

Synthesis, Crystal Structure, and Application of the Oxonium Acid $[H(OEt_2)_2]^+[B(C_6F_5)_4]^-$

Peter Jutzi,* Christian Müller, Anja Stammer, and Hans-Georg Stammer

Faculty of Chemistry, University of Bielefeld, Universitätsstrasse 25,
D-33615 Bielefeld, Germany

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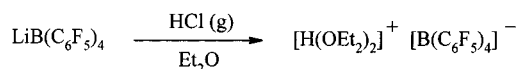
Summary: The reaction of $LiB(C_6F_5)_4$ with HCl in diethyl ether afforded the new oxonium acid $[H(OEt_2)_2]^+[B(C_6F_5)_4]^-$ (**1**) as a colorless crystalline solid, which was characterized by NMR spectroscopy, by elemental analysis, and by single-crystal X-ray diffraction. The application of **1** is demonstrated in the generation of the complex $\{[\eta^5-C_5H_3(CH_2CH_2NMe_2)CMe_2-\eta^5-C_{13}H_8]ZrCH_3\}^+[B(C_6F_5)_4]^-$ (**3**), containing an intramolecularly donor-stabilized alkylzirconocene cation.

Introduction

Cationic species with main group and transition metal centers have attracted considerable interest because of their activity in certain catalytic C–C bond formation reactions;¹ their detailed investigation has led to a much better understanding of the interaction between catalyst and substrate. For the stabilization of highly electrophilic cations, unreactive and noncoordinating (or weakly coordinating) counteranions are prerequisite.

Anions such as $[PF_6]^-$, $[BF_4]^-$, $[SO_3CF_3]^-$, $[SbF_6]^-$, and $[BPh_4]^-$ are regarded as noncoordinating (or weakly coordinating) counterions, but they react with highly electrophilic cations.² The hexabromo carborane anion $CB_{10}H_{12}Br_6^{2-}$ and the perfluorinated tetraarylborate $[B(C_6F_5)_4]^-$,³ however, are very poorly coordinating, fairly nonreactive anions. $[B(C_6F_5)_4]^-$ is much more stable than the chemically labile tetraphenylborate or the related tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.^{2d,e} Thus, it is frequently used as counteranion for electrophilic cations. In the chemistry of transition metal alkyl and olefin complexes, the tetraarylborate anion can be introduced by reaction with reagents such as $[Ag]^+[B(C_6F_5)_4]^-$, $[Cp_2Fe]^+[B(C_6F_5)_4]^-$, $[Ph_3C]^+$

Scheme 1



1

$[B(C_6F_5)_4]^-$, $[HNR_3]^+[B(C_6F_5)_4]^-$, $[HNMe_2Ph]^+[B(C_6F_5)_4]^-$, $[C_5Me_5Sn]^+[B(C_6F_5)_4]^-$, or $[H(OEt_2)_2]^+[3,5-(CF_3)_2-C_6H_3_4B]^-$.^{4–6} We now wish to report on the synthesis and crystal structure of an oxonium salt containing the cation $[H(OEt_2)_2]^+$ and the anion $[B(C_6F_5)_4]^-$. Furthermore, we describe an application of this compound in zirconocene chemistry.

Results and Discussion

According to the procedure described by Massey and Park, $LiB(C_6F_5)_4$ was prepared by reaction of LiC_6F_5 with $B(C_6F_5)_3$ in pentane.³ This compound, which is soluble in diethyl ether, reacted with HCl under precipitation of $LiCl$ to give the desired product $[H(OEt_2)_2]^+[B(C_6F_5)_4]^-$ (**1**) (Scheme 1). By crystallization from a concentrated ether solution at $-60^\circ C$, **1** was obtained as colorless crystals. **1** is slightly air- and moisture-sensitive but can be handled in air for a short period of time. It is stable at room temperature and soluble in

(1) For example see: (a) Brintzinger, H.-H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143, and references therein. (b) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428–447. (c) Aulbach, M.; Küber, F. *Chem. Unserer Zeit* **1994**, *28*, 197–208. (d) Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1997**, *119*, 8125–8126. (e) Bochmann, M.; Dawson, D. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2226–2228.

