Inorg. Chem. **2002**, *41*, 4090–4092

Inorganic Chemistry
Communication

Tetraarylpentaborates, $[B_5O_6Ar_4]^-$ (Ar = C_6H_4OMe-4, $C_6H_3Me_2$-2,6): Their Formation from the Reaction of Arylboronic Acids with an Aryloxorhodium Complex, Structure, and Chemical Properties

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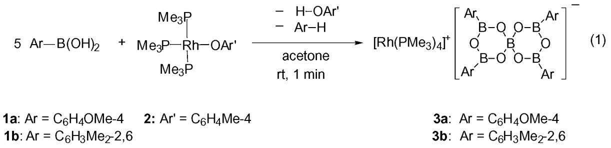
Received December 28, 2001

The reactions of (4-methoxyphenyl)boronic acid (**1a**) and of (2,6-dimethylphenyl)boronic acid (**1b**) with $(PMe_3)_3Rh$-$(OC_6H_4Me$-4) (**2**) in a 5:1 molar ratio result in the formation of cationic rhodium complexes with new tetraarylpentaborates $[Rh(PMe_3)_4]^+[B_5O_6Ar_4]^-$ (**3a**, Ar = C_6H_4OMe-4; **3b**, Ar = $C_6H_3Me_2$-2,6). The characterization of **3a** is as follows: orthorhombic space group $P2_12_12_1$, a = 14.7600(5) Å, b = 17.1675(5) Å, c = 19.8654(5) Å; V = 5033.7(3) Å^3; Z = 4. The characterization of **3b** is as follows: orthorhombic space group *Pnma*, a = 23.704(6) Å, b = 17.254(8) Å, c = 13.304(2) Å; V = 5441(2) Å^3; Z = 4. An intermediate complex, $[Rh(PMe_3)_4]^+[Ph_3B_3O_3(OC_6H_4Me\text{-}4)]^-$ (**4**), was isolated from the reaction of phenylboroxine, $(PhBO)_3$, with **2**. The tetraarylpentaborates smoothly undergo hydrolysis to give $[Rh(PMe_3)_4]^+[B_5O_6(OH)_4]^-$ (**5**).

Pentaborate $[B_5O_6(OH)_4]^-$, which is a stable anion with a unique spiro bicyclic structure, was prepared from the reaction of potassium fluoride with boric acid.[1] Analogous substituted pentaborates such as tetraarylpentaborate $[B_5O_6Ar_4]^-$ would be of a hydrophobic nature and suited as a counteranion of cationic organotransition metal complexes. There have been few reports on isolation of the organopentaborates and their use as the boron-containing anions. In this paper, we report the preparation of new organic tetraarylpentaborates via aryloxorhodium(I) complex-promoted condensation of arylboronic acids.

Reactions of (4-methoxyphenyl)boronic acid (**1a**) and of (2,6-dimethylphenyl)boronic acid (**1b**) with $(PMe_3)_3Rh$-$(OC_6H_4Me$-4) (**2**)[2] in a 5:1 molar ratio lead to the isolation of rhodium complexes with new tetraarylpentaborates $[Rh(PMe_3)_4]^+[B_5O_6Ar_4]^-$ (**3a**, Ar = C_6H_4OMe-4; **3b**, Ar = $C_6H_3Me_2$-2,6) at room temperature (eq 1).[3] The yield of **3a** is 62% based on Rh, which is improved to 73% in the reaction with addition of PMe_3 equimolar to **1a**.



(1)

Figure 1 shows structures of the anions $[B_5O_6Ar_4]^-$ of **3a** and **3b** by X-ray crystallography.[4] The spiro structure of the two planar six-membered rings is similar to that of $[B_5O_6(OH)_4]^-$.[1a] The B−O bonds between tetracoordinate boron atom and oxygen (1.46(1)−1.478(8) Å in **3a** and 1.46(1)−1.474(7) Å in **3b**) are longer than the other B−O bonds in the six-membered rings (1.304(9)−1.392(9) Å in **3a** and 1.33(1)−1.39(1) Å in **3b**). The cationic rhodium part is separated completely from the borate in both complexes. It contrasts with complexes $M^+[B_5O_6(OH)_4]^-$ (M = K, NH_4) which show a significant interaction between the cation and

