Synthesis of a New Tridentate Anthracene Ligand Bearing (*i*-Pr)$_2$P Group at 1,8-Positions: Facile Bond Switch on Tetracoordinate Boron Atom

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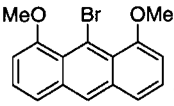
9-Borylanthracene **12** was prepared from 1,8-bis(diisopropylphosphino)-9-bromoanthracene (**5**) and the X-ray structure of **12** shows a tetrahedral boron atom coordinated by only one of the two (*i*-Pr)$_2$P groups. However, anthracene protons were observed symmetrically in ^{1}H NMR even at –80 °C, clearly indicating that the intramolecular bond-switching process is taking place very rapidly in solution.

Recently, we reported synthesis of a novel ligand (**1**) bearing the OMe group at 1,8-positions and a Br atom at 9-position, and the ligand was utilized to give hypervalent pentacoordinate boron compounds (**2**).[1] On the other hand, anthracene bearing the diphenylphosphino group at 1,8-positions (**3**) has been synthesized by Haenel et al.[2] Although some Pd or Ni compounds (**4**) could be prepared by the reaction of **3** with Pd(II) or Ni(II), introduction of various main group elements to 9-position of the anthracene have never been reported. Here we report on synthesis of a new diphosphine ligand with a Br atom at 9-position (**5**). The bromide was easily lithiated with *n*-BuLi and was utilized to introduce a boron atom to the 9-position.



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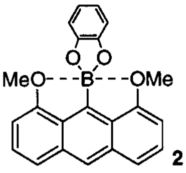

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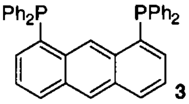

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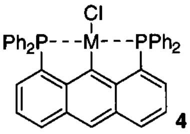

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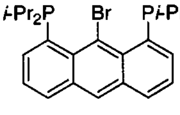
M = Ni, Pd



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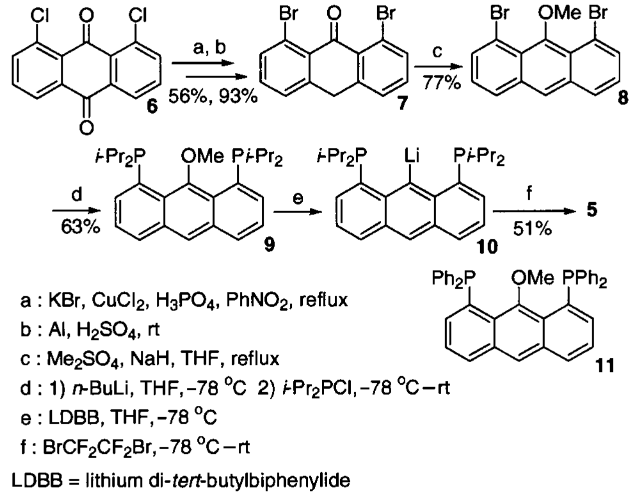
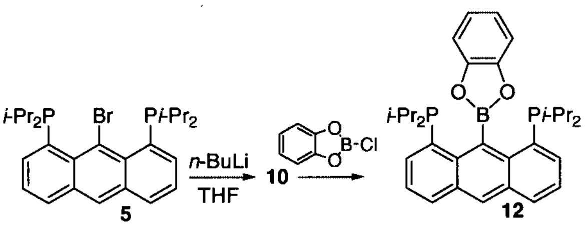
Synthesis of **5** is illustrated in Scheme 1. Bromination[3] and reduction[4] of commercially available quinone **6** afforded dibromoanthrone **7**. Deprotonation of **7** followed by methylation gave 1,8-dibromo-9-methoxyanthracene **8**.[5] After dilithiation of **8** by 2 equiv of *n*-BuLi, 2 equiv of (*i*-Pr)$_2$PCl was added to the reaction mixture to give **9**.[6] LDBB (lithium di-*tert*-butylbiphenylide) could remove the methoxy group from 9-position of **9** selectively. Trapping of the generated lithium derivative **10** with BrCF$_2$CF$_2$Br gave the novel anthracene ligand **5** bearing two (*i*-Pr)$_2$P groups in 51% yield.[7] It is interesting to note that the LDBB reduction of the OMe group is a novel procedure but the similar reduction from the corresponding Ph$_2$P derivative (**11**) by LDBB was not successful probably due to the ortho-lithiation at the Ph$_2$P group.



Scheme 1. Synthesis of **5**.

After quantitative regeneration of lithium derivative **10** by the reaction of **5** with *n*-BuLi in THF, **10** was reacted with *B*-chlorocatecholborane to give a boryl derivative **12** (Scheme 2).[8] The boryl derivative **12** was air and moisture stable, and the single crystals of **12** suitable for X-ray analysis were obtained by recrystallization from CH$_2$Cl$_2$.



Scheme 2. Introduction of a boron substituent.

ORTEP drawing of **12** is shown in Figure 1.[9] Shorter P–B bond length is 2.14(1) Å and the longer P-B length is 3.17(1) Å. Although the former is longer than the sum (1.98 Å)[10] of covalent radius of boron and phosphorus, the latter is shorter than that of the van der Waals radii (3.98 Å).[10] The structure of the boron atom should be regarded to be tetracoodinated. Thus, only one of the two (*i*-Pr)$_2$P groups is coordinating toward the boron atom in the solid state.

