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Synthesis, structure, and unprecedented solubility of lipophilic borate salts

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ABSTRACT

The multi-gram scale preparation of halide free lipophilic borate salts from inexpensive precursor compounds 3,3′,5,5′-tetra-*tert*-butyl-2,2′-biphenol and tetrahydridoboranate salts is reported. The so-called "*bortebate*" anion is more stable against water and bases than its aluminum analog "*altebate*", but *bortebate* formation is significantly slower. *Bortebate* salts are highly soluble in hydrocarbon solvents, e.g. >35 mmol/L lithium *bortebate* in pentane at 20 °C. Quantitative salt metathesis reactions between sodium *bortebate* and halide salts can be easily achieved by precipitation of the sodium halide in methylene chloride.

1. Introduction

Salts are very rarely lipophilic in nature. The charge separation of cations and anions is best stabilized by a polar and hydrophilic environment. However, lipophilic ions are made possible by a low charge, large molecular dimensions and a lipophilic molecular surface. The solubility of salts in aprotic or even unpolar solvents reflects the lipophilicity of its ionic components [1]. Thus, we consider the solubility of alkali salts in pentane as the ultimate test for the lipophilicity of an anion.

Weakly coordinating anions (WCA) [2] such as $[B(C_6F_5)_4]^-$ ("$BArF_{20}$") and $[B\{3,5\text{-}C_6H_3(CF_3)_2\}_4]^-$ ("$BArF_{24}$") are more lipophilic than chloride or sulfate (Fig. 1 top left) [1,3]. Fluoroalkyl substituents in silylated tetraphenylborate salts lead to an increased solubility in hexanes, indicative for the applicability of lipophilic salts in supercritical CO_2 (Fig. 1 down left) [4]. The high costs and the persistence of C–F bonds in the environment, however, are disadvantages. A permethylated carborane of the Michl group can be classified as very lipophilic, halide free, but expensive anion (Fig. 1 top center) [5]. Krossing's perfluorated tetraalkoxy aluminate derives its exceptionally low nucleophilicity from the 36 fluorine substituents (Fig. 1 top right) [6]. Spiroborates derived from 2,2′-dihydroxybiphenyl have been structurally characterized, and the relative stability and interconversion of the chiral and achiral isomers has been discussed [7]. Lipophilic spiroborates have been successfully tested for wood protection based on their termiticidal activity and leach resistance [8]. The Waldvogel group has synthesized halogenated spiroborates by electrochemical oxidation of aryl borate esters [9]. We have recently reported aluminate salts comprising two sterically demanding *tert*-butylated 2,2′-biphenolate ligands (Fig. 1 down right) [10]. Their low reactivity against electrophiles such as tritylium cations originates in the steric shielding of the aluminate center.

Salts of the so-called *altebate* anion (aluminate with eight *tert*-butyl substituents) feature a so far unique solubility in alkanes [10]. Due to the steric demand of eight *tert*-butyl groups, the aluminate structure is locked in the achiral S_4-symmetric conformation. Most importantly, alkali metal *altebates* are easily available in two high yielding steps from cheap chemicals. However, exposure to aqueous acids and bases leads to rapid hydrolysis of the aluminate. In this article, we report salts of the analogous borate ester anion "*bortebate*" (borate with eight *tert*-butyl substituents) that displays both higher stability towards water as well as a higher solubility of its lithium salt in pentane.

2. Experimental

2.1. General methodology

Starting materials were used as supplied by Acros-Fisher, Aldrich Chemical Company without further purification. Reactions involving air-sensitive reagents were carried out under an atmosphere of dinitrogen or argon using standard Schlenk techniques. Absolute solvents were dried in an MBRAUN MB SCS-800 solvent purification system. NMR spectra were recorded using Bruker DRX-200, Bruker ARX-250, Bruker Avance 300 and Bruker Avance 500 spectrometers. Chemical shifts are reported in ppm relative to tetramethylsilane for ^1H and ^{13}C, and were determined by reference to ^{13}C and residual ^1H solvent peaks ($CDCl_3$ 77.0 and 7.26

