Notes

Increasing the Lipophilic Character of Tetraphenylborate Anions through Silyl Substituents

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Summary: Trimethylsilyl- and dimethyl(1H,1H,2H,2H-perfluorooctyl)silyl substituents have been introduced in the para position of tetraphenylborate anions, resulting in enhanced solubility of their complexes n-$Bu_4N[B(C_6H_4\text{-}SiMe_2R\text{-}4)_4]$ *(R = Me,* $CH_2CH_2C_6F_{13}$*) and* $[Rh(dppe)_2][B(C_6H_4SiMe_2R\text{-}4)_4]$ *(dppe = 1,2-bis(diphenylphosphino)ethane, R = Me,* $CH_2CH_2C_6F_{13}$*) in apolar organic solvents.*

Introduction

Weakly coordinating anions are of interest for a range of applications that require generation and stabilization of highly reactive cationic species.[1,2] A lot of research has been directed at reducing the nucleophilicity of such anions by increasing their steric requirements, as in $[B(C_6F_4SiR_3)_4]^-$ [3] and $[MeB(2\text{-}C_6F_4C_6F_5)_3]^-$,[4] or by using polyhedral carboranes such as $[CB_{11}H_{12}]^-$, $[CB_{11}H_6Cl_6]^-$, and $[CB_{11}HF_{11}]^-$.[1a,b] However, relatively simple tetraphenylborates such as $[B\{3,5\text{-}C_6H_3(CF_3)_2\}_4]^-$ (TFPB) and $[B(C_6F_5)_4]^-$ remain the most widely used,[1a] because of their easy synthesis. Another interesting implication of the use of TFPB and $[B(C_6F_4SiR_3)_4]^-$ is their lipophilic behavior.[3,5] Especially TFPB is known for increasing the solubility of transition metal complexes in apolar media such as super critical carbon dioxide.[5a,b] Herein we report the preparation of large and weakly coordinating trimethylsilyl- and perfluoroalkylsilyl-substituted tetraphenylborate anions, which are more lipophilic than $[BPh_4]^-$, but in a chemical sense very similar to this anion.

Results and Discussion

Starting from *p*-bromo(trimethylsilyl)benzene and *p*-bromo[dimethyl(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silyl]benzene, **1a** and **1b** were prepared. Ion exchange with *n*-Bu_4NF and $[Rh(dppe)_2]Cl$ yielded the corresponding complexes **3** and **4** (Scheme 1). To assess the influence of the silyl substitution on the tetraphenylborate, single crystals of **2a** and **4a** were obtained. Their molecular structures in the solid state were determined by single-crystal X-ray diffraction (Figures 1 and 2, respectively).[6]

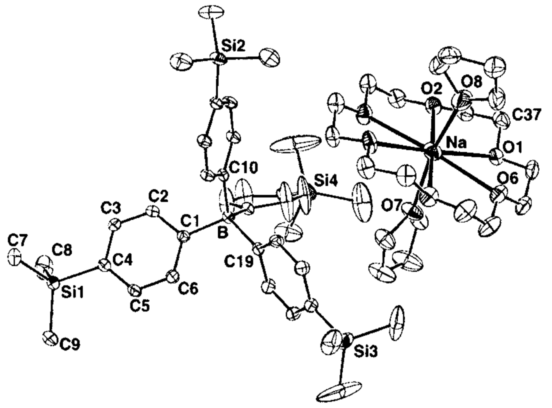

Figure 1. Molecular structure of **2a** with ellipsoids at 30% probability level. H atoms were omitted. Selected bond lengths (Å) and angles (deg): B−C(1) = 1.658(4), B−C(10) = 1.643(5), B−C(19) = 1.647(4), B−C(28) = 1.655(4), Na−O(1) = 2.685(3), Na−O(2) = 2.712(3), Na−O(3) = 2.712(3), Na−O(4) = 2.704(4), Na−O(5) = 2.822(3), Na−O(6) = 2.786(3), Na−O(7) =2.268(5), Na−O(8) = 2.284(4), C(1)−B−C(10) = 106.6(3), C(1)−B−C(19) = 111.9(2), C(1)−B−C(28) = 108.8(2), C(10)−B−(C19) = 110.9(2), C(10)−B−C(28) = 111.1(2), C(19)−B−C(28) = 107.6 (3).

