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Tetrakis{3,5-bis(perfluorohexyl)phenyl}borate: a highly fluorous anion

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Abstract—In search of new possibilities for rendering catalysts soluble in fluorous solvents, the preparation of a sodium derivative of tetrakis{3,5-bis(perfluorohexyl)phenyl}borate, a new and highly fluorous anion, is described. This weakly coordinating anion exhibits substantial affinity for perfluorinated solvents and is therefore expected to make a broad range of cationic transition-metal catalysts compatible with fluorous biphasic recycling techniques. © 2001 Elsevier Science Ltd. All rights reserved.

In recent years, economic and environmental considerations have led to the development of a number of advanced procedures for the recycling of homogeneous catalysts.[1] Fluorous Biphasic Catalyst Separation (FBCS) as a mild method for catalyst recovery and an alternative to aqueous biphasic separation[2], was first reported in the open literature in 1994 and has received increasing attention ever since.[1a] A well established method for adapting a catalyst to the requirements of FBCS is the attachment of perfluoroalkyl substituents to its ligand system.[1a,3,4] In our search for new ways of rendering ionic catalysts compatible with FBCS, we decided to investigate the perfluoroalkyl- substitution of a weakly-coordinating anion, instead of substituting a coordinated ligand.[5] The major advantage of this approach is the absence of interference of the perfluoroalkyl- substitution with the properties of the often very carefully optimised set of spectator ligands. Furthermore, this approach offers the possibility of making a broad range of catalysts available for use in FBCS by developing a single fluorous anion. Another advantage is the stabilisation of the anion by the electron withdrawing fluorinated alkyl groups, whereas in strongly-coordinated ligands this effect is often disadvantageous and requires insulating spacers to prevent a negative influence on the catalytic activity.[1a]

As catalytically relevant tetrakis{3,5-bis(trifluoromethyl)phenyl}borate (TFPB)[6] is known to increase the solubility of metal complexes in $scCO_2$,[7] we set out to prepare a related anion with a significantly increased proportion of fluorine. Empirically, approximately 60 wt% of fluorine is required to achieve preferential solubility of a compound in the fluorous phase of a fluorous biphasic solvent system.[1a,4] When charge separation is neglected, this implies for a typical catalyst such as $[Rh(L_2)(COD)]X$, in which L_2 is a diphosphine with a molecular weight up to ca 400, e.g. dimethyl-phospholanobenzene (Me-DuPhos) and X represents the fluorous tetraphenylborate anion, a requirement of at least 70 wt% of fluorine in the anion. Therefore, we decided to replace the trifluoromethyl groups in TFPB with perfluorohexyl groups (Scheme 1), yielding a tetraphenylborate with the desired level of fluorous character.

Using copper-mediated cross coupling,[8] 1,3-bis(perfluorohexyl)benzene (**1**) was prepared from 1,3-diiodobenzene and a slight excess of IC_6F_{13}.[9] The relatively mild conditions employed here, yield the desired product in 83% yield, with only the 1,3-product being observed. This is in contrast to the previously described synthesis of 1,3-bis(perfluorohexyl)benzene, in which **1** was isolated as an isomerisation product in the synthesis of 1,2-bis(perfluorohexyl)benzene.[10]

Electrophilic aromatic bromination of **1** is complicated by the presence of the strongly electron withdrawing perfluorohexyl substituents. The use of a powerful bromination mixture, NBS/trifluoroacetic acid/sulphuric acid,[11] resulted, after optimisation of reaction