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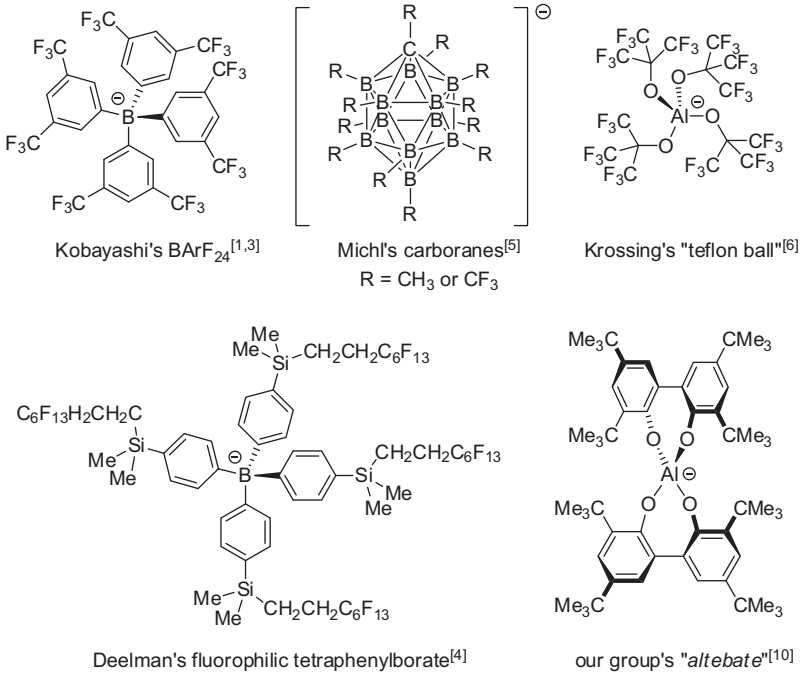


Fig. 1. Overview of selected lipophilic arylborates, carboranes, and aluminates with low nucleophilicity.

ppm; d_6-acetone 30.83 and 2.05 ppm). ^{11}B chemical shifts are reported in ppm relative to $BF_3{\cdot}OEt_2$. Melting points were determined using a Gallenkamp hot-stage microscope and are uncorrected. An optimized preparation protocol for 3,3′,5,5′-tetra-(*tert*-butyl)-2,2′-biphenol has already been reported in the literature [10,11].

2.2. Synthesis and characterization

2.2.1. Synthesis of lithium tetrakis(tetrahydrofuran) bis[3,3′,5,5′-tetra-(tert-butyl)-2,2′-diphenolato]borate(III)

Under argon atmosphere, $LiBH_4$ (2 M, 6.1 mL, 12 mmol) was diluted in 15 mL THF (obtained by distillation from Na/Ph_2CO). A solution of 3,3′,5,5′-tetra-(*tert*-butyl)-2,2′-biphenol (10 g, 24 mmol) in 15 mL THF was added slowly. The reaction mixture was heated for 8 d under reflux conditions, and filtered over Celite. The solvent was removed *in vacuo*. Excess 3,3′,5,5′-tetra-(*tert*-butyl)-2,2′-biphenol was removed by sublimation (6 h, 120 °C, 0.5 mbar). 8.74 g (7.8 mmol, 65%) of a colorless powder were obtained. ^1H NMR (500.13 MHz, d_6-acetone, 25 °C) δ = 7.13 (d, 4H, $^4J_{H,H}$ = 2.5 Hz, Ar), 7.02 (d, 4H, $^4J_{H,H}$ = 2.5 Hz, Ar), 3.63 (m, 16H, THF), 1.79 (m, 16H, THF), 1.31 (s, 36H, Me), 1.24 (s, 36H, Me) ppm. $^{13}C\{^1H\}$ NMR (125.77 MHz, d_6-acetone, 25 °C) δ = 155.9 (C_{Ar}), 139.4 (C_{Ar}), 139.2 (C_{Ar}), 133.6 (C_{Ar}), 126.0 (C_{Ar}), 121.8 (C_{Ar}), 68.1 (THF), 35.7 ($CCMe_3$), 34.6 ($CCMe_3$), 32.3 (Me), 31.7 (Me), 26.2 (THF-C) ppm. $^{11}B\{1H\}$ NMR (64.14 MHz, d_6-acetone, 25 °C) δ = 6.45 (s) ppm. Mp. 241 °C. IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3426, 2959, 2904, 2870, 1637, 1476, 1435, 1411, 1389, 1360, 1282, 1267, 1242, 1102, 1048, 974, 935, 912, 878. (%) 4·THF (1123.41): *Anal.* Calc. for $C_{56}H_{80}BLiO_4$: C, 76.98; H, 10.05. Found: C, 77.23; H, 9.84%. HR-MS (ESI−) *m/z* (%): calcd.: 827.61497 found: 827.61309 (100) $[M-Li(thf)_4^+]^-$.