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(1) Recent reviews: (a) Lupinetti, A. J.; Strauss, S. H. *Chemtracts* **1998**, *11*, 565. (b) Reed, C. A. *Acc. Chem. Res.* **1998**, *32*, 1025. (c) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927.

(2) Selected references: (a) Lancaster, S. J.; Walker, D. A.; Thornton-Pett, M.; Bochmann, M. *Chem. Commun.* **1999**, 1533. (b) Xie, Z.; Manning, J.; Reed, R. W.; Mathur, R.; Boyd, P. D. W.; Benesi, A.; Reed, C. A. *J. Am. Chem. Soc.* **1996**, *118*, 2922. (c) Giardello, M. A.; Eisen, M. S.; Stern, S. L.; Marks, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 3326. (d) Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920.

(3) Jia, L.; Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 842.

(4) Chen, Y.-X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 2582.

(5) (a) Kainz, S.; Brinkmann, A.; Leitner, W.; Pfaltz, A. *J. Am. Chem. Soc.* **1999**, *121*, 6421. (b) Burk, M. J.; Feng, S.; Gross, M. F.; Tumas, W. *J. Am. Chem. Soc.* **1995**, *117*, 8277. (c) Iwamoto, H.; Sonoda, T.; Kobayashi, H. *Tetrahedron Lett.* **1983**, *24*, 4703.

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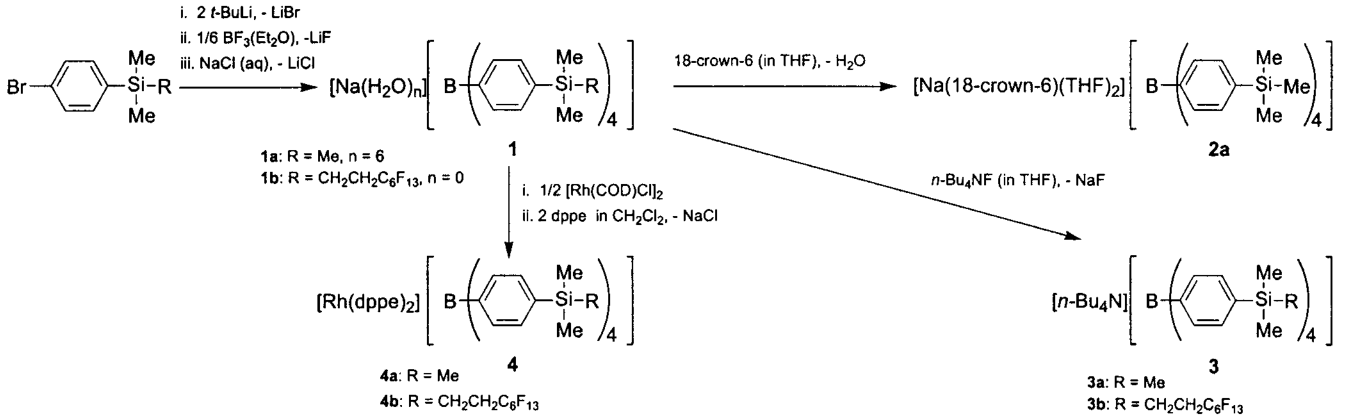
Scheme 1. Synthesis of the Various *p*-Silyl-Substituted Tetraaryl Borate Complexes



The structural similarity of the borate anions in **2a** and **4a** with those in [Na(18-crown-6)(H_2O)$_2$][BPh_4],[7a] [Na(benzo-15-crown-5)$_2$][BPh_4],[7b] and [Rh(HOCH(CH_2-PPh_2)$_2$)$_2$][BPh_4][8] indicates that the influence of the silyl substitution on the geometry of the borate anion is not significant, and its weakly coordinating character is at least comparable to [BPh_4]$^-$. This is further supported by ^{11}B NMR spectroscopy in solution; the chemical shifts measured in methanol-d_4 for all compounds described herein hardly deviate from that measured for sodium tetraphenylborate.[9]

A difference between fluorous borate **1b** and nonfluorous **1a** was observed in the IR spectra of these compounds. The spectrum of **1a** shows the presence of coordinated water resulting from the aqueous workup, whereas **1b** is isolated as a solvent-free salt. The absence of coordinated H_2O in **1b** is confirmed by elemental analysis and is remarkable, as sodium borates are usually obtained free of solvent only after thorough drying.[10] The lack of solvent coordination in **1b** could be caused by the presence of stabilizing Na···F–C interactions[11,12] between the Na^+ cation and the perfluoroalkyl tail, thereby eliminating the need for polar solvent (i.e., H_2O) coordination. IR data were inconclusive in this respect, as no changes in the C–F stretching region (1200–1350 cm^{-1}) of the IR spectrum of **1b** relative to that of **3b** were observed.[11a,13] Attempts to detect these interactions either by ^{19}F NMR spectroscopy in solution or by determination of a molecular structure in the solid state were hampered by the low solubility of **1b** in apolar solvents as well as the impossibility to obtain **1b** in single crystalline form.

