EurJOC
European Journal of Organic Chemistry

A Journal of
ChemPubSoc Europe

Accepted Article

Title: Synthesis of a Chiral Borate Counteranion, its Trityl Salt, and Application Thereof in Lewis-Acid Catalysis

Authors: Phillip Pommerening, Jens Mohr, Jonas Friebel, and Martin Oestreich

To be cited as: *Eur. J. Org. Chem.* 10.1002/ejoc.201700239

Link to VoR: http://dx.doi.org/10.1002/ejoc.201700239

Supported by
ACES Asian Chemical Editorial Society

WILEY-VCH

10.1002/ejoc.201700239

WILEY-VCH

Synthesis of a Chiral Borate Counteranion, its Trityl Salt, and Application Thereof in Lewis-Acid Catalysis

Phillip Pommerening, Jens Mohr, Jonas Friebel, and Martin Oestreich*[a]

Abstract: The preparation of a chiral derivative of $[B(C_6F_5)_4]^-$ where the fluorine atom in the *para* position of each of the C_6F_5 groups is replaced by a 1,1'-binaphthalen-2-yl group is described. The new counteranion is isolated as its lithium, sodium, and trityl salt. The chiral trityl salt is then used as a catalyst in selected counteranion-directed Diels–Alder reactions and a Mukaiyama aldol addition but no asymmetric induction is achieved. Application of the chiral trityl salt to the generation of silicon cations by silicon-to-carbon hydride transfer from hydrosilanes failed, presumably as a result of the incompatibility of the relatively electron-rich naphthyl groups in the borate and cationic silicon electrophiles.

Introduction

Weakly coordinating anions (WCAs) have become an enabling technology,[1] being widely used in fundamental inorganic and organic chemistry[2] as well as finding broad application in polymer science.[3] Various types of these counteranions with different elements as the central atom, e.g., boron and aluminum, have been reported.[1] Boron-based systems with electron-deficient aryl groups are particularly popular, and the fluorinated borates tetrakis[3,5-bis(trifluoromethyl)phenyl] borate ([**1**]$^-$; $[BAr^F_4]^-$)[4] and tetrakis(pentafluorophenyl) borate ([**2**]$^-$; $[B(C_6F_5)_4]^-$)[5] are the typical congeners of this class of compounds (Figure 1). Asymmetric catalyses with and without transition metals where a chiral counteranion is the source of chirality have recently witnessed tremendous growth[6] but none make use of a chiral tetraaryl-substituted borate.[7] The majority of chiral borates are derived from catechols and binols[7,8] while just a few borates without boron–oxygen linkages are known[9,10] (e.g., [**3**]$^-$; Figure 1). We are not aware of an application of [**3**]$^-$ or related compounds in asymmetric counteranion-directed catalysis.[6] With our interest in silicon-cation-catalyzed enantioselective Diels–Alder reactions of cyclohexa-1,3-diene,[11–14] we entertained the idea of replacing weakly coordinating $[B(C_6F_5)_4]^-$ ([**2**]$^-$) by the chiral, partially fluorinated counteranion [**4**]$^-$ (Figure 1).[15] The oxophilicity of silicon cations precludes the use of the prevalent oxygen-containing borates, and the enormous electrophilicity of these Lewis acids could be incompatible with the relatively electron-rich naphthyl groups in [**4**]$^-$. We therefore also considered testing the corresponding trityl salt $[Ph_3C]^+\cdot$[**4**]$^-$ as catalyst in asymmetric Diels–Alder reactions.[16–18] Franzén and co-workers had recently shown that trityl cations promote challenging Diels–Alder reactions of cyclohexa-1,3-diene,[17a,b] and the same group accomplished a related enantioselective Diels–Alder reaction of 2,3-dimethylbuta-1,3-diene directed by a chiral counteranion.[16a]

We report here the preparation of the chiral counteranion [**4**]$^-$ as its lithium and sodium salts $[Li]^+\cdot$[**4**]$^-$ and $[Na]^+\cdot$[**4**]$^-$ and the transformation of the latter into $[Ph_3C]^+\cdot$[**4**]$^-$. The chiral trityl salt was then applied as a catalyst in representative Diels–Alder reactions and a Mukaiyama aldol addition while the generation of cognate silicon cations by Corey's hydride abstraction[19] from hydrosilanes had failed.