The solubility of the product was determined by stirring lithium *bortebate* in pentane under an argon atmosphere, and filtering off the solution by canula transfer into a second Schlenk flask. In a first experiment, the solution temperature was determined to 20 °C. In a second experiment, the temperature was 22 °C. 50.0 mL (±0.2 mL) of the saturated solution was measured off into a syringe, the solvent was removed in vacuo and the mass of the residue was determined to 1.9723 g (20 °C) and 2.1592 g (22 °C). A sample of the residue was dissolved in d_6-acetone, and found ^1H NMR-spectroscopically to be >97% pure with a THF/*bortebate* ratio of 4.0 ± 0.05. The determination of the lithium *bortebate* solubility in pentane under an atmosphere of air was not reproducible, possibly due to partial hydrolysis of the thf adduct of the lithium counterion.

2.2.2. Synthesis of sodium pentakis(tetrahydrofuran) bis[3,3′,5,5′-tetra-(tert-butyl)-2,2′-diphenolato]borate(III)

Under inert gas conditions, $NaBH_4$ (0.69 g, 18 mmol) was suspended in 15 mL THF. A solution of 3,3′,5,5′-tetra-(*tert*-butyl)-2,2′-biphenol (15 g, 37 mmol) in 15 mL THF was slowly added. The reaction mixture was heated for 8 d under reflux conditions, and filtered over Celite. Removal of the solvent gave 20 g of a colorless powder (17 mol, 92%). ^1H NMR (199.92 MHz, d_6-acetone, 25 °C) δ = 7.13 (d, 4H, $^4J_{H,H}$ = 2.6 Hz, Ar), 7.01 (d, 4H, $^4J_{H,H}$ = 2.6 Hz, Ar), 3.62 (m, 20H, THF), 1.79 (m, 20H, THF), 1.31 (s, 36H, Me), 1.24 (s, 36H, Me) ppm. $^{13}C\{^1H\}$ NMR (50.27 MHz, d_6-acetone, 25 °C) δ = 155.9 (C_{Ar}), 139.3 (C_{Ar}), 139.2 (C_{Ar}), 133.6 (C_{Ar}), 126.0 (C_{Ar}), 121.8 (C_{Ar}), 68.1 (THF), 35.7 ($CCMe_3$), 34.6 ($CCMe_3$), 32.3 (Me), 31.7 (Me), 26.2 (THF) ppm. $^{11}B\{1H\}$ NMR (64.14 MHz, CD_2Cl_2, 25 °C) δ = 6.44 (s) ppm. Decomp. >89 °C. IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 2959, 2907, 2869, 1623, 1476, 1464, 1435, 1410, 1390, 1361, 1332, 1282, 1240, 1201, 1132, 1101, 975, 934, 909, 879. *Anal.* Calc. for $C_{56}H_{80}BNaO_4{\cdot}2$ THF (after THF elimination) (995.24): C, 77.24; H, 9.72. Found: C, 77.30; H, 9.74%. HR-MS (ESI−) *m/z* (%): calcd.: 827.61497 found: 827.61412 (100), $[M-Na(thf)_5^+]^-$.