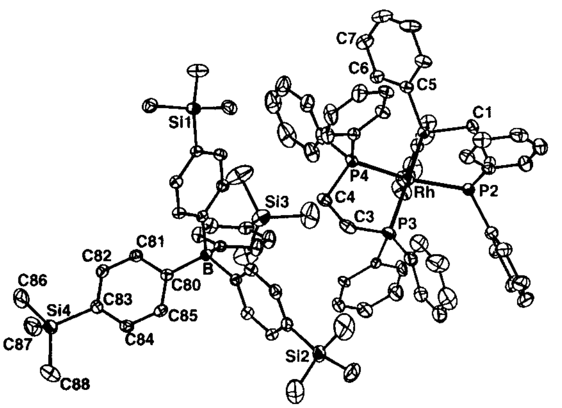


Figure 2. Molecular structure of **4a** with ellipsoids at 30% probability level. H atoms were omitted. Selected bond lengths (Å) and angles (deg): B–C(53) = 1.637(3), B–C(62) = 1.637(3), B–C(71) = 1.662(3), B–C(80) = 1.653(3), Rh–P(1) = 2.2979(6), Rh–P(2) = 2.2997(6), Rh–P(3) = 2.2833(6), Rh–P(4) = 2.2956(6), Rh–C(57) = 6.260(2), C(53)–B–C(62) = 109.03(16), C(53)–B–C(71) = 108.89(17), C(53)–B–C(80) = 108.02(16), C(62)–B–C(71) = 108.75(16), C(62)–B–C(80) = 110.75(17), C(71)–B–C(80) = 111.35(16), P(1)–Rh–P(2) = 83.74(2), P(1)–Rh–P(3) = 163.09(2), P(1)–Rh–P(4) = 98.68(2), P(2)–Rh–P(3) = 99.07(2), P(3)–Rh–P(4) = 83.54(2).

The solubility of **1**, **3**, and **4** in various solvents was explored, which revealed that the introduction of per-

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(6) Crystal data for **2a**: $C_{56}H_{92}BNaO_8Si_4$, monoclinic, spacegroup $P2_1/c$ (no. 14), with a = 13.540(2), b = 20.606(3), c = 27.693(3) Å, β = 118.86(2)°, V = 6767.1(16) Å^3, Z = 4, D_{calcd} = 1.020 g cm^{-3}. All data, where relevant, are given without disordered solvent contribution; 44 964 reflections measured (Nonius KappaCCD diffractometer, 150 K, Mo Kα radiation), 12 222 unique. The structure was solved by automated direct methods (SHELXS86) and refined on F^2 (SHELXL-97-2, 631 parameters). A disordered solvent area (792 Å, 187 e, probably THF) was incorporated in the model using PLATON/SQUEEZE. Several of the $SiMe_3$ groups and one of the phenyl rings of the anion display conformational disorder. The available data did not allow for the refinement of a disorder model. w$R2$ = 0.2304, $R1$ = 0.0793 for 9530 $I > 2\sigma(I)$, S = 1.069, $-0.48 < \Delta\rho < 0.96$ e Å^{-3}. Crystal data for **4a**: $C_{88}H_{100}BP_4RhSi_4$, monoclinic, spacegroup $P2_1$ (no. 4), with a = 14.7259(2), b = 20.1809(2), c = 16.4196(2) Å, β = 96.5775(4)°, V = 4847.49(10) Å^3, Z = 2, D_{calcd} = 1.033 g cm^{-3}. All data, where relevant, are given without disordered solvent contribution; 96 384 reflections measured (as for **2a**), 22 082 unique. The structure was solved by automated direct methods (SHELXS97) and refined on F^2 (SHELXL-97-2, 992 parameters). A disordered solvent area (1001 Å, 376 e) was incorporated in the model using PLATON/SQUEEZE. A two-site disorder model was introduced to describe the rotational disorder of the phenyl moieties around C3–P3; the occupancy of the major component refined to 0.537(9). w$R2$ = 0.0880, $R1$ = 0.0348 for 19688$I > 2\sigma(I)$, S = 1.039, $-0.36 < \Delta\rho < 0.39$ e Å^{-3}.