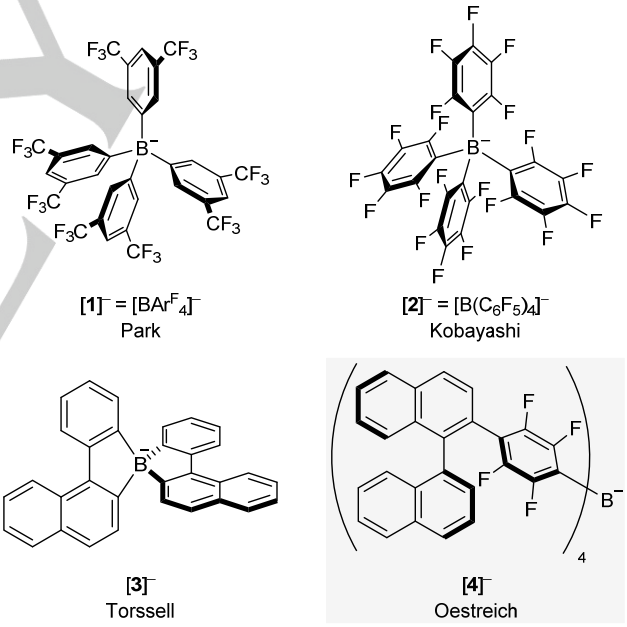


Figure 1. Typical weakly coordinating borates [**1**]$^-$ and [**2**]$^-$ by Park and Kobayashi, respectively, as well as known and targeted chiral borates [**3**]$^-$ and [**4**]$^-$.

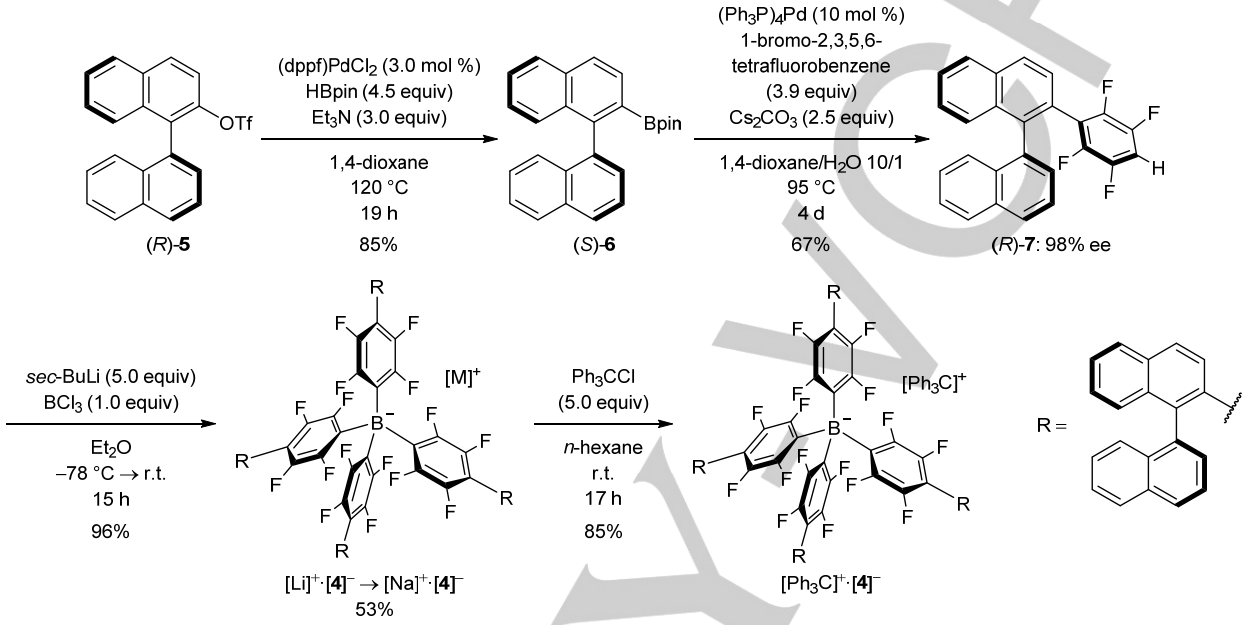
Results and Discussion

We decided to replace the four *para* fluorine atoms in $[B(C_6F_5)_4]^-$ ([**2**]$^-$) by 1,1'-binaphthalen-2-yl groups. The required precursor (*R*)-**7** was prepared from binol-derived (*R*)-**5**[20] (Scheme 1, top). The aryl boronic ester (*S*)-**6** was made from (*R*)-**5** by palladium-catalyzed coupling with pinacolborane[21] [(*R*)-**5** → (*S*)-**6**].[22] Desired (*R*)-**7** was then obtained by subsequent Suzuki–Miyaura coupling of (*S*)-**6** with 1-bromo-2,3,5,6-tetrafluorobenzene [(*S*)-**6**

[a] P. Pommerening, Dr. J. Mohr, J. Friebel, Prof. Dr. M. Oestreich
Institut für Chemie, Technische Universität Berlin
Straße des 17. Juni 115, 10623 Berlin (Germany)
E-mail: martin.oestreich@tu-berlin.de
Homepage: http://www.organometallics.tu-berlin.de

Supporting information for this article is given via a link at the end of the document.