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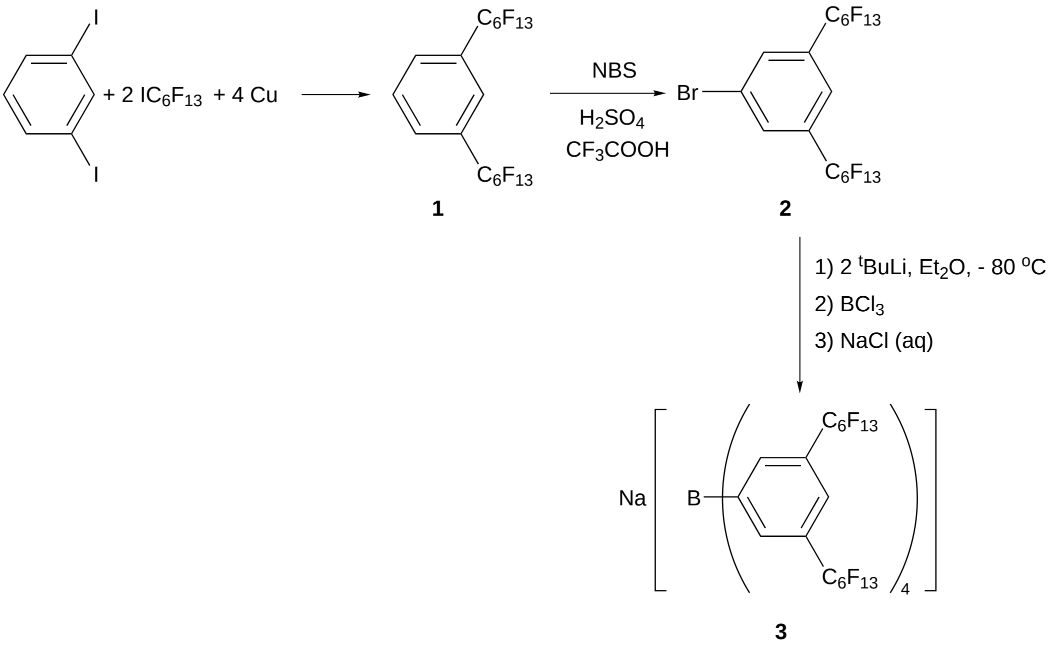

Scheme 1. Synthesis of sodium tetrakis{3,5-bis(perfluorohexyl)phenyl}borate.

conditions, in a mixture of 3,5-bis(perfluorohexyl)-bromobenzene (**2**) and unreacted **1** (4:1 molar ratio, 54% non isolated yield of **2**).[12] Since the separation of **1** and **2** was difficult, the mixture was used without further purification.

Reaction of 3,5-bis(trifluoromethyl)bromobenzene with magnesium, followed by coupling with a boron reagent, is the preferred way of preparing TFPB.[13] As **2** could not be converted into the corresponding Grignard, the use of *tert*-butyllithium was explored. **2** was reacted with 2 equiv. of ^{t}BuLi in Et_2O at −80°C, followed by the addition of BCl_3 to the aryllithium intermediate in situ (**Caution**: perfluoroalkyllithium compounds are potentially explosive and should not be isolated or warmed to room temperature).[13] Work-up with brine yielded the desired sodium tetrakis{3,5-bis(perfluorohexyl)phenyl}borate (**3**) as a spectroscopically and analytically pure compound.[14] The ^{11}B NMR spectrum is especially indicative of the formation of **3**, as the observed resonance corresponds well with those observed for tetraarylborates.[5,15]

The sodium salt **3** proved soluble in perfluorinated butyltetrahydrofuran (FC-75),[16] which demonstrates the high fluorophilicity of this salt despite the presence of a highly positively charged sodium ion. Stabilisation of such a cation in solution could in principle take place through interaction with the anion or solvation. ^1H and ^{19}F NMR analysis of **3** in FC-75 showed no indication for interaction of the sodium with either the phenyl groups or the perfluorohexyl groups of the anion.[17] As FC-75 contains an ether function, this appears to solvatate the cation. Addition of 12-crown-4 (1.5 equiv.) to the solution did not result in any changes in the chemical shifts (^1H, ^{11}B and ^{19}F NMR) of the anion, which corresponds with the above interpretation.

As we have previously observed that transition-metal complexes of related perfluoroalkylated tetraphenylborates are more soluble in apolar solvents in comparison with their corresponding sodium salts,[5] the tetrakis{3,5-bis(perfluorohexyl)phenyl}borate appears to offer significant potential in FBCS and possibly for catalysis in supercritical solvents as well.[7] Studies directed at using this anion in FBCS are currently underway.

In summary, using existing synthetic procedures, new and highly fluorinated sodium tetrakis{3,5-bis(perfluorohexyl)phenyl}borate has been prepared, which shows substantial solubility in the perfluorinated solvent FC-75. At 71 wt% of fluorine, it will introduce a fluorous character which is likely to be sufficient to render cationic transition-metal catalysts compatible with fluorous biphasic recycling techniques.