(7) (a) Seik Weng Ng. *Z. Kristallogr.–New Cryst. Struct.* **1998**, *213*, 159. (b) Owen, J. D. *J. Chem. Soc., Dalton Trans.* **1980,** 1066.

(8) Scherer, J.; Huttner, G.; Buchner, M.; Bakos, J. *J. Organomet. Chem.* **1996**, *520*, 45.

(9) The ^{11}B NMR spectrum of $NaBPh_4$ in CD_3OD shows a resonance at δ −2.76, which is similar to the chemical shifts of the ^{11}B resonances found for **1b** (δ −2.77), **2a** (δ −2.60), **3a** (δ −2.79), **3b** (δ −2.79), **4a** (δ −2.80), and **4b** (δ −2.80).

(10) (a) Wittig, G.; Raff, P. *Liebigs Ann. Chem.* **1950**, *573*, 195. (b) Nishida, H.; Takada, N.; Yoshimura, M.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600. (c) Bahr, S. R.; Boudjouk, P. *J. Org. Chem.* **1992**, *57*, 5545.

(11) (a) For a Na···F–C interaction, see: Samuels, J. A.; Lobkovsky, E. B.; Streib, W. E.; Folting, K.; Huffman, J. C.; Zwanziger, J. W.; Caulton, K. G. *J. Am. Chem. Soc.* **1993**, *115*, 5093. (b) For a Zr···F–C interaction, see: Karl, J.; Erker, G.; Fröhlich, R. *J. Am. Chem. Soc.* **1997**, *119*, 11165.

(12) Another possible interaction of Na with the borate anion would be η^6-coordination with a phenyl group. This is a well-known coordination mode of [BPh_4]$^-$ toward metal ions (ref 1c and Aresta, M.; Quaranta, E.; Tommasi, I. *New J. Chem.* **1997**, *21*, 595.). However, the ease with which **1b**, compared to **1a**, is obtained free of water suggests involvement of the perfluoroalkyl groups.

Table 1. Solubility of the Borate Complexes in Hexanes[a]

compound	μmol/L[b]	mg/L[b]
[n-Bu_4N][BPh_4][c]	<11	<7
3a[c]	<8	<7
3b[d]	4.0×10^3	8.7×10^3
[Rh(dppe)$_2$][BPh_4][c]	<0.4	<0.7
4a	0.4	0.7
4b	5.8	17

[a] A mixture of hexane isomers, predominantly *n*-hexane and methylcyclopentane, was used. [b] Expressed as the amount of borate complex that can be dissolved in 1 L of pure solvent at 25 °C. Determined by ICP/AAS analysis for [B] and [Rh]. [c] Below the detection limit for ICP-AAS. [d] Solubility determined using gravimetric methods.

fluoroalkylsilyl groups in BPh_4^- has a marked effect on the solubility of the borate complexes. Introduction of both trimethylsilyl and perfluoroalkylsilyl groups results in poor solubility in water for sodium salts **1a** and **1b** (<0.14 mmol/L), whereas $NaBPh_4$ shows excellent solubility (>0.30 mol/L) in this solvent.[14] However, solubility of **1a** and **1b** in a noncoordinating solvent, such as hexanes, remains low too (<0.14 mmol/L). Exchange of sodium for a tetrabutylammonium cation results in increased solubility of fluorous compound **3b** in hexanes, whereas nonfluorous **3a** remains essentially insoluble (Table 1). The influence of the fluorous tail on the solubility of the rhodium complex is less dramatic, but does result in an increased solubility in hexanes for **4b** (6 μmol/L) when compared to **4a** (0.4 μmol/L) and reference compound [Rh(dppe)$_2$]BPh_4[15] (<0.4 μmol/L). The increased solubility of **4b** was also visible to the naked eye, as only **4b** gave a distinctly yellow-colored hexane layer. Although the hexane solutions of **3b** and **4b** appear to be real solutions to the naked eye, the presence of colloidal aggregates or micelles cannot be excluded a priori and will be the subject of further research.