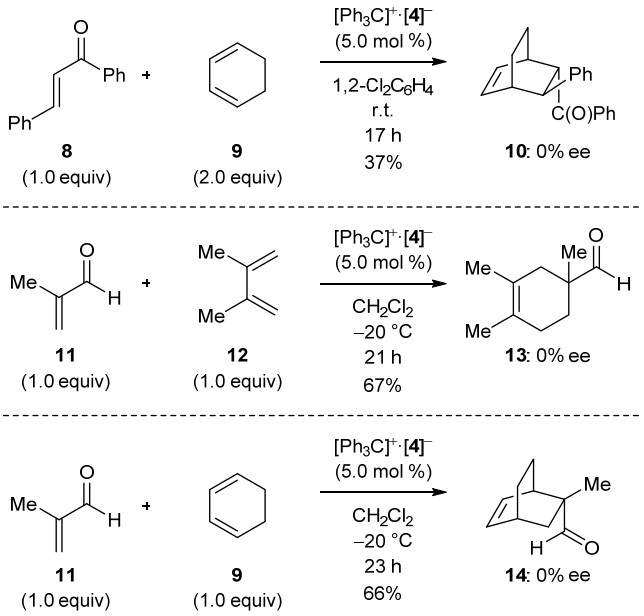
→ (*R*)-**7**]. High catalyst loading, excess of the aryl bromide, strict exclusion of oxygen, and long reaction times were mandatory to furnish (*R*)-**7** in decent 67% yield. HPLC analysis of (*R*)-**7** (98% ee) on a chiral stationary phase shows no thermally induced racemization. Also, crystals suitable for X-ray diffraction were obtained from a solution of (*R*)-**7** in CH_2Cl_2 by slow evaporation of the solvent at room temperature and ambient atmosphere (see the Supporting Information). Attempts to directly arrive at (*R*)-**7** from (*R*)-**5** were unsuccessful.



Scheme 1. Preparation of precursor (*R*)-**7** and its transformation into various borate salts of [**4**]$^-$.

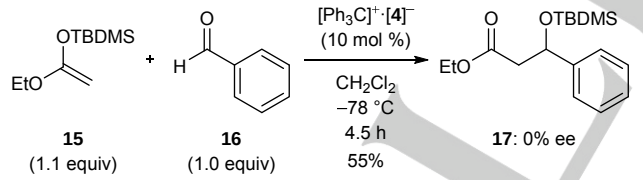
We had initially planned to install one chiral unit in $[B(C_6F_5)_4]^-$-type borates starting from $B(C_6F_5)_3$ and, e.g., [1,1'-binaphthalen]-2-yllithium but the targeted heteroleptic borate was formed along with $[Li]^+\cdot[\mathbf{2}]^-$, indicating transfer of a C_6F_5 group.[23] Therefore, we turned directly toward the preparation of homoleptic [**4**]$^-$ (Scheme 1, bottom). Deprotonation of (*R*)-**7** with *sec*-butyllithium[24] followed by the reaction with BCl_3 led to the air- and water-stable lithium borate $[Li]^+\cdot[\mathbf{4}]^-$ in near-quantitative yield {(*R*)-**7** → $[Li]^+\cdot[\mathbf{4}]^-$}. The direct conversion of $[Li]^+\cdot[\mathbf{4}]^-$ into $[Ph_3C]^+\cdot[\mathbf{4}]^-$ with trityl chloride was feasible but resulted in the difficult separation of $[Ph_3C]^+\cdot[\mathbf{4}]^-$ from LiCl due to its solubility in organic solvents. Preceding salt metathesis with excess NaCl ($[Li]^+\cdot[\mathbf{4}]^-$ → $[Na]^+\cdot[\mathbf{4}]^-$) allowed for straightforward filtration of difficultly soluble NaCl after the reaction of $[Na]^+\cdot[\mathbf{4}]^-$ with trityl chloride ($[Na]^+\cdot[\mathbf{4}]^-$ → $[Ph_3C]^+\cdot[\mathbf{4}]^-$). This procedure provided access to lithium-free $[Ph_3C]^+\cdot[\mathbf{4}]^-$.[25]

As mentioned above, Franzén and co-workers had recently shown that trityl cations catalyze Diels–Alder reactions, even those involving cyclohexa-1,3-diene as enophile.[17a,b] With the LiCl-free trityl salt $[Ph_3C]^+\cdot[\mathbf{4}]^-$ in hand, we tested the difficult Diels–Alder reaction of cyclohexa-1,3-diene (**9**) and chalcone (**8**) (Scheme 2, top).[12b] Cycloadduct **10** was isolated in moderate yield. The trityl cation with [**4**]$^-$ as counteranion is promoting this Diels–Alder reaction at lower rate than parent $[Ph_3C]^+\cdot[B(C_6F_5)_4]^-$; the yield obtained with $[Ph_3C]^+\cdot[B(C_6F_5)_4]^-$ is 84%. We note here that Franzén and co-workers had also tested **9** in the enantioselective counteranion-directed Diels–Alder reaction with methacrolein (**11**) with no success (traces of the Diels–Alder adduct).[16a] However, the same catalyst promoted the cycloaddition of another diene/dienophile combination, **12**/**11**, with 53% ee at low conversion (cf. Scheme 2, middle).[12b] For comparison, we also investigated the reactions of 2,3-dimethylbuta-1,3-diene (**12**) as well as cyclohexa-1,3-diene (**9**) with methacrolein (**11**, Scheme 2, middle and bottom). In both cases, we isolated the cycloadducts **13** and **14** in moderate yield without enantiomeric excess.



