torsional motion. These low frequency vibrations of BToIF are highly populated at the temperature of the GED experiment (162 °C). As a consequence the vibrationally averaged torsional angle is apparently larger for BTolF (56.8(4)°) than for BCF (40.6(3)°). However, these determined values for the torsional angle are highly dependent of the distinct dynamics of the molecule and their least-square errors should not be considered to represent a limit range of the torsional angles.

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Figure 3. Gas-phase structures of BCF (left) and BToIF (right) and corresponding experimental (circles O) and model (solid red line) radial distribution functions of BCF and BToIF. The difference curves are shown below. Vertical bars indicate interatomic distances in the modelled geometry.

A suitable correction for vibrational effects was attempted but failed due to physically insensibly large correction terms calculated by the usually applied procedures.^[26] A modeling of this molecular dynamics was not attempted, as the three torsions of the C₆F₄ groups plus three of the CF₃ groups are highly correlated and would thus require at least a six-dimensional treatment, which is beyond the present resources.

To further investigate the effect of the conjugation between the aromatic π -system on the barrier of rotation of the two different perfluoroaryl groups we calculated the potential energy (TPSS/6-311G(2d)^[27]) for the rotation of the aryl groups for both species under – a simplifying – maintenance of C_3 and D_3 symmetry of the corresponding minimum structures. These potential energy curves show a 12 kJ mol⁻¹ lower barrier of rotation at 90° torsion for the perfluorotolyl substituents compared to the perfluorophenyl groups (Figure 4). This supports the experimental findings of an apparently wider vibrationally averaged torsional angle found for BToIF. Due to the steric interaction between the *ortho*-fluorine atoms when decreasing the torsional angle towards 0°, the energy rises dramatically. This results in a substantially unsymmetrical potential and therefore in an anharmonic rotation of the perfluoroaryl groups.

In contrast, the quantum-chemically predicted structures [TPSS/6-311G(2d)], represent minimum structures and do not take zero-point vibrations into account. They suggest no differrence in the magnitude of the torsional angle C(2)–C(1)–B(1)–C(1)' for BCF (38.0°) and BToIF (38.2°). They also predict very similar B–C distances at 1.566 Å and 1.568 Å, respectively. In contrast, the B–C distance of BCF ($r_{h1} = 1.546(3)$ Å) determined in the electron diffraction experiment is shorter than that determined for BToIF ($r_{h1} = 1.564(2)$ Å). This reflects again vibrational averaging of a real system with elongating B–C distances when the molecule performs its aryl group torsions. At larger torsional angles the π -interaction between the perfluorotolyl group and the empty boron p-orbital is decreased and thus the B–C bonds become elongated.

We demonstrated this also for a set of simplified model compounds $(p-R^1C_6F_4)BR_2^2$ [R¹ = F, CF₃; R² = H, F; TPSS/6-311G(2d) avoiding the complications of correlated aryl torsions] by investigating the dependence of the B–C distance on the dihedral angle, which is fully consistent with the described behavior of BCF and BToIF (for details see ESI).



Figure 4. Calculated potential energy (TPSS/6-311G(2d)) of the D_3 symmetric minima of BCF and C_3 symmetric minima of BToIF in dependence of predefined dihedral angles between the aryl planes and the BC₃ plane.

In essence, the synthesis and isolation of tris(perfluorotolyl)borane (BToIF) gives access to a new boron Lewis acid. It is 9% stronger Lewis acidic than BCF (Gutmann-Beckett method) and has a 10% higher calculated fluoride ion affinity (FIA) than BCF. A higher FIA than SbF₅ characterizes BToIF as Lewis superacid, and to the best of our knowledge the most Lewis acidic singlesite triorganoborane. The clearly higher electron withdrawal of the perfluorotolyl groups in the absence of an electron donation ability of the *para*-fluorine group has observable structural consequences in gas-phase experiments. It makes in particular the torsional/vibrational behavior of BCF and BToIF different. Being

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the more Lewis acidic analogue to BCF, BTolF might find a wide scope of application in many fields of chemistry.

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Conflict of interest

The authors declare no conflict of interest.