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(3) Data for **3a**. ^1H NMR (300 MHz, acetone-d_6, 25 °C): δ = 7.98 (d, J(HH) = 9 Hz, 8H, *ortho*-H(B)), 6.87 (d, J(HH) = 9 Hz, 8H, *meta*-H(B)), 3.78 (s, 12H, OCH_3), 1.53 (m, 36H, PCH_3). $^{31}P\{^1H\}$ NMR (121.5 MHz, acetone-d_6, 25 °C): δ = −15.4 (d, J(PRh) = 134 Hz). ^{11}B NMR (160.4 MHz, acetone-d_6, 25 °C): δ = 28.18 (s, br, 4B), 4.76 (s, 1B). $^{13}C\{^1H\}$ NMR (100.4 MHz, acetone-d_6, 25 °C): δ = 162.1 (*para*-*C*(B)), 137.2 (*ortho*-*C*(B)), 113.4 (*meta*-*C*(B)), 55.1 (O*C*H_3), 20.7 (P*C*H_3), the ipso carbons were not observed. Anal. Calcd (%) for $C_{40}H_{64}B_5O_{10}P_4Rh$: C, 48.74; H, 6.54. Found: C, 48.28; H, 6.28. Data for **3b**: see Supporting Information.

(4) Crystallographic data for **3a**: formula $C_{40}H_{64}B_5O_{10}P_4Rh$, MW = 985.79, orthorhombic, space group $P2_12_12_1$ (No. 19), a = 14.7600(5) Å, b = 17.1675(5) Å, c = 19.8654(5) Å, V = 5033.7(3) Å^3, Z = 4, T = 213 K, μ = 0.515 mm^{-1}, F(000) = 2056, ρ_{calcd} = 1.301 Mg/m^3, total of 39189 reflections were collected, for observed data R = 0.056, R_w = 0.075 for 5268 reflections with $I > 3\sigma(I)$. Crystallographic data for **3b**: formula $C_{44}H_{72}B_5O_6P_4Rh$, MW = 977.90, orthorhombic, space group *Pnma* (No. 62), a = 23.704(6) Å, b = 17.254(8) Å, c = 13.304(2) Å, V = 5441(2) Å^3, Z = 4, T = 296 K, μ = 0.470 mm^{-1}, F(000) = 2056, ρ_{calcd} = 1.194 Mg/m^3, total of 5326 reflections were collected, for observed data R = 0.056, R_w = 0.050 for 3311 reflections with $I > 3\sigma(I)$. Crystallographic data (excluding structure factors) of the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-170093-170094. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: int. code +(49) 1223-336-033. E-mail: deposit@ccdc.cam.ac.uk.)

10.1021/ic015630w CCC: $22.00

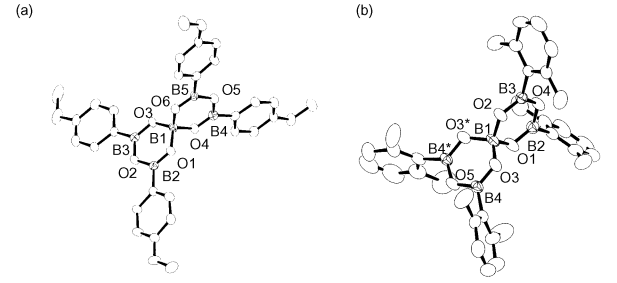


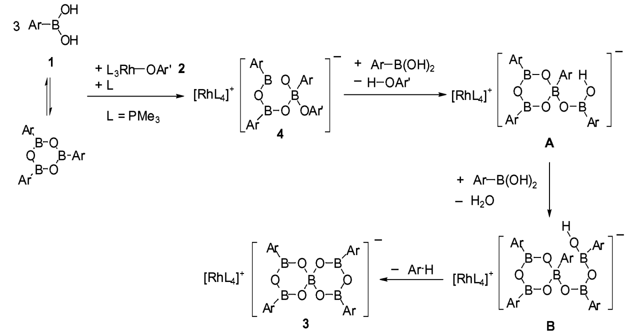
Figure 1. Molecular structures of the anions of (a) **3a** and (b) **3b** determined by X-ray crystallography with 30% thermal ellipsoidal plotting. B1, B2, B3, O1, O2, O4, and O5 atoms of **3b** are included in a crystallographic mirror plane. Selected bond distances (Å) and angles (deg): (a) O1−B1 1.462(9), O1−B2 1.337(9), O2−B2 1.404(9), O2−B3 1.392(9), O3−B1 1.472(9), O3−B3 1.304(9), O4−B1 1.478(8), O4−B4 1.33(1), O5−B4 1.41(1), O5−B5 1.375(9), O6−B1 1.46(1), and O6−B5 1.345(9); O1−B1−O3 111.5(6), O1−B1−O4 107.7(6), O1−B1−O6 108.6(6), O3−B1−O4 107.7(6), O3−B1−O6 108.6(6), and O4−B1−O6 112.0(6); (b) O1−B1 1.47(1), O1−B2 1.34(1), O2−B1 1.46(1), O2−B3 1.33(1), O3−B1 1.474(7), O3−B4 1.348(7), O4−B2 1.36(1), O4−B3 1.39(1), O5−B4 1.363(8), and O5−B4 1.363(8); O1−B1−O2 111.9(8), O1−B1−O3 107.5(6), O1−B1−O3 107.5(6), O2−B1−O3 109.3(6), O2−B1−O3 109.3(6), and O3−B1−O3 111.4(8).