Scheme 2. Representative trityl-cation-catalyzed Diels–Alder reactions of cyclohexa-1,3-diene (top/bottom) and 2,3-dimethylbuta-1,3-diene (middle).

We also applied $[Ph_3C]^+\cdot[\mathbf{4}]^-$ to the typical Mukaiyama aldol reaction of **15** and **16** (Scheme 3).[26,27] Examples of enantioselective Mukaiyama aldol additions have been reported with chiral triarylcarbenium ions as catalysts[28] or in the presence of chiral counteranions.[29] Our catalyst yielded adduct **17** with moderate efficiency in racemic form. It is worth mentioning that we also observed rapid decoloration of the reaction mixture,[28] an indication of competing trityl-cation and silicon-cation catalysis.[27]



Scheme 3. Representative trityl-cation-catalyzed Mukaiyama aldol addition.

We also probed $[Ph_3C]^+\cdot[\mathbf{4}]^-$ in Corey's silicon-to-carbon hydride transfer.[19] Treatment of Et_3SiH with $[Ph_3C]^+\cdot[\mathbf{4}]^-$ in C_6D_6 to form $[Et_3Si(benzene)]^+\cdot[\mathbf{4}]^-$ failed.[30] Although we detected the diagnostic resonance signal of the methine proton of triphenylmethane in the ^1H NMR spectrum, the $[Et_3Si(benzene)]^+\cdot[\mathbf{4}]^-$ was not be observed.[31] Several resonance signals in the ^{29}Si NMR spectrum hinted decomposition of $[Et_3Si(benzene)]^+\cdot[\mathbf{4}]^-$, probably due to interactions of the strong silicon electrophile and the relatively electron-rich naphthyl groups in counteranion $[\mathbf{4}]^-$. The generation of our intramolecularly stabilized, ferrocenyl-substituted silicon cation $[FcSi(t\mathrm{Bu})Me]^+$ (Fc = ferrocenyl) from the corresponding hydrosilane in $1,2\text{-}Cl_2C_6D_4$[14b,32] was also unsuccessful. Decomposition of both the ferrocene backbone and the borate $[\mathbf{4}]^-$ was assumed based on several resonance signals in the ^1H and ^{11}B NMR spectra.

Conclusions

In summary, we presented a reliable synthesis of an air- and water-stable (potentially weakly coordinating) chiral borate $[\mathbf{4}]^-$ with various countercations, i.e., $[Li]^+\cdot[\mathbf{4}]^-$, $[Na]^+\cdot[\mathbf{4}]^-$, and $[Ph_3C]^+\cdot[\mathbf{4}]^-$. To demonstrate its usefulness, we tested $[Ph_3C]^+\cdot[\mathbf{4}]^-$ as a catalyst in representative trityl-cation-catalyzed Diels–Alder reactions and a Mukaiyama aldol addition but there was no enantiomeric excess. We also verified whether $[Ph_3C]^+\cdot[\mathbf{4}]^-$ could be used in Corey's silicon-to-carbon hydride transfer for the generation of silicon cations from hydrosilanes. However, unlike commonly employed $[Ph_3C]^+\cdot[B(C_6F_5)_4]^-$, the highly electrophilic silicon cations were not compatible with the chiral counteranion $[\mathbf{4}]^-$ wrapped in relatively electron-rich naphthyl groups.

Experimental Section

For general remarks as well as experimental procedures and spectroscopic data for literature-known compounds see the Supporting Information.

(*S*)-2-([1,1'-Binaphthalen]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*S*)-6]