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- [1] a) A. G. Massey, A. J. Park, F. H. A. Stone, *Proc. Chem. Soc.* 1963, 212–213; b) A. G. Massey, A. J. Park, *J. Organomet. Chem.* 1964, 2, 245–250.
- [2] W. E. Piers, T. Chivers, Chem. Soc. Rev. 1997, 26, 345–354.
- [3] a) H. Yamamoto, *Lewis Acids in Organic Synthesis*, Wiley-VCH, Weinheim, **2000**; b) K. Ishihara, H. Yamamoto, *Eur. J. Org. Chem.* **1999**, 527–538.
- [4] a) X. Yang, C. L. Stern, T. J. Marks, J. Am. Chem. Soc. 1991, 113, 3623–3625; b) X. Yang, C. L. Stern, T. J. Marks, J. Am. Chem. Soc. 1994, 116, 10015–10031; c) E. Y.-X. Chen, T. J. Marks, Chem. Rev. 2000, 100, 1391–1434.
- [5] a) G. C. Welch, Juan, Ronan R. San, J. D. Masuda, D. W. Stephan, *Science* 2006, *314*, 1124–1126; b) P. A. Chase, G. C. Welch, T. Jurca, D. W. Stephan, *Angew. Chem. Int. Ed.* 2007, *46*, 8050–8053; c) G. C. Welch, D. W. Stephan, *J. Am. Chem. Soc.* 2007, *129*, 1880–1881; d) D. W. Stephan, *Dalton Trans.* 2009, 3129–3136; e) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* 2010, *49*, 46–76; f) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* 2015, *54*, 6400–6441; g) D. W. Stephan, *J. Am. Chem. Soc.* 2015, *137*, 10018–10032.
- G. C. Welch, L. Cabrera, P. A. Chase, E. Hollink, J. D. Masuda, P. Wei, D. W. Stephan, *Dalton Trans.* 2007, 3407–3414.
- a) M. Ullrich, A. J. Lough, D. W. Stephan, Organometallics, 2010, 29, 3647–3654; b) M. Ullrich, A. J. Lough, D. W. Stephan, J. Am. Chem. Soc. 2009, 131, 52–53; c) D. Winkelhaus, B. Neumann, H.-G. Stammler, N. W. Mitzel, Dalton Trans. 2012, 41, 8609–8614.
- [8] a) I. B. Sivaev, V. I. Bregadze, *Coord. Chem. Rev.* 2014, 270-271, 75–88; b) A. E. Ashley, T. J. Herrington, G. G. Wildgoose, H. Zaher, A. L. Thompson, N. H. Rees, T. Kramer, D. O'Hare, *J. Am. Chem. Soc.* 2011, 133, 14727–14740; c) R. J. Blagg, T. R. Simmons, G. R. Hatton, J. M. Courtney, E. L. Bennett, E. J. Lawrence, G. G. Wildgoose, *Dalton Trans.* 2016, 45, 6032–6043; d) R. J. Blagg, E. J. Lawrence, K. Resner, V. S. Oganesyan, T. J. Herrington, A. E. Ashley, G. G. Wildgoose, *Dalton Trans.* 2016, 45, 6023–6031; e) J. A. Nicasio, S. Steinberg, B. Ines, M. Alcarazo, *Chem. Eur. J.* 2013, *19*, 11016–11020; f) L. Greb, C. G.

Daniliuc, K. Bergander, J. Paradies, Angew. Chem. Int. Ed. 2013, 52, 5876–5879; g) M. M. Morgan, A. J. V. Marwitz, W. E. Piers, M. Parvez, Organometallics 2013, 32, 317–322; h) G. J. P. Britovsec, J. Ugolotti, A. J. P. White, Organometallics 2005, 24, 1685–1691; i) D. Naumann, H. Butler, R. Gnann, Z. Anorg. Allg. Chem. 1992, 618, 74–76, j) H. Großekappenberg, M. Reißmann, M. Schmidtmann, T. Müller, Organometallics 2015, 34, 4952–4958, k) H. Zhao, J. H. Reibenspies, F. P. Gabbaï, Dalton Trans. 2013, 42, 608–610.