2.2.3. Synthesis of sodium mono(tetrahydrofuran) bis[3,3′,5,5′-tetra-tert-butyl-2,2′-diphenolato]borate(III)

THF elimination from the *pentakis*(tetrahydrofuran) sodium *bortebate* proceeded at 120 °C and 0.1 mbar over a period of 12 h 14 g (16 mmol, 98%) of a colorless powder were obtained. ^1H NMR (250.13 MHz, d_6-acetone, 25 °C) δ = 7.13 (d, 4H, $^4J_{H,H}$ = 2.5 Hz, Ar), 7,02 (d, 4H, $^4J_{H,H}$ = 2.5 Hz, Ar), 3.62 (m, 4H, THF), 1.78 (m, 4H, THF), 1.30 (m, 36H, Me), 1.24 (m, 36H, Me) ppm. $^{13}C\{^1H\}$ NMR

(500.13 MHz, d_6-acetone, 25 °C) δ = 156.7 (C_{Ar}), 140.2 (C_{Ar}), 139.9 (C_{Ar}), 134.4 (C_{Ar}), 126.8 (C_{Ar}), 122.6 (C_{Ar}), 68.9 (THF), 36.5 ($CCMe_3$), 35.5 ($CCMe_3$), 33.2 (Me), 32.5 (Me), 27.0 (THF) ppm. $^{11}B\{H\}$ (64.14 MHz, d_6-acetone, 25 °C) δ = 5.74 (s) ppm. Decomp. >218 °C. IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3424, 2959, 2906, 2870, 1467, 1462, 1435, 1411, 1390, 1361, 1282, 1265, 1240, 1210, 1201, 1132, 1101, 974, 934, 910, 878. HR-MS (ESI−) *m/z* (%): calcd.: 827.61497 found: 827.61320 (100) $[M-Na(thf)^+]^-$.

2.2.4. Synthesis of tetraphenylphosphonium bis[3,3′,5,5′-tetra-(tert-butyl)-2,2′-diphenolato]borate(III)

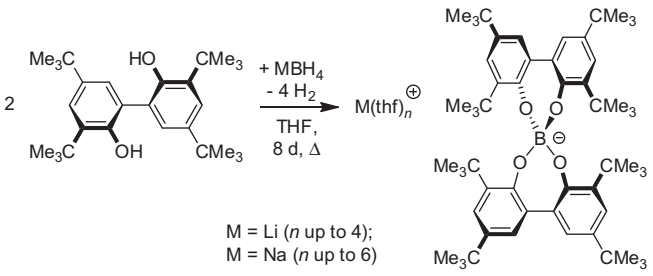
Tetraphenylphosphonium bromide (0.53 g, 1.3 mmol) was dissolved in 15 mL CH_2Cl_2. A solution of sodium *bortebate* (1.3 g, 1.4 mmol) in 10 mL CH_2Cl_2 was added. Immediately, a colorless solid (NaBr) precipitated. The suspension was filtered over Celite. Removal of the solvent *in vacuo* gave a colorless powder. The product was washed with a small amount of pentane. 1.1 g of a colorless powder (0.94 mmol, 75%) were isolated. ^1H NMR (500.13 MHz, CD_2Cl_2, 25 °C) δ = 7.77 (t, 4H, $^3J_{H,H}$ = 6.6 Hz, Ar), 7.62 (m, 8H, Ar), 7.47 (m, 8H, Ar), 7.10 (d, 4H, $^4J_{H,H}$ = 2.3 Hz, Ar), 7.01 (d, 4H, $^4J_{H,H}$ = 2.3 Hz, Ar), 1.25 (s, 36H, Me), 1.13 (s, 36H, Me) ppm. $^{13}C\{^1H\}$ NMR (125.77 MHz, CD_2Cl_2, 25 °C) δ = 154.9 (C_{Ar}), 139.2 (C_{Ar}), 138.9 (C_{Ar}), 136.0 (C_{Ar}), 135.9 (C_{Ar}), 134.5 (C_{Ar}), 134.4 (C_{Ar}), 132.5 (C_{Ar}), 130.8 (C_{Ar}), 130.7 (C_{Ar}), 125.7 (C_{Ar}), 121.7 (C_{Ar}), 117.9 (C_{Ar}), 117.2 (C_{Ar}), 35.0 ($CCMe_3$), 34.2 ($CCMe_3$), 31.7 (Me), 30.8 (Me) ppm. $^{11}B\{^1H\}$ NMR (64.14 MHz, CD_2Cl_2, 25 °C) δ = 6.31 (s) ppm. ^{31}P NMR (202.47 MHz, CD_2Cl_2, 25 °C) δ = 22.9 (s) ppm. Mp. >300 °C. IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 2951, 2903, 2867, 1583, 1476, 1463, 1437, 1411, 1388, 1359, 1282, 1243, 1109, 996, 967, 934, 911, 875, 724, 690, 528. *Anal.* Calc. for $C_{80}H_{100}BO_4P$ (1167.43): C, 82.31; H, 8.63. Found: C, 82.44; H, 8.72%. HR-MS (ESI+) *m/z* (%): calcd.: 339.12971 found: 339.12978 $[PPh_4]^+$. HR-MS (ESI−) *m/z* (%): calcd.: 827.61497 found: 827.61432 (100), $[M-Ph_4P^+]^-$.