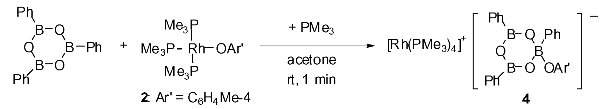
anion in the crystals.[1] Aryl substituted anions of **3a** and **3b** probably show weaker coordination ability than $[B_5O_6(OH)_4]^-$ with OH groups.[5]

The $^{31}P\{^{1}H\}$ NMR spectra of **3a** and **3b** in acetone-d_6 show a simple doublet at a position (δ −15.4, J(RhP) = 134 Hz) similar to that reported for $[Rh(PMe_3)_4]^+Cl^-$ (δ −14.5, J(RhP) = 125.6 Hz in D_2O).[6] The ^{11}B NMR spectra of **3a** and **3b** contain the two signals that are assigned to the tetracoordinate boron (δ 4.76 and 4.67) and tricoordinate boron (δ 28.18 and 29.73) nuclei. These results suggest that **3a** and **3b** exist as ionic complexes in solution, similar to $[Rh(PMe_3)_4]^+Cl^-$.

An equimolar reaction of **1a** with **2** produces **3a** in 20% yield, indicating that the Rh complex-promoted activation of an arylboronic acid is slower than the subsequent condensation of arylboronic acid molecules, forming the tetraarylpentaborates. One of the intermediate complexes of the formation of the bicyclic anion was isolated from the reaction of phenylboroxine $(PhBO)_3$[7] with **2** (eq 2). The obtained complex $[Rh(PMe_3)_4]^+[Ph_3B_3O_3(OC_6H_4Me\text{-}4)]^-$ (**4**)[8] was characterized by NMR (^1H, ^{11}B, and $^{13}C\{^1H\}$) and elemental analyses to have the anion with the monocyclic structure. This reaction involves the transfer of the aryloxide ligand from rhodium to boron. The migration of anionic ligand from transition metal to boron was postulated as a part of the transmetalation step in the metal-catalyzed synthetic organic reactions,[9] although the reaction in this study does not cause aryl group transfer from boron to rhodium.

Scheme 1. Plausible Sequences of Steps for Formation of **3**





(2)

Scheme 1 depicts plausible sequences of steps for the formation of **3** on the basis of the described results. The aryloxo ligand of **2** is known to be highly basic and nucleophilic, similar to the ligand of Pd(II) and Pt(II) aryloxo complexes with PMe_3 ligands.[2,10] The transfer of the aryloxide group to the electrophilic boronic acid or boroxine leads to the formation of **4** which undergoes stepwise condensation with aryl boronic acid to give the intermediates **A** and then **B**. Intramolecular metathesis reaction of O−H and B−C bonds of **B** results in formation of **3** and extrusion of Ar−H.

The role of the Rh complex is limited to donating the nucleophilic aryloxide ligand to a boron atom of the boroxine (or arylboronic acid) at the initial step of the reaction. In fact, the reaction of **1b** with another nucleophilic aryloxide anion of $[PPN]^+[OC_6H_4Me\text{-}4]^-$ (PPN = bis(triphenylphos-

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(5) References of weakly coordinating boron-containing anions, see: (a) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927. (b) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 133. (c) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.*, **2000**, *100*, 1169. (d) Olah, G. A.; Schlosberg, R. H. *J. Am. Chem. Soc.* **1968**, *90*, 2726. (e) Nishida, H.; Takada, N.; Yoshimura, M.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600. (f) Zanirato, P. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2789. (g) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920. (h) Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. *Science* **1993**, *260*, 1917. (i) Jia, L.; Yong, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 842. (j) Reed, C. A.; Fackler, N. L. P.; Kim, K. C.; Stasko, D.; Evans, D. R.; Boyd, P. D. W.; Rickard, C. E. F. *J. Am. Chem. Soc.* **1999**, *121*, 6314. (k) Jutzi, P.; Müller, C.; Stammler, A.; Stammler, H.-G. *Organometallics* **2000**, *19*, 1442. (l) van den Broeke, J.; Lutz, M.; Koojiman, H.; Spek, A. L.; Deelman, B. J.; van Koten, G. *Organometallics* **2001**, *20*, 2114.