According to a modified procedure by Masuda,[21a] a mixture of (*R*)-(1,1'-binaphthalen)-2-yl trifluoromethanesulfonate [(*R*)-**5**, 0.87 g, 2.2 mmol, 1.0 equiv] and triethylamine (0.90 mL, 0.65 g, 6.5 mmol, 3.0 equiv) in 1,4-dioxane (6.0 mL) was added to a solution of [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (48 mg, 65 µmol, 3.0 mol %) in 1,4-dioxane (3.0 mL). Pinacolborane (1.4 mL, 1.3 g, 9.8 mmol, 4.5 equiv) was added, and the resulting mixture was maintained at 120 °C for 19 h. The reaction was quenched by the addition of water (30 mL), and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (2 × 30 mL), and the combined organic phases were dried over Na_2SO_4. After evaporation of the volatiles under reduced pressure, the residue was purified by flash column chromatography on silica gel using cyclohexane/ethyl acetate = 30/1 as eluent to afford the title compound (*S*)-**6** (0.7 g, 85%) as a white solid. M.p. = 114 °C. R_f = 0.42 (cyclohexane/ethyl acetate = 20/1). GLC (SE-54): t_R = 29.0 min. IR (ATR): nu(tilde) = 1471, 1378, 1354, 1301, 1264, 1134, 1109, 964, 850, 818, 800, 774, 745 cm^{-1}. HRMS (APCI) for $C_{26}H_{26}BO_2^+$ [(M+H)$^+$]: calculated 381.2020, found 381.2023. ^1H NMR (500 MHz, $CDCl_3$): δ/ppm = 0.80 (s, 6H), 0.93 (s, 6H), 7.24–7.35 (m, 3H), 7.41–7.53 (m, 4H), 7.56–7.61 (m, 1H), 7.87–7.99 (m, 5H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ/ppm = 24.3, 24.4, 83.3, 125.1, 125.5, 125.8, 125.9, 126.6, 126.7, 126.9, 127.37, 127.4, 127.9, 128.0, 128.2, 130.0, 132.9, 133.6, 134.1, 134.7, 139.1, 144.9. The C_q–Bpin signal could not be detected. The spectroscopic data are in accordance with those previously reported.[21b]

(*R*)-2-(2,3,5,6-Tetrafluorophenyl)-1,1'-binaphthalene [(*R*)-7]

A mixture of (*S*)-2-([1,1'-binaphthalen]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*S*)-**6**, 1.50 g, 3.94 mmol, 1.00 equiv], tetrakis(triphenylphospine)palladium(0) (456 mg, 0.395 mmol, 10.0 mol %), bromo-2,3,5,6-tetrafluorobenzene (1.87 mL, 3.52 g, 15.4 mmol, 3.90 equiv), and Cs_2CO_3 (3.16 g, 9.70 mmol, 2.46 equiv) in 1,4-dioxane/water (10/1, 22 mL) was heated at 95 °C for 4 d. The reaction mixture was filtered through Celite®, and the volatiles were removed under reduced pressure. Purification of the residue by flash column chromatography on silica gel using cyclohexane/toluene = 10/1 as eluent afforded the title compound (*R*)-**7** (1.07 g, 67%, 98% ee) as a white solid. M.p. = 158 °C. R_f = 0.30 (cyclohexane). GLC (SE-54): t_R = 29.0 min. IR (ATR): nu(tilde) = 1491, 1387, 1365, 1281, 1255, 1170, 968, 934, 871, 849, 821, 803, 781, 755, 711 cm^{-1}. HRMS (APCI) for $C_{26}H_{14}F_4$ $[M]^+$: calculated 402.1026, found 402.1033. ^1H NMR (500 MHz, $CDCl_3$): *δ*/ppm = 6.77 (m_c, 1H), 7.27–7.61 (m, 9H), 7.83–7.89 (m, 2H), 8.03 (m_c, 1H), 8.10 (m_c, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): *δ*/ppm = 105.0 (m_c), 121.9 (m_c), 125.1, 125.7 (m_c), 126.0, 126.1, 126.2, 126.2, 126.8, 127.0, 127.2, 127.3, 128.1, 128.1, 128.2, 128.4, 132.5, 133.3, 133.4, 133.8, 135.5, 139.1, 142.4–143.0 (m), 144.3–144.9 (m, 2C), 146.3–146.6 (m). $^{19}F\{^1H\}$ NMR (471 MHz, $CDCl_3$): *δ*/ppm = –140.0–(–139.8) (m, 2F), –139.5–(–139.3) (m, 1F), –138.8–(–138.6) (m, 1F). Optical rotation: $[\alpha]^{20}_D$ = –1128 (c = 1.05, $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-RH column, 20 °C, acetonitrile/H_2O = 60/40, flow rate 0.40 mL/min, λ = 254 nm): t_R = 52.0 min for (*S*)-**7**, t_R = 63.6 min for (*R*)-**7**. The crystallographic data is available online in the CCDC database under number CCDC 1521041.