The solubility of perfluoroalkyl-substituted borates **3b** and **4b** in the fluorocarbon solvent FC-72[16] was also explored. This was found to be low for both compounds (**3b**, 52 μmol/L; **4b**, no color change observed in FC-72, implicating solubility well below 6 μmol/L). This can be explained by the combination of a relatively low fluorine content of these compounds, 45 and 35 wt %, respectively, and their ionic nature. It has been reported that the fluorine content of neutral phosphines and metal−phosphine complexes should be ca. 60% or higher to achieve high or preferential solubility in fluorous solvents.[17]

In conclusion, the present results show that the solubility of ionic tetraphenylborate complexes, especially tetrabutylammonium tetraphenylborate, in alkane solvents can be improved by the introduction of dimethyl(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silyl substituents in the anion. These lipophilic tetraphenylborate anions with a more complex structure can be obtained through a facile synthetic procedure by using the silyl center as a connecting point.[18] A further increase of the fluorous content of these borates is needed to achieve the desired solubility in apolar and fluorous (e.g., FC-72) solvents. Most importantly, it was shown that the introduction of these fluorous silyl substituents leaves the structural properties and the coordination behavior of these anions almost unaffected, thus rendering them alternatives for the TFPB anion and of interest for application in biphasic catalysis using apolar media or for catalysis in supercritical CO_2.

Experimental Section

General Procedures. All reactions were performed under dry N_2 atmosphere using standard Schlenk techniques. Tetrahydrofuran (THF), diethyl ether (Et_2O), hexane, and pentane were distilled from sodium benzophenone ketyl. *p*-Bromo(trimethylsilyl)benzene[19] and *p*-bromo(dimethyl(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silyl)benzene[17b,c] were synthesized according to literature procedures. All other chemicals were used as received. NMR spectra were recorded on Varian Mercury 200 (^1H and ^{31}P) and Varian Inova 300 (^1H, ^{11}B, ^{13}C, and ^{19}F) spectrometers with TMS (^1H, ^{13}C), $CFCl_3$ (^{19}F), $BF_3{\cdot}Et_2O$ (^{11}B), and H_3PO_4 (85%) (^{31}P) as external references. Elemental analyses and ICP/AAS analyses were carried out by H. Kolbe, Mikroanalytisches Laboratorium, Mühlheim an der Ruhr. Infrared spectra were recorded on a Mattson Galaxy FT-IR 5000 spectrometer.

Sodium Tetrakis[*p*-(trimethylsilyl)phenyl]borate Hexahydrate (1a) and 18-Crown-6-bis(tetrahydrofuran)−Sodium Tetrakis[*p*-(trimethylsilyl)phenyl]borate (2a). To a solution of *p*-bromo(trimethylsilyl)benzene (9.00 g, 39.1 mmol) in Et_2O (100 mL) was slowly added *t*-BuLi (52 mL, 1.5 M in pentane, 79.2 mmol) at −78 °C. The resulting solution was stirred for 3 h and allowed to warm to 0 °C. After cooling to −78 °C, $BF_3{\cdot}Et_2O$ (0.82 mL, 6.53 mmol) was added, and the solution was allowed to reach room temperature over a period of 16 h. The resulting clear yellow solution was slowly poured into a saturated aqueous NaCl solution (100 mL) and the Et_2O layer separated. After extraction of the aqueous layer with Et_2O (3 × 50 mL), the combined organic layers were washed with H_2O (50 mL) and dried over $MgSO_4$. Removal of the solvent and washing with pentane yielded 3.75 g (82% yield, based on boron) of a white solid. ^1H NMR (methanol-d_4, 300.1 MHz): δ 7.36 (m, 8H, Ar_o), 7.17 (d, $^3J_{HH} = 6.0$ Hz, 8H, Ar_m), 4.85 (s, 12H, H_2O), 0.22 (s, 36H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (methanol-d_4, 75.5 MHz): δ 167.3 (q, $^1J_{BC} = 49.3$ Hz, C−B), 137.7 (Ar_o), 132.9 (C−Si), 132.3 (Ar_m), 0.27 ($SiCH_3$). $^{11}B\{^1H\}$ NMR (methanol-d_4, 96.3 MHz): δ −2.55 (t, $^1J_{BC} = 24.4$ Hz). IR (KBr, cm^{-1}): 3485 (s), 3045 (m), 2955 (s), 1635 (w), 1577 (m), 1259 (s), 1143 (s), 1087 (m), 841 (s), 804 (m).