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(8) Data for **4**. Yield 60%. ^1H NMR (400 MHz, acetone-d_6, 25 °C): δ = 8.11 (d, J = 8 Hz, 4H), 7.72 (d, J = 8 Hz, 2H), 7.34 (m, 6H), 7.04 (d, J = 8 Hz, 2H), 6.95 (d, J = 8 Hz, 2H), 6.92 (t, J = 8 Hz, 1H), 6.73 (d, J = 8 Hz, 2H), 2.09 (s, 3H, p−CH_3), 1.42 (br, 36H PCH_3). $^{31}P\{^1H\}$ NMR (121.5 MHz, acetone-d_6, −50 °C): δ = −16.1 (d, J(PRh) = 133 Hz). ^{11}B NMR (160.4 MHz, acetone-d_6, 25 °C): δ = 28.50 (br, 2B), 4.47 (s, 1B). $^{13}C\{^1H\}$ NMR (100.4 MHz, acetone-d_6, 25 °C): δ = 135.6, 133.1, 130.2, 127.8, 126.7, 124.8, 120.4, 20.6 (br, PCH_3). The CH_3 carbon was not observed because of overlapping with that of PMe_3. The spectrum at −50 °C showed the signals of CH_3 carbon (δ 20.4) and PMe_3 carbons (δ 19.9) separately. The *ipso* carbon signals were not observed because of their low intensity. Anal. Calcd (%) for $C_{37}H_{58}B_3O_4P_4Rh$: C, 53.80; H, 7.08. Found: C, 53.48; H, 7.17.

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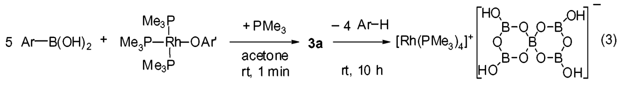
phino)iminium, $Ph_3P{=}N{=}PPh_3$) in a 5:1 molar ratio produces $[PPN]^+[B_5O_6(C_6H_3Me_2\text{-}2,6)_4]^-$ which shows the same NMR signals as the anion part of **3b**.

A prolonged reaction (10 h) of **1a** with **2** in acetone leads to deposition of a yellow insoluble solid. The ^1H NMR spectra and elemental analyses of the product revealed the structure, $[Rh(PMe_3)_4]^+[B_5O_6(OH)_4]^-$ (**5**) (eq 3).[11]



(3)

1a: Ar = C_6H_4OMe-4 **2**: Ar' = C_6H_4Me-4 **5**

Complex **5** is obtained also by standing an acetone solution of the isolated **3a** for 9 days at room temperature. In the former reaction, the initially formed **3a** undergoes hydrolysis of the B−Ar bonds by water contained in the reaction mixture.

In summary, this work demonstrates the preparation of unprecedented tetraarylpentaborates $[B_5O_6Ar_4]^-$ from arylboronic acids and an aryloxorhodium complex. This reaction involves metathesis reaction among the arylboronic acid, the boroxine, and the intermediate anionic species. The thermodynamically favorable B−O bond formation renders the sequential reactions, which involve activation of Rh−O or B−C bonds, facile.

Acknowledgment. This work was supported by the Grant-in-Aid for Scientific Research on Priority Areas, Molecular Physical Chemistry, from the Ministry of Education, Culture, Sports, Science and Technology, Japan (11166221). We are grateful to Prof. Norio Miyaura (Hokkaido University) for helpful discussion on the reaction mechanism. We also thank Prof. Munetaka Akita (Tokyo Institute of Technology) for X-ray crystal analysis of **3a** with imaging plate.

Supporting Information Available: Synthetic procedure for **2**−**5** and $[PPN]^+[B_5O_6(C_6H_3Me_2\text{-}2,6)_4]^-$. X-ray crystallographic file (for **3a** and **3b**) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Complex **5** was isolated as orange crystals in 58% yield from the reaction of **1a** with **2** in a 5:1 molar ratio for 10 h. ^1H NMR (300 MHz, acetone-d_6, 25 °C): $\delta = 3.76$ (s, 4H, O*H*), 1.55 (s, br, 36H, PC*H*$_3$). $^{31}P\{^1H\}$ NMR (121.5 MHz, acetone-d_6, 25 °C): $\delta = -15.4$ (d, J(PRh) = 134 Hz). ^{11}B NMR (160.4 MHz, acetone-d_6, 25 °C): $\delta = 20.22$ (s, br, 4B), 2.24 (s, 1B). $^{13}C\{^1H\}$ NMR (100.4 MHz, acetone-d_6, 25 °C): $\delta = 20.7$ (P*C*H$_3$). Anal. Calcd (%) for $C_{12}H_{40}B_5O_{10}P_4Rh$: C, 23.05; H, 6.45. Found: C, 23.10; H, 5.96.