However, ^{1}H NMR of **12** showed a symmetrical anthracene pattern {two kinds of doublets (δ 7.72, 8.10; 4H), and a triplet (δ 7.48; 2H)} at room temperature. In addition, only one signal was

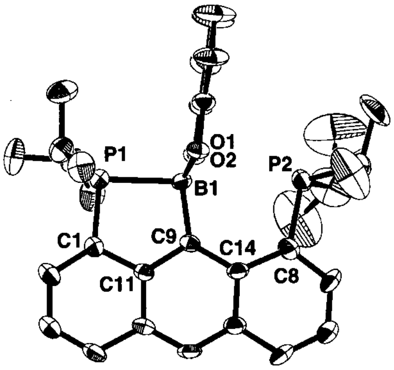
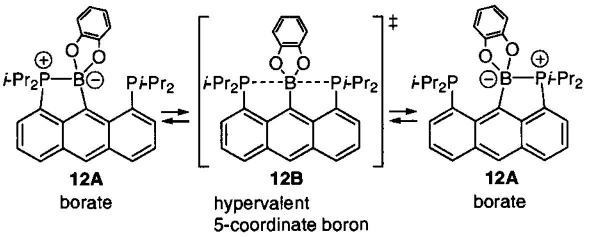


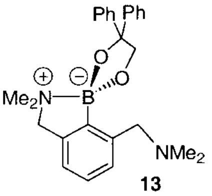
Figure 1. X-ray structure of **12** (30% thermal ellipsoid). Selected bond lengths (Å) and angles (deg): P1-B1 = 2.14(1); P2-B1 = 3.17(1); B1-O1 = 1.46(1); O2-B1 = 1.48(1); P1-C1-C11 = 113.5(6); P2-C8-C14 = 124.1(8); B1-C9-C11 = 114.1(8); B1-C9-C14 = 127.5(7). Sum of the angles around the boron atom (deg) = 345.6.

observed in the ^{31}P NMR. The peaks kept its sharpness and symmetrical pattern even at –80 °C. These NMR data indicate that the very rapid bond switching process is taking place in solution as illustrated in Scheme 3.



Scheme 3. Very rapid P–B bond switching equilibrium in **12**.

Since the energy barrier of the P–B bond switching process in **12** was too small to measure by coalescence method, the energy difference between the unsymmetrical tetracoordinate compound **12A** and the pentacoordinate boron **12B**, which should be the transition state of the bond switching process, must be very small. The small activation energy in **12** indicates that our newly prepared rigid anthracene ligand system stabilizes the 5-coordinate boron transition state. The result is in contrast to the relatively high energy barrier ($\Delta G^‡$ = 13.4 kcal/mol) of the similar S_N2 type reaction of **13** with 2,6-bis(dimethylaminomethyl)phenyl ligand.[11]



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Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

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5 THF (15 mL) was added to a mixture of 0.703 g (2.0 mmol) of **7** and 0.194 g (4.8 mmol) of NaH (60% in oil) at 0 °C under Ar. Me_2SO_4 (0.38 mL, 4 mmol) was added dropwise at 0 °C. The reaction mixture was stirred for 20 h at 80 °C and filtered through Celite pad (Celite 545, Katayama Chemical Co. ltd.). Crude **8** was purified by column chromatography (CH_2Cl_2:hexane = 1:15 – 1:7) to give 0.564 g (77%) of **8** as a yellow solid; mp 179–181 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 3.86 (s, 3H), 7.26 (dd, 2H, *J* = 8Hz, 8Hz), 7.86 (d, 2H, *J* = 8Hz), 7.93 (d, 2H, *J* = 8Hz), 8.25 (s, 1H); ^{13}C NMR (99 MHz, $CDCl_3$, 25 °C) δ 65.3, 116.3, 123.3, 124.0, 125.9, 128.4, 133.5, 133.9, 153.1; MS (FAB$^+$) M$^+$ = 364, 366, 368.

6 *n*-BuLi in *n*-hexane solution (4.0 mL, 1.50 M, 6.0 mmol) was added to the THF (30 mL) solution of 1.10 g (3.0 mmol) of **8** at –78 °C under Ar. After the reaction mixture was stirred for 2 h at –78 °C, 0.954 mL (6.0 mmol) of $(i\text{-Pr})_2$PCl was added to the solution at –78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h at room temperature. The crude product was treated with water and then purified with column chromatography (SiO_2; CH_2Cl_2:hexane = 1:15 – 1:10 – 1:7) to give yellow solid of **9** (0.873 g, 63%); mp 132–134 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 0.81 (dd, 6H, *J* = 8 Hz, 8 Hz), 1.33 (dd, 6H, *J* = 8 Hz, 8 Hz), 1.24–1.31 (m, 12H), 1.80–1.98 (m, 2H), 2.28–2.42 (m, 2H), 3.84 (s, 3H), 7.40 (dd, 2H, *J* = 8 Hz, 8Hz), 7.58 