2.2.5. Synthesis of tetraphenylphosphonium bis[3,3′,5,5′-tetra-(tert-butyl)-2,2′-diphenolato]aluminate(III)

Tetraphenylphosphonium bromide (0.5 mg, 1.2 mmol) was dissolved in 15 mL CH_2Cl_2. A solution of sodium *altebate* (1.3 g, 1.4 mmol) in 10 mL CH_2Cl_2 was added. A colorless solid (NaBr) precipitated immediately. The suspension was filtered over Celite. Removal of the solvent *in vacuo* gave a colorless powder. The product was washed with a small amount of pentane. 1.2 g of a colorless powder (1.0 mmol, 86%) were obtained. ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C) δ = 7.69 (t, 4H, $^3J_{H,H}$ = 6.0 Hz, Ar), 7.37–7.53 (m, 16H, Ar), 7.16 (d, 4H, $^4J_{H,H}$ = 2.5 Hz, Ar), 7.01 (d, 4H, $^4J_{H,H}$ = 2.5 Hz, Ar), 1.24 (s, 36H, Me), 1.19 (s, 36H, Me) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$, 25 °C) δ = 156.0 (C_{Ar}), 138.0 (C_{Ar}), 137.6 (C_{Ar}), 135.9 (C_{Ar}), 135.9 (C_{Ar}), 134.1 (C_{Ar}), 133.9 (C_{Ar}), 132.6 (C_{Ar}), 130.9 (C_{Ar}), 130.7 (C_{Ar}), 128.0 (C_{Ar}), 121.6 (C_{Ar}), 117.7 (C_{Ar}), 116.5 (C_{Ar}), 35.1 ($CCMe_3$), 34.1 ($CCMe_3$), 31.9 (Me), 30.6 (Me) ppm. ^{31}P NMR (101.26 MHz, $CDCl_3$, 25 °C) δ = 24.2 (s) ppm. Mp. >300 °C. IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 2951, 2904, 2867, 1463, 1437, 1405, 1386, 1359, 1281, 1242, 1109, 871, 803, 783, 769, 724, 690, 621, 607, 528. *Anal.* Calc. for $C_{80}H_{100}AlO_4P$ (1083.60): C, 81.18; H, 8.52. Found: C, 81.18; H, 8.49%. HR-MS (ESI+) *m/z* (%): calcd.: 339.12971 found: 339.12982 $[PPh_4]^+$. MS (ESI−) *m/z* (%): calcd.: 843.58775 found: 843.58690 (100) $[M-Ph_4P^+]^-$.