(2) For weakly coordinating anions see for example: (a) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927–942, and references therein. (b) Noirot, M. D.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1987**, *26*, 2216–2223, and references therein. (c) Shelley, K.; Reed, C. A.; Lee, Y. J.; Scheidt, W. R. *J. Am. Chem. Soc.* **1986**, *108*, 3117–3118. (d) Reed, C. A. *Acc. Chem. Res.* **1998**, *3*, 133–139. (e) Reed, C. A. *Acc. Chem. Res.* **1998**, *6*, 325–332. (f) Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1025. (g) Bochmann, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1181–1182. (h) Lambert, J. B.; Zhan, S. J. *Chem. Soc., Chem. Commun.* **1993**, 383–384. (i) Reedijk, J. *Comm. Inorg. Chem.* **1982**, *1*, 379. (j) Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718. (k) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728–2729.

(3) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1962**, *2*, 245.

(4) For example see: (a) Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, *26*, 345–354, and references therein. (b) Turner, H. W. European Patent No. 277 004, 1988. (c) Turner, H. W. United States Patent No. 5 599 761, 1997. (d) Bochmann, M.; Lancaster, S. J. *J. Organomet. Chem.* **1992**, *434*, C1–C5. (e) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255–270. (f) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325–387, and references therein. (g) Chien, J. C. W.; Tsai, W.-M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570–8571. (h) Rhodes, B.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1998**, *17*, 1931–1933. (i) Jia, L.; Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 842–857. (j) Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920–3922. (k) Taube, R.; Wache, S. *J. Organomet. Chem.* **1992**, *428*, 431–442.

(5) The strong Brønsted acid $[C_6Me_5H_4]^+[B(C_6F_5)_4]^-$ might also be a suitable reagent for protonolysis of M–CH₃ bonds or protonation of metal olefin complexes: Reed, C. A.; Fackler, N. L. P.; Kim, K.-C.; Stasko, D.; Evans, D.; Boyd, P. D. W.; Rickard, C. E. *J. Am. Chem. Soc.* **1999**, *121*, 6314–6315.

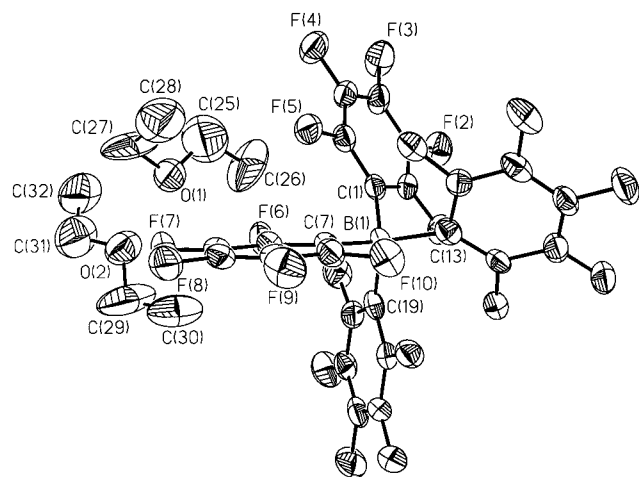
(6) The related anions $[RB(C_6F_5)_3]^-$ (R = alkyl) and $[(C_6F_5)_3B(\mu-OH)B(C_6F_5)_3]^-$ are obtained upon reaction of metal alkyl complexes with $B(C_6F_5)_3$ or metal complexes with $B(C_6F_5)_3$ in the presence of H_2O . See for example ref 4a and: Danopoulos, A. A.; Galsworthy, J. R.; Green, M. L. H.; Cafferkey, S.; Doerr, L. H.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1998**, 2529–2530.