Light yellow crystals of borate **2a** were grown by slow diffusion of hexane into a solution of **1a** (0.40 g, 0.57 mmol) and THF (15 mL) in the presence of 18-crown-6 (0.29 g, 1.10 mmol). ^1H NMR (methanol-d_4, 300.1 MHz): δ 7.36 (m, 8H, Ar_o), 7.19 (d, $^3J_{HH} = 6.0$ Hz, 8H, Ar_m), 3.72 (m, 8H, THF), 3.59 (s, 24H, 18-crown-6), 1.86 (m, 8H, THF), 0.21 (s, 36H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (methanol-d_4, 75.5 MHz): δ 167.3 (q, $^1J_{BC} = 49.3$ Hz, C−B), 137.7 (Ar_o), 132.8 (C−Si), 132.4 (Ar_m), 71.9 (18-crown-6), 67.7 (α-THF), 27.4 (β-THF), 0.36 ($SiCH_3$). $^{11}B\{^1H\}$ NMR (methanol-d_4, 96.3 MHz): δ −2.60 (t, $^1J_{BC} = 24.4$ Hz).

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(13) (a) Adams, D. M. *Metal−Ligand and Related Vibrations*; Edward Arnold (Publishers) Ltd: London, 1967. (b) Douay, M. C.; Bopegedera, A. M. R. P.; Brazier, C. R.; Bernath, P. F. *Chem. Phys. Lett.* **1998**, *148*, 1.

(14) Bueechl, H. In *Advances in Analytical Chemistry and Instrumentation*; Reilly, C. N., Ed.; Wiley: New York, 1960; Vol. 1, p 10.

(15) Faraone, F. *J. Chem. Soc., Dalton Trans.* **1975**, 541.

(16) FC-72 is a mixture of perfluorohexanes.

(17) (a) Horváth, I. T. *Acc. Chem. Res.* **1998**, *31*, 641. (b) Richter, B.; Deelman, B.-J.; van Koten, G. *J. Mol. Catal. (A)* **1999**, *145*, 317. (c) Richter, B.; de Wolf, E.; van Koten, G.; Deelman, B.-J. *J. Org. Chem.* **2000**, *65*, 3885.

(18) (a) Richter, B.; Spek, A. L.; van Koten, G.; Deelman, B.-J. *J. Am. Chem. Soc.* **2000**, *122*, 3945. (b) Richter, B.; Deelman, B.-J.; van Koten, G. European Patent Appl. 98203308.6.

(19) Wu, R.; Schumm, J. S.; Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1996**, *61*, 6906.

Anal. Calcd for $C_{56}H_{92}BNaO_8Si_4$: C, 64.71; H, 8.92; Si, 10.81. Found: C, 64.71; H, 8.93; Si, 11.74.

Sodium Tetrakis[*p*-{dimethyl(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silyl}phenyl]borate (1b). Preparation of compound **1b** was carried out using a procedure similar to that employed for the preparation of **1a**. Starting from *p*-bromo{dimethyl-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silyl}benzene (2.88 g, 5.12 mmol) in a Et_2O/hexane mixture (1:1, 50 mL), *t*-BuLi (6.8 mL, 1.5 M in pentane, 10.2 mmol), and $BF_3{\cdot}Et_2O$ (0.11 mL, 0.85 mmol) yielded 1.60 g (97% yield, based on boron) of a white solid. ^1H NMR (methanol-d_4, 300.1 MHz): δ 7.34 (m, 8H, Ar_o), 7.20 (d, $^3J_{HH} = 7.8$ Hz, 8H, Ar_m), 2.05 (m, 8H, CH_2CF_2), 0.86 (m, 8H, $SiCH_2$), 0.30 (s, 24H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (methanol-d_4, 75.5): δ 168.7 (C−B), 137.7 (Ar_o), 132.5 (Ar_m), 129.7 (C−Si), 28.0 (CH_2CF_2), 7.3 ($SiCH_2$), −2.3 ($SiCH_3$). $^{11}B\{^1H\}$ NMR (methanol-d_4, 96.3 MHz): δ −2.77 (s). ^{19}F NMR (methanol-d_4, 282.5 MHz): δ −79.0 (m, 3F), −113.6 (m, 2F), −119.5 (m, 2F), −120.5 (m, 2F), −121.0 (m, 2F), −123.9 (m, 2F). IR (KBr, cm^{-1}): 3045 (w), 2980 (w), 1361 (w), 1317 (w), 1240 (s), 1213 (s), 1143 (m), 1069 (m), 898 (m), 841 (s), 798 (s), 530 (s). Anal. Calcd for $C_{64}H_{56}BF_{52}NaSi_4$: C, 39.23; H, 2.88; B, 0.55; F, 50.42; Na, 1.17. Found: C, 39.18; H, 3.02; B, 0.54; F, 50.27; Na, 1.25.