Lithium Tetrakis(2-[2,3,5,6-tetrafluorophenyl]-1,1'-binaphthalene)-borate ($[Li]^+\cdot[4]^-$)

To a solution of (*R*)-2-(2,3,5,6-tetrafluorophenyl)-1,1'-binaphthalene [(*R*)-**7**, 0.50 g, 1.2 mmol, 5.5 equiv] in diethyl ether (20 mL), *sec*-butyllithium (1.3 M in cyclohexane, 0.90 mL, 1.1 mmol, 5.0 equiv) was added dropwise at –78 °C, and the resulting mixture was stirred for 3 h. BCl_3 (1.0 M in *n*-heptane, 0.20 mL, 0.23 mmol, 1.0 equiv) was added dropwise, and the resulting mixture was stirred overnight by allowing the solution to slowly warm to room temperature. The reaction was quenched by the addition of water (20 mL), and the volatiles were removed under reduced pressure to give $[Li]^+\cdot[\mathbf{4}]^-$ (0.35 g, 96%) as a colorless solid. M.p. = 219 °C. IR (ATR): nu(tilde) = 3650, 3045, 1611, 1505, 1437, 1365, 1276, 1174, 962, 822, 758, 704 cm^{-1}. HRMS (APCI) for $C_{104}H_{52}BF_{16}^-$ $[M^-]$: calculated 1615.3912, found 1615.3850. ^7Li NMR (194 MHz, $CDCl_3$): *δ*/ppm = –1.94. ^{11}B NMR (160 MHz, $CDCl_3$): *δ*/ppm = –17.1.

Sodium Tetrakis(2-[2,3,5,6-tetrafluorophenyl]-1,1'-binaphthalene)-borate ($[Na]^+$ $[4]^-$)

To freshly prepared brine (5 mL), a solution of lithium tetrakis(2-[2,3,5,6-tetrafluorophenyl]-1,1'-binaphthalene)borate $[Li]^+\cdot[\mathbf{4}]^-$ (377 mg, 0.232 mmol) in CH_2Cl_2 (5 mL) was added and stirred overnight. The reaction mixture was diluted with water (10 mL), the phases were separated, and the aqueous phase extracted with CH_2Cl_2 (2 × 10 mL). The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel using ethyl acetate as eluent to afford the title compound $[Na]^+\cdot[\mathbf{4}]^-$ (202 mg, 53%) as a gray solid. M.p. > 220 °C. R_f = 0.07 (ethyl acetate). IR (ATR): nu(tilde) = 3651, 3048, 1611, 1506, 1438, 1365, 1277, 1176, 962, 823, 759, 705 cm^{-1}. HRMS (APCI) for $C_{104}H_{52}BF_{16}^-$ $[M^-]$: calculated 1615.3912, found 1615.3878. ^{11}B NMR (160 MHz, $CDCl_3$): *δ*/ppm = –17.3. Optical rotation: $[\alpha]^{20}_D$ = –14 (c = 0.98, $CHCl_3$).

Triphenylcarbenium Tetrakis(2-[2,3,5,6-tetrafluorophenyl]-1,1'-binaphthalene)borate ($[Ph_3C]^+\cdot[4]^-$)

According to a modified procedure by Schulz,[33] sodium tetrakis(2-[2,3,5,6-tetrafluorophenyl]-1,1'-binaphthalene)borate $[Na]^+\cdot[\mathbf{4}]^-$ (0.10 g, 60 µmol 1.0 equiv) and triphenylmethyl chloride (0.86 mg, 0.31 mmol 5.0 equiv) were suspended in *n*-hexane (6 mL) and stirred overnight at room temperature. The solution was filtered under nitrogen atmosphere and the resulting precipitate washed with *n*-hexane (2 × 5 mL). The brown solid was dissolved in CH_2Cl_2 (10 mL), and the resulting solution was concentrated under reduced pressure to approximately one third of its volume. *n*-Pentane (20 mL) was added rapidly, and the supernatant was removed via syringe. This procedure was repeated three times. The resulting precipitate was dried under high vacuum to afford the title compound $[Ph_3C]^+\cdot[\mathbf{4}]^-$ (95 mg, 85%) as an orange to brown solid. M.p. = 189 °C. IR (ATR): nu(tilde) = 3046, 1579, 1506, 1481, 1440, 1356, 1277, 1182, 964, 824, 760, 703 cm^{-1}. HRMS (APCI) for $C_{104}H_{52}BF_{16}^-$ $[M^-]$: calculated 1615.3912, found 1615.3849. HRMS (APCI) for $C_{19}H_{15}^+$ $[M^+]$: calculated 243.1168, found 243.1174. ^{11}B NMR (161 MHz, CD_2Cl_2): *δ*/ppm = –17.3. Optical rotation: $[\alpha]^{20}_D$ = +49 (c = 1.0, $CHCl_3$).

Acknowledgments

M.O. is indebted to the Einstein Foundation (Berlin) for an endowed professorship. We thank Dr. Elisabeth Irran (TU Berlin) for the X-ray analysis.

Keywords: Cations • Chirality • Diels–Alder reaction • Lewis acids • Trityl group

[1] For leading reviews, see: a) I. Raabe, I. Krossing, *Angew. Chem. Int. Ed.* **2004**, *43*, 2066–2090; b) S. H. Strauss, *Chem. Rev.* **1993**, *93*, 927–942.