Table 1. Crystallographic Data for 1

empirical formula	C ₃₂ H ₂₁ BF ₂₀ O ₂
fw	828.30
cryst size, color and habit	0.8 × 0.5 × 0.3 mm ³ , colorless needles
cryst syst, space group	orthorhombic <i>Pbca</i>
temperature	173(2) K
wavelength	0.71073 Å
unit cell dimens	<i>a</i> = 18.714(9) Å, <i>α</i> = 90° <i>b</i> = 16.871(10) Å, <i>β</i> = 90° <i>c</i> = 21.315(9) Å, <i>γ</i> = 90°
volume	6730(6) Å ³
<i>Z</i> , calcd density	8, 1.635 Mg/m ³
abs coeff	0.176 mm ⁻¹
<i>θ</i> range for data collection	1.89–25.02°
index ranges	0 ≤ <i>h</i> ≤ 22, 0 ≤ <i>k</i> ≤ 20, –25 ≤ <i>l</i> ≤ 0
no. of rflns collected/unique	5928/5927 [<i>R</i> (int) = 0.0367]
abs corr	none
no. of data/restraints/params	5927/0/504
goodness-of-fit on <i>F</i> ²	1.006
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0812, <i>wR</i> 2 = 0.1587 [2780]
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1843, <i>wR</i> 2 = 0.2054
largest diff peak and hole	0.433 and –0.392 e Å ⁻³
diffractometer used	Siemens P2(1) diffractometer
programs used	Siemens SHELXTL plus/ SHELXL-97
refinement method	full-matrix least-squares on <i>F</i> ²

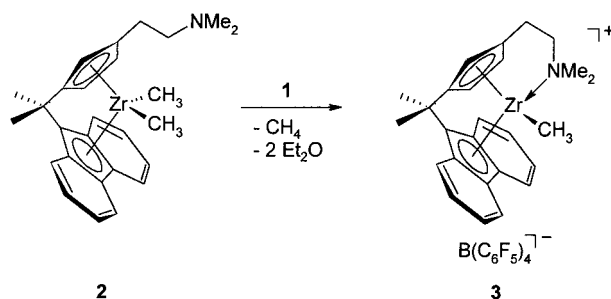
Table 2. Selected Bond Lengths and Atomic Distances [Å] for 1

B(1)–C(1)	1.657(9)
B(1)–C(7)	1.651(9)
B(1)–C(13)	1.665(8)
B(1)–C(19)	1.673(9)
O(1)···O(2)	2.445(9)
O(1)···F(6)	3.460(7)

**Figure 1.** Molecular structure of [H(OEt₂)₂]⁺[B(C₆F₅)₄][–] (**1**) (ORTEP diagram; 50% probability ellipsoids).

polar organic solvents such as ethers and dichloromethane. ¹H NMR spectroscopy as well as elemental analysis indicate that **1** is a dietherate. This is confirmed by an X-ray crystal structure determination. Crystallographic data for **1** are presented in Table 1; selected bond length and atomic distances are given in Table 2. The molecular structure of **1** is depicted in Figure 1. The *R* factor of the crystal structure and the thermal parameters of the C atoms of the ether molecules do not allow a definite predication whether the proton is located symmetrically or unsymmetrically between O(1) and O(2).⁷

The application of **1** in organometallic and organic chemistry seems to be promising.⁸ Due to its easy access,

Scheme 2

1 is a useful reagent for the preparation of ionic species containing the [B(C₆F₅)₄][–] counteranion. Concerning metallocene chemistry, the lack of proton resonances in the aromatic region is valuable for monitoring reactive species in NMR tube experiments. As an example, **1** was reacted with the 2-(*N,N*-dimethylamino)ethyl-function-alized zirconocene dimethyl **2** to give complex **3**, containing an intramolecularly donor-stabilized 16-VE zirconocene cation (Scheme 2).⁹

Experimental Section

General Data. All manipulations were carried out under a purified argon atmosphere using standard Schlenk techniques. The solvents were commercially available, purified by conventional means, and distilled immediately prior to use. The melting point determination was performed using a Büchi 510 melting point apparatus. The elemental analyses were performed by the Microanalytical Laboratory of the Universität Bielefeld. The NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer (¹H 500.1 MHz; ¹³C{¹H} 125.8 MHz; ¹⁹F{¹H} 470.6 MHz). Chemical shifts are reported in ppm and are referenced to the solvent as internal standard.