Acknowledgements

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9. A mixture of 121 mmol of copper powder, 56.3 mmol IC_6F_{13}, 21.4 mmol of 1,3-diiodobenzene, 4.1 mmol of 2,2′-bipyridine, 15 mL of DMSO and 32 mL of C_6F_6 was stirred at 50°C for 6 days. After addition of H_2O (50 mL) the mixture was extracted with CH_2Cl_2 (2×50 mL) and C_6F_6 (5 mL) After removal of all volatiles, the residue was taken up in acetone (50 mL) and extracted with FC-72 (2×20 mL). Drying in vacuo yielded 12.66 g (83 %) of a light yellow oil. ^{1}H NMR ($CDCl_3$:C_6F_6, 1:1): δ 7.88 (d, $J=7.2$ Hz, 2H), 7.87 (s, 1H), 7.76 (t, $J=7.2$ Hz, 1H). $^{13}C\{^{19}F\}$ ($CDCl_3$:C_6F_6, 1:1): δ 130.5 (s), 130.4 (d, $^1J_{C,H}=165.0$ Hz), 129.2 (d, $^1J_{C,H}=165.8$ Hz), 125.8 (d, $^1J_{C,H}=158.5$ Hz), 119.1 (CF_3), 115.5 (CF_2), 111.5 (CF_2), 111.0 (CF_2), 110.6 (CF_2), 108.8 (CF_2). ^{19}F NMR ($CDCl_3$:C_6F_6, 1:1): δ −93.5 (m, 3F), −123.6 (m, 2F), −133.6 (m, 2F), −134.1 (m, 2F), −135.0 (m, 2F), −138.5 (m, 2F). Anal. calcd for $C_{18}H_4F_{26}$: C, 30.27; H, 0.56. Found: C, 30.08; H 0.49.
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14. To a mixture consisting of **2** and **1** (0.83 g, molar ratio 83:17) containing 0.88 mmol of **2** and Et_2O (50 mL) was added ^{t}BuLi (1.2 mL, 1.5 M in pentane, 1.8 mmol) at −78°C followed by BCl_3 (0.17 mL, 1.0 M in hexane, 0.17 mmol) after 60 min. After warming to room temperature, the mixture was poured into H_2O (50 mL) and the water layer saturated with NaCl. After extraction with Et_2O (3×25 mL), drying over $MgSO_4$ and removal of all volatiles, a residue was obtained which was taken up in FC-72 (2 mL) and extracted with acetone (5 mL). Evaporation of acetone yielded 0.29 g (46 %) of a light-green oil. ^{1}H NMR (acetone-d_6): δ 7.76 (s, 8H, Ar_o) 7.59 (s, 4H, Ar_p). $^{13}C\{^{19}F\}$ (acetone-d_6): δ 162.7 (q, Ar-B, $^1J_{B,C}=50.2$ Hz), 130.4 (d, Ar_o, $^1J_{C,H}=159.2$ Hz), 129.2 (s, Ar_m), 122.3 (d, Ar_p, $^1J_{C,H}=165.4$ Hz), 120.5 (CF_3), 117.7 (CF_2), 113.0 (CF_2), 112.6 (CF_2), 112.1 (CF_2), 110.6 (CF_2). $^{11}B\{^1H\}$ NMR (acetone-d_6): δ −11.9 (s, $^1J_{BC=}$49.4 Hz). ^{19}F NMR (acetone-d_6): δ −88.6 (m, 3F), −118.2 (m, 2F), −128.5 (m, 2F), −129.0 (m, 2F), −129.4 (m, 2F), −129.9 (m, 2F), −133.5 (m, 2F). Anal. calcd for $C_{72}H_{12}BF_{104}Na$: C, 27.55; H, 0.43; F, 70.81. Found: C, 27.28; H, 0.52; F, 70.32.
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16. Using gravimetric methods, the solubility of **3** in FC-75 was determined to be 37 mmol per L of solvent at 25°C.
17. **3**: ^{1}H NMR (FC-75): δ 7.72 (s, 8H, Ar_o), 7.47 (s, 4H, Ar_p). ^{11}B NMR (FC-75): δ −12.9 (s). **3**+12-crown-4 (1.5 equiv.): ^{1}H NMR (FC-75): δ 7.65 (s, 8H, Ar_o) 7.44 (s, 4H, Ar_p), 3.28 (s, 16 H, 12-crown-4). ^{11}B NMR (FC-75): δ −12.9 (s). Spectra were externally referenced against acetone-d_6 (^{1}H NMR) and $BF_3{\cdot}Et_2O$ (^{11}B NMR) by using sealed capillaries.