[2] For representatives examples, see: a) T. J. Barbarich, S. T. Handy, S. M. Miller, O. P. Anderson, P. A. Grieco, S. H. Strauss, *Organometallics* **1996**, *15*, 3776–3778; b) S. Moss, B. T. King, A. de Meijere, S. I. Kozhushkov, P. E. Eaton, J. Michl, *Org. Lett.* **2001**, *3*, 2375–2377; c) L. L. Anderson, J. Arnold, R. G. Bergman, *J. Am. Chem. Soc.* **2005**, *127*, 14542–14543; d) Y. Li, B. Diebl, A. Raith, F. E. Kühn, *Tetrahedron Lett.* **2008**, *49*, 5954–5956; e) T.-T.-T. Nguyen, D. Türp, M. Wagner, K. Müllen, *Angew. Chem. Int. Ed.* **2013**, *54*, 669–673; f) S. Fischer, J. Schmidt, P. Strauch, A. Thomas, *Angew. Chem. Int. Ed.* **2013**, *52*, 12174–12178.

[3] a) J. A. S. Roberts, M.-C. Chen, A. M. Seyam, L. Li, C. Zuccaccia, N. G. Stahl, T. J. Marks, *J. Am. Chem. Soc.* **2007**, *129*, 12713–12733; b) M.-C. Chen, J. A. S. Roberts, A. M. Seyam, L. Li, C. Zuccaccia, N. G. Stahl T. J. Marks, *Organometallics* **2006**, *25*, 2833–2850; c) M. Mager, S. Becke, H. Windisch, U. Denninger, *Angew. Chem. Int. Ed.* **2001**, *40*, 1898–1902.

[4] A. G. Massey, A. J. Park, *J. Organomet. Chem.* **1964**, *2*, 245–250.

[5] H. Kobayashi, T. Sonoda, H. Iwamoto, *Chem. Lett.* **1981**, 579–580.

[6] For authoritative reviews, see: a) M. Mahlau, B. List, *Angew. Chem. Int. Ed.* **2013**, *52*, 518–533; b) R. J. Phipps, G. L. Hamilton, F. D. Toste, *Nat Chem.* **2012**, *4*, 603–614.

[7] For a review, see: J. Lacour, V. Hebbe-Viton, *Chem. Soc. Rev.* **2003**, *32*, 373–382.

[8] For an example of a binol-derived borate as a counteranion in a copper-catalyzed reaction, see: D. B. Llewellyn, D. Adamson, B. A. Arndtsen, *Org. Lett.* **2000**, *2*, 4165–4168.

[9] K. Torssell, *Acta Chem. Scand.* **1962**, *16*, 87–93.

[10] D. J. Owen, D. VanDerveer G. B. Schuster, *J. Am. Chem. Soc.* **1998**, *120*, 1705–1717.

[11] For planar chiral, ferrocene-stabilized silicon cations as catalysts, see: R. K. Schmidt, H. F. T. Klare, R. Fröhlich, M. Oestreich, *Chem. Eur. J.* **2016**, *22*, 5376–5383.

[12] For axial chiral, sulfur-stabilized silicon cations as catalysts, see: a) V. H. G. Rohde, M. F. Müller, M. Oestreich, *Organometallics* **2015**, *34*, 3358–3373; b) P. Shaykhutdinova, M. Oestreich, *Organometallics* **2016**, *35*, 2768–2771.

[13] For an axial chiral, acetonitrile-stabilized silicon cation as catalyst, see: M. Johannsen, K. A. Jørgensen, G. Helmchen, *J. Am. Chem. Soc.* **1998**, *120*, 7637–7638.

[14] For silicon-cation-catalyzed Diels–Alder reactions in the racemic series, see: a) K. Hara, R. Akiyama, M. Sawamura, *Org. Lett.* **2005**, *7*, 5621–5623; b) H. F. T. Klare, K. Bergander, M. Oestreich, *Angew. Chem. Int. Ed.* **2009**, *48*, 9077–9079; c) R. K. Schmidt, K. Müther, C. Mück-Lichtenfeld, S. Grimme, M. Oestreich, *J. Am. Chem. Soc.* **2012**, *134*, 4421–4428.

[15] For silicon-cation-catalyzed enantioselective Diels–Alder reactions of cyclopentadiene using a new chiral counteranion, see: T. Gatzenmeier, M. van Gemmeren, Y. Xie, D. Höfler, M. Leutzsch, B. List, *Science* **2016**, *351*, 949–952

[16] For trityl-cation-catalyzed enantioselective Diels–Alder reactions using chiral counteranions, see: a) S. Ni, V. R. Naidu, J. Franzén, *Eur. J. Org. Chem.* **2016**, 1708–1713; for trityl-cation-catalyzed enantioselective hetero-Diels–Alder reactions using chiral counteranions, see: b) J. Lv, Q. Zhang, X. Zhong, S. Luo, *J. Am. Chem. Soc.* **2015**, *137*, 15576–15583.