Preparation of [H(OEt₂)₂]⁺[B(C₆F₅)₄][–] (1**).** A solution of LiB(C₆F₅)₄ (3.00 g, 4.25 mmol) in diethyl ether (12 mL) was transferred via syringe to a 500 mL Schlenk flask containing HCl(g) (25.0 mmol) at –30 °C. Immediately LiCl precipitated, and the flask was allowed to stand at –30 °C for 4 h. After filtration the solution was concentrated to 10 mL and stored at –60 °C. Colorless crystals (2.30 g, 2.78 mmol, 65%) of **1** were formed and isolated by decanting the supernatant and by evaporating the residual solvent under reduced pressure. Mp: 148 °C.

¹H NMR (CD₂Cl₂ *T* = 298 K): δ 15.50 (v br, 1 H, Et₂OH), 7.55 (q, ³*J* = 7.2 Hz, 8 H, CH₂), 1.42 (t, ³*J* = 7.2 Hz, 12 H, CH₃). ¹³C NMR (CD₂Cl₂): δ 148.5 (d, ¹*J*_{C–F} = 240.83 Hz), 138.6 (d, ¹*J*_{C–F} = 244.72 Hz), 136.7 (d, ¹*J*_{C–F} = 241.58 Hz), 124.5 (br),

(7) (a) Kolesnikov, S. P.; Sizov, A. I.; Soleveichik, G. L.; Bulychev, B. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1985**, 1, 79–86. (b) Mootz, D.; Steffen, M. *Z. Anorg. Allg. Chem.* **1981**, 482, 193–299. (c) Cotton, F. A.; Fair, C. K.; Lewis, G. E.; Mott, G. N.; Ross, F. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1984**, 106, 5319–5323.

(8) For the application of [H(OEt₂)₂]⁺[3,5-(CF₃)₂C₆H₃][–] see: (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, 117, 6414–6415. (b) Cámpora, J.; López, J. A.; Palma, P.; Valerga, P.; Spillner, E.; Carmona, E. *Angew. Chem., Int. Ed.* **1999**, 38, 147–151. (c) Widenhoefer, R. A.; Vadehra, A.; Cheruvu, P. K. *Organometallics* **1999**, 18, 4614–4618.

(9) Müller, C.; Jutzi, P. Manuscript in preparation. NMR spectroscopic data for **3**: ¹H NMR (CD₂Cl₂, *T* = 298 K): δ –0.70 (s, 3 H, Zr–CH₃), 0.21 (s, 4 H, CH₂), 1.18 (t, ³*J* = 7.1 Hz, (CH₃CH₂)₂O), 1.22, 1.97, 2.17, 2.38 (4×s, 4×3 H, C(CH₃)₂, N(CH₃)₂), 2.39, 2.42, 2.70, 3.25, (4×m, 4×1 H, –CH₂–CH₂–), 3.52 (q, ³*J* = 7.1 Hz, (CH₃CH₂)₂O), 5.42, 5.69, 6.65 (3×m, 3×1 H, Cp–H), 7.36, 7.46, 7.53 (3×m, 3×1 H, fluorenyl–H), 7.67 (d, ³*J* = 8.9 Hz, 1 H, fluorenyl–H), 7.75 (m, 1 H, fluorenyl–H), 8.07 (d, ³*J* = 8.8 Hz, 1 H, fluorenyl–H), 8.30 (d, ³*J* = 8.2 Hz, 1 H, fluorenyl–H), 8.33 (d, ³*J* = 8.4 Hz, 1 H, fluorenyl–H).

70.4 (CH₂), 13.9 (CH₃). ¹⁹F NMR (CD₂Cl₂): δ 76.78 (s, br, *o*-F), 46.30 (t, *J*_{F-F} = 20.28 Hz, *p*-F), 42.36 (m, *m*-F). ¹¹B NMR (CD₂-Cl₂): δ -17.28. Anal. Calcd for C₃₂H₂₁BF₂₀O₂: C, 46.40; H, 2.56. Found: C, 46.20; H, 2.74.

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Supporting Information Available: Tables of crystal data, positional and thermal parameters, and selected bond lengths and angles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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