- [9] a) U. Mayer, V. Gutmann, W. Gerger, *Monatsh. Chem.* **1975**, *106*, 1235–1257; b) V. Gutmann, *Coord. Chem. Rev.* **1976**, *18*, 225–255; c) M. A. Beckett, D. S. Brassington, M. E. Light, M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.* **2001**, 1768–1772; d) M. A. Beckett, G. C. Strickland, J. R. Holland, K. Sukumar Varma, *Polymer* **1996**, *37*, 4629–4631.
- [10] R. F. Childs, D. L. Mulholland, A. Nixon, Can. J. Chem. 1982, 60, 801– 808.
- [11] a) T. J. Herrington, A. J. Thom, A. J. White, A. E. Ashley, *Dalton Trans.* **2012**, *41*, 9019–9022; b) Z. Lu, Z. Cheng, Z. Chen, L. Weng, Z. H. Li, H
 Wang, *Angew. Chem. Int. Ed.* **2011**, *50*, 12227–12231.
- [12] a) Y.-X. Chen, C. L. Stern, S. Yang, T. J. Marks, *J. Am. Chem. Soc.* **1996**, *118*, 12451–12452; b) S. C. Binding, H. Zaher, C. F. Mark, D. O'Hare, *Dalton Trans.* **2012**, *41*, 9061–9066.
- [13] H. Böhrer, N. Trapp, D. Himmel, M. Schleep, I. Krossing, *Dalton Trans.* 2015, 44, 7489–7499.
- [14] a) C. Fan, W. E. Piers, M. Parvez, Angew. Chem. Int. Ed. 2009, 48, 2955–2958; b) P. A. Chase, W. E. Piers, B. O. Patrick, J. Am. Chem. Soc. 2000, 122, 12911–12912.
- [15] M. Nagase, Y. Kuninobu, M. Kanai, J. Am. Chem. Soc. 2016, 138, 6103–6106.
- a) C. G. Swain, E. C. Lupton, *J. Am. Chem. Soc.* **1968**, *90*, 4328–4337;
 b) C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **1991**, *91*, 165–195; c) B. Hoge, J. Bader, *J. Fluorine Chem.* **2007**, *128*, 857–861.
- [17] a) A. Cairncross, H. Omura, W. A. Sheppard, J. Am. Chem. Soc. 1971, 93, 248–249; b) A. Cairncross, W. A. Sheppard, E. Wonchoba, Org. Synth. 1979, 59, 122.
- [18] A. Sundararaman, F. Jäkle, J. Organomet. Chem. 2003, 681, 134–142.
- [19] V. F. Cherstkov, S. R. Sterlin, L. S. German, Russ. Chem. Bull. 1985, 34, 2452.
- [20] b) A. Sundararaman, R. A. Lalancette, L. N. Zakharov, A. L. Rheingold, F. Jäkle, Organometallics 2003, 22, 3526–3532.
- [21] L. O. Müller, D. Himmel, J. Stauffer, G. Steinfeld, J. Slattery, G. Santiso-Quiñones, V. Brecht, I. Krossing, *Angew. Chem. Int. Ed.* 2008, 47, 7659–7663.
- [22] D. J. Parks, W. E. Piers, G. P. A. Yap, Organometallics 1998, 17, 5492–5503.
- [23] a) W. Liu, K. Welch, C. O. Trindle, M. Sabat, W. H. Myers, W. D. Harman, *Organometallics*, **2007**, *26*, 2589–2597. b) W. Adcock, G. T. Binmore, A. R. Krstic, J. C. Walton, J. Wilkie, *J. Am. Chem. Soc.*, **1995**, *117*, 2758–2766.
- [24] a) R. J. F. Berger, M. Hoffmann, S. A. Hayes, N. W. Mitzel, Z. Naturforsch. B 2009, 64; b) C. G. Reuter, Yu. V. Vishnevskiy, S. Blomeyer, N W. Mitzel, Z. Naturforsch. B 2016, 71, 1–13.
- [25] a) Yu. V. Vishnevskiy, J. Mol. Struct. 2007, 833, 30–41; b) Yu. V. Vishnevskiy, J. Mol. Struct. 2007, 871, 24–32; c) Yu. V. Vishnevskiy, UNEX, 2013, http://unexprog.org.
- [27] a) V. A. Sipachev, J. Mol. Struct. 2001, 567–568, 67–72; b) V. A. Sipachev, J. Mol. Struct. 2004, 693, 235–240.
- [26] a) J. M. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, *Phys. Rev. Lett.* **2003**, *91*,146401. b) R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650.

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Superacidic tris(tetrafluoro-4-(trifluoromethyl)phenyl)borane (BToIF) was prepared from BBr₃ and $F_3CC_6F_4$ -Cu(I). It is a stonger Lewis acid than tris(pentafluorophenyl)borane (BCF) and has a higher fluoride ion affinity than SbF₅. The structures of BToIF and – for the first time – of the widely used BCF were determined by gas electron diffraction and reflect the different electronic situations.



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