[17] For trityl-cation-catalyzed Diels–Alder and hetero-Diels–Alder reactions in the racemic series, see: a) J. Bah, J. Franzén, *Chem. Eur. J.* **2014**, *20*, 1066–1072; b) J. Bah, V. R. Naidu, J. Teske, J. Franzén, *Adv. Synth. Catal.* **2015**, *357*, 148–158; c) M. A. A. El Remaily, V. R. Naidu, S. Ni, J. Franzén, *Eur. J. Org. Chem.* **2015**, 6610–6614.

[18] For a recent review of trityl cations in Lewis-acid catalysis, see: V. R. Naidu, S. Ni, J. Franzén, *ChemCatChem* **2015**, *7*, 1896–1905.

[19] J. Y. Corey, *J. Am. Chem. Soc.* **1975**, *97*, 3237–3238.

[20] Y. Uozumi, N. Suzuki, A. Ogiwara, T. Hayashi, *Tetrahedron* **1994**, *50*, 4293–4302.

[21] According to a reported procedure: a) M. Murata, T. Oyama, S. Watanabe, Y. Masuda, *J. Org. Chem.* **2000**, *65*, 164–168; for another (recent) cross-coupling approach to (*S*)-**6** from (*S*)-**5** using bis(pinacolato)diboron, see: b) X. Yang, G. Xu, W. Tang, *Tetrahedron* **2016**, *72*, 5178–5183.

[22] For an alternative synthesis of (*S*)-**6**: B. Schilling, V. Kaiser, D. E. Kaufmann, *Chem. Ber.* **1997**, *130*, 923–932.

[23] J. Mohr, *Master Thesis*, Westfälische Wilhelms-Universität Münster, **2012**.

[24] R. Roesler, B. J. N. Har, W. E. Piers, *Organometallics* **2002**, *21*, 4300–4302.

[25] No resonance signal was detected by ^{7}Li NMR spectroscopy.

[26] a) T. Mukaiyama, S. Kobayashi, M. Murakami, *Chem. Lett.* **1985**, 447–450; b) S. Kobayashi, M. Murakami, T. Mukaiyama, *Chem. Lett.* **1985**, 1535–1538.

[27] For mechanistic investigation, see: a) S. E. Denmark, C.-T. Chien, *Tetrahedron Lett.* **1994**, *35*, 4327–4330; b) T. K. Hollis, B. Bosnich, *J. Am. Chem. Soc.* **1995**, *117*, 4570–4581.

[28] C.-T. Chien, S.-D. Chao, K.-C. Yen, C.-H. Chen, I.-C. Chou, S.-W. Hon, *J. Am. Chem. Soc.* **1997**, *119*, 11341–11342.

[29] a) P. García-García, F. Lay, P. García-García, C. Rabalakos, B. List, *Angew. Chem. Int. Ed.* **2009**, *48*, 4363–4366; b) M. Sai, H. Yamamoto, *J. Am. Chem. Soc.* **2015**, *137*, 7091–7094.

[30] For $[Et_3Si(benzene)]^{+}\cdot[B(C_6F_5)_4]^{-}$, see: J. B. Lambert, S. Zhang, C. L. Stern, J. C. Huffman, *Science* **1993**, *260*, 1917–1918.

[31] J. B. Lambert, S. Zang, S. M. Ciro, *Organometallics* **1994**, *13*, 2430–2443.

[32] K. Müther, R. Fröhlich, C. Mück-Lichtenfeld, S. Grimme, M. Oestreich, *J. Am. Chem. Soc.* **2011**, *133*, 12442–12444.

[33] M. Lehmann, A. Schulz, A. Villinger, *Angew. Chem. Int. Ed.* **2009**, *48*, 7444–7447.

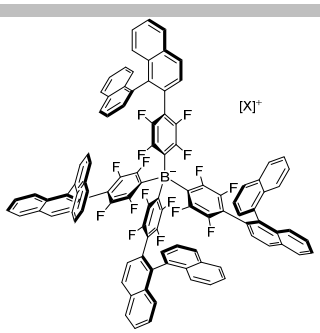
10.1002/ejoc.201700239

WILEY-VCH

Suggestion for the Entry for the Table of Contents

FULL PAPER

Chiral Counteranion. Chiral modification of the popular perfluorinated borate counteranion $[B(C_6F_5)_4]^-$ resulted in an air- and water-stable, potentially weakly coordinating borate with various countercations. Its utility is shown in trityl-cation-catalyzed Diels–Alder reactions and a Mukaiyama aldol addition.



*P. Pommerening, J. Mohr, J. Friebel, M. Oestreich**

Page No. – Page No.

Synthesis of a Chiral Borate Counteranion, its Trityl Salt, and Application Thereof in Lewis-Acid Catalysis