3. Results and discussion

The synthesis of the 3,3′,5,5′-tetra-(*tert*-butyl)-2,2′-biphenol ligand can be easily achieved in a high yield 100 g-scale from inexpensive 2,4-di-*tert*-butylphenol and MnO_2. The reaction of the resulting 2,2′-biphenol with $LiBH_4$ or $NaBH_4$ in THF takes several days under reflux conditions (Scheme 1). The *bortebate* formation



Scheme 1. Preparation of thf adducts of alkali metal *bortebate* salts [9].

from $LiBH_4$ or $NaBH_4$ took place orders of magnitude more slowly than the respective *altebate* formation from $LiAlH_4$ or $NaAlH_4$. The different rate of H_2 formation originates from the increased steric hindrance of the overall eight *tert*-butyl groups due to the smaller boron center, and the lower polarity of the B–H bonds compared to the more ionic Al–H bonds.

The S_4 symmetric *bortebate* anion is an achiral *meso* structure due to an inner racemate of its two atropisomeric 2,2′-biphenolate ligands. The D_2 diastereomer is predicted to be 46.3 kJ mol^{-1} higher in energy at the B3LYP/LACV3P**++ level of theory due to the disadvantageous repulsion of two pairs of *tert*-butyl groups in *ortho*-position to the phenolate oxygen [12]. This value is even higher than the energetic difference between D_2/S_4 for the *altebate* ion (19.1 kJ mol^{-1}) [10]. A strong intramolecular steric repulsion occurs between two pairs of *tert*-butyl groups in the D_2 structure. The smaller radius of the lighter earth metal translates into a tighter packing of the substituents, thus favoring the more sterically balanced S_4 structure. Indeed, X-ray structure determinations always revealed the S_4 symmetry of the *bortebate* anion (Fig. 2).

At room temperature, the *bortebate* anion does neither hydrolyze in THF/H_2O solution nor does addition of aqueous NaOH cause hydrolytic degradation. The solid thf adducts of lithium and sodium bortebate can be handled in air. However, addition

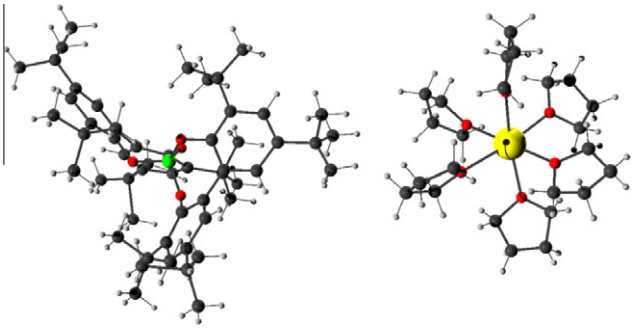
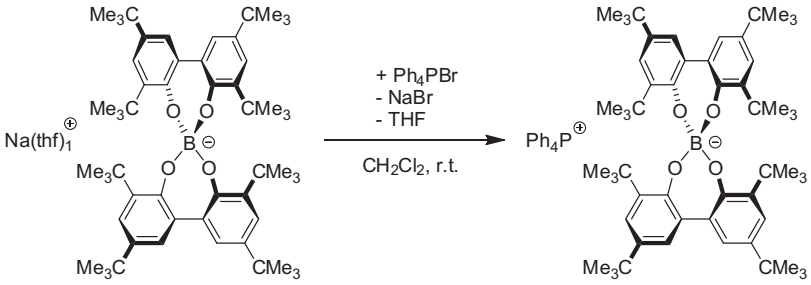


Fig. 2. Structural proof of the hexakis(thf) adduct of sodium bortebate by a single-crystal X-ray structure of mediocre quality (wR_2 = 0.306); C black, H gray, O red, Na yellow, B green [13]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Content of thf ligands in sodium *bortebate* and sodium *altebate*, according to integration in ^1H NMR spectra.

T and p	Ratio thf/bortebate	Ratio thf/altebate
50 °C at 300 mbar	7.0	7.5
r.t. at 0.1 mbar	3.2	2.5 (after 8 h)
60 °C at 0.1 mbar	1.36 (after 8 h)	1.6 (after 8 h)
90 °C at 0.1 mbar	0.6 (after 12 h)	0.6 (after 8 h)
120 °C at 0.1 mbar	0.6 (110 °C, after 8 h)	0.4 (after 8 h)



Scheme 2. Preparation of the tetraphenylphosphonium *bortebate*.