Tetrabutylammonium Tetrakis[*p*-(trimethylsilyl)phenyl]borate (3a). *n*-Bu_4NF (0.86 mL, 1 M in THF, 0.86 mmol) was added to a solution of **1a** (0.32 g, 0.43 mmol) in THF (25 mL). After stirring for 1.5 h, the solution was evaporated to dryness. H_2O (10 mL) was added, and the mixture was stirred for 30 min. The solid was collected and washed with H_2O (10 mL). The resulting solid was dried in vacuo, yielding 0.24 g (65%) of a white solid. ^1H NMR (methanol-d_4, 300.1 MHz): δ 7.35 (m, 8H, Ar_o), 7.19 (d, 8H, $^3J_{HH} = 7.5$ Hz, Ar_m), 3.13 (m, 8H, NCH_2), 1.58 (m, 8H, NCH_2CH_2), 1.37 (m, 8H, $CH_2CH_2CH_2$), 1.02 (t, 12H, CH_2CH_3), 0.22 (s, 36H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (methanol-d_4, 75.5 MHz): δ 166.3 (q, C−B), 137.8 (Ar_o), 133.0 (C−Si), 132.4 (Ar_m), 60.4 (NCH_2), 25.6 (NCH_2CH_2), 21.6 ($CH_2CH_2CH_3$), 14.8 (CH_2CH_3), 0.3 ($SiCH_3$). $^{11}B\{^1H\}$ NMR (methanol-d_4, 96.3 MHz): δ −2.79 (s). Anal. Calcd for $C_{52}H_{88}BNSi_4$: C, 73.44; H, 10.43; N, 1.65. Found: C, 73.15; H, 10.51; N, 1.68.

Tetrabutylammonium Tetrakis[*p*-{dimethyl(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silyl}phenyl]borate (3b). Preparation of compound **3b** was carried out using a procedure similar to that employed for the preparation of **3a**. Starting from **1b** (0.23 g, 0.12 mmol) and *n*-Bu_4NF (0.24 mL, 1 M in THF, 0.24 mmol) yielded 0.12 g (46%) of an off-white waxy solid. ^1H NMR (methanol-d_4, 200.1 MHz): δ 7.34 (m, 8H, Ar_o), 7.15 (d, 8H, $^3J_{HH} = 7.4$ Hz, Ar_m), 3.29 (m, 8H, NCH_2), 2.01 (m, CH_2CF_2), 1.64 (m, 8H, NCH_2CH_2), 1.41 (m, 8H, $CH_2CH_2CH_2$), 1.01 (t, 12H, CH_2CH_3), 0.86 (m, 8H, $SiCH_2$) 0.19 (s, 36H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (methanol-d_4, 75.5 MHz): δ 169.2 (q, C−B), 138.2 (Ar_o), 132.9 (C−Si), 130.3 (Ar_m), 60.6 (NCH_2), 28.2 (t, CH_2CF_2), 25.8 (NCH_2CH_2), 12.7 ($CH_2CH_2CH_3$), 14.9 (CH_2CH_3), 7.5 ($SiCH_2$), −2.1 ($SiCH_3$). $^{11}B\{^1H\}$ NMR (methanol-d_4, 96.3 MHz): δ −2.79 (s). IR (KBr, cm^{-1}): 3045 (w), 2962 (w), 1579 (w), 1479 (w), 1363 (m), 1248 (s), 1209 (s), 1143 (m), 1066 (m), 1022 (m), 896 (m), 839 (s), 794 (s), 530 (s). Anal. Calcd for $C_{80}H_{92}BF_{52}NSi_4$: C, 44.10; H, 4.26; N, 0.64; F, 45.35. Found: C, 43.83; H, 4.34; N, 0.56; F, 45.26.

Rhodium(I) [Bis(1,2-bis(diphenylphosphino)ethane)] Tetrakis[*p*-(trimethylsilyl)phenyl]borate (4a). 1,2-Bis-(diphenylphosphino)ethane (0.46 g, 1.17 mmol) in CH_2Cl_2 (5 mL) was slowly added to a solution of $[Rh(1,5\text{-}COD)Cl]_2$ (135.6 mg, 0.28 mmol) in CH_2Cl_2 (5 mL). After stirring for 1 h, **1a** (0.41 g, 0.57 mmol) suspended in 1-propanol (5 mL) was added slowly. The resulting mixture was stirred for 4 h and filtered, and volatiles were removed in vacuo. The solid was taken up in acetone, the resulting solution was filtered, and upon addition of hexane, 0.63 g (76%) of a light orange solid precipitated. Crystals were grown by slow diffusion of Et_2O into a $CHCl_3$ solution of **4a**. ^1H NMR ($CDCl_3$, 300.1 MHz): δ 7.44 (m, 8H, Ar_o), 7.34 (m, 8H, $^3J_{HH} = 6.0$ Hz, Ar_m), 7.18 (m, 40H, P−Ph) 2.07 (m, 8H, $P{-}(CH_2)_2{-}P$), 0.14 (s, 36H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 165.5 (q, $^1J_{BC} = 48.8$ Hz, B−C), 136.0(s), 134.6(s), 133.4(s), 131.5 (m, P−C), 131.3(s), 130.9(s), 128.8(s), 28.7 (m, $P{-}(CH_2)_2{-}P$), −0.3 ($SiCH_3$). $^{11}B\{^1H\}$ NMR (methanol-d_4, 96.3 MHz): δ −2.80 (s). ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ 58.3 (d, $^1J_{RhP} = 132.5$ Hz). Anal. Calcd for $C_{88}H_{100}BP_4RhSi_4$: C, 70.10; H, 6.69; P, 8.22; Si, 7.45. Found: C, 69.97; H, 6.82; P, 8.15; Si, 7.36.

Rhodium(I) [Bis(1,2-bis(diphenylphosphino)ethane)] Tetrakis[*p*-{dimethyl (1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silyl}phenyl]borate (4b). To a solution of $[Rh(COD)Cl]_2$ (51.8 mg, 0.12 mmol) in CH_2Cl_2 (5 mL) was slowly added dppe (0.18 g, 0.45 mmol) in CH_2Cl_2 (2 mL). After stirring for 1 h, **1b** (0.24 g, 0.12 mmol) dissolved in methanol (2 mL) was added slowly. The resulting mixture was stirred for 1.5 h and filtered, and volatiles were removed in vacuo. The solid was then taken up in $CHCl_3$, the resulting solution was filtered, and upon addition of diethyl ether, 0.46 g (68%) of a bright yellow solid precipitated. ^1H NMR ($CDCl_3$, 300.1 MHz): δ 7.44 (m, 8H, Ar_o), 7.34 (d, 8H, $^1J_{HH} = 6.0$ Hz, Ar_m), 7.18 (m, 40H, P−Ph), 2.12 (m, 8H, $P{-}(CH_2)_2{-}P$), 2.05 (m, 8H, CH_2CF_2), 0.90 (m, 8H, CH_2Si), 0.14 (s, 24H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 165.5 (q, $^1J_{BC} = 48.8$ Hz, B−C), 136.0(s), 134.6(s), 133.4(s), 132.3, 131.5 (m, P−C), 131.3(s), 130.9(s), 128.8(s), 28.7 (CH_2CF_2), 26.3 (t, $^1J_{PC} = 23.7$ Hz, $P{-}(CH_2)_2{-}P$), 5.7 ($SiCH_2$), −0.3 ($SiCH_3$). $^{11}B\{^1H\}$ NMR (methanol-d_4, 96.3 MHz): δ −2.80 (s). ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ 58.3 (d, $^1J_{RhP} = 132.5$ Hz). Anal. Calcd for $C_{116}H_{104}BF_{52}P_4RhSi_4$: C, 49.13; H, 3.70; F, 34.84; P, 4.37; Si, 3.96. Found: C, 49.25; H, 3.66; F, 34.67; P, 4.85; Si, 4.05.

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Supporting Information Available: Solubility studies, crystal data, and structure refinement details for **2a** and **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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