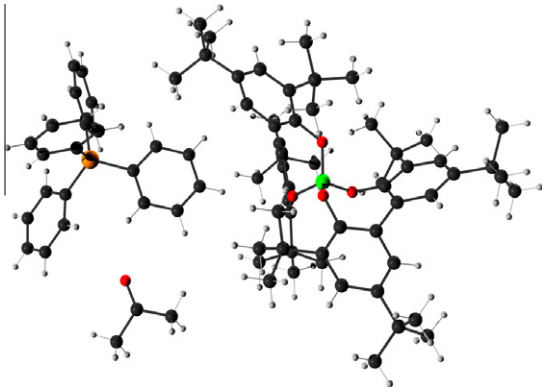


Fig. 3. Single-crystal X-ray structure of the tetraphenylphosphonium *bortebate*; C black, H gray, O red, Na yellow, B green P orange [13]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

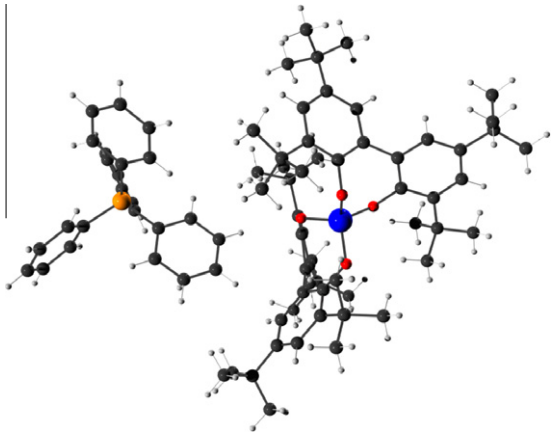


Fig. 4. Single-crystal X-ray structure of the tetraphenylphosphonium *altebate*; C black, H gray, O red, Na yellow, Al blue, P orange [13]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of aqueous acids leads to instantaneous hydrolysis. This behavior correlates with boron's favorite coordination numbers 3 and 4, and aluminum's favorite coordination numbers 4–6. Presumably, a hydroxide nucleophile expands the coordination sphere of aluminum in the *altebate* anion, while it is unable to do so in *bortebates*.

Tetrahydrofuran ligands of sodium bortebate can be eliminated by heating to at least 90 °C at 0.1 mbar for two days to a level of 0.6 thf per sodium bortebate. THF elimination proceeds under similar conditions for *bortebate* and *aluminate* salts (Table 1). The relative influence of the size of the anion, and of the possible coordination of the anion to unsaturated, "naked" sodium appears to be small.

In salt metathesis reactions, alkali metal cations can easily be exchanged by more lipophilic cations. As an example, addition of tetraphenylphosphonium bromide to sodium bortebate in CH_2Cl_2 gives a precipitate of NaBr (Scheme 2).

For a structural comparison of the *bortebate* and the *altebate* anion, we obtained single-crystals suitable for X-ray diffraction studies of the tetraphenylphosphonium salts, respectively. Besides the shorter B–O bonds (146.7 ± 1 pm) compared to the Al–O bonds (174.5 ± 1.1 pm), the structural differences between *bortebate* and *altebate* are insignificant (Figs. 3 and 4).

The high solubility of *bortebate* salts in hydrocarbon solvents is evidence for its anion's high lipophilicity. Lithiumtetrakis(tetrahydrofuran) *bortebate* was dissolved in pentane at saturation concentrations of 39.5 g/L (20 °C) and 43 g/L (22 °C) under an argon atmosphere. The pentane solubility of the analogous lithium *altebate* amounts to a significantly lower value of only 7 g/L (24 °C).

4. Conclusion

Bortebate salts display an unprecedented lipophilicity that even surpasses that of its aluminum analog, reflected in an approximately sixfold lithium *bortebate* solubility in pentane. The synthetic access to *bortebates*, however, is hampered by the prolongued reaction time of the 2,2′-biphenol precursor with BH_4^-, and the required harsh reaction conditions. *Bortebates* are more resistant towards hydrolysis compared to *altebates* in alkaline solution. In our experience, *bortebates* share the high tendency towards crystallization with its aluminum sibling.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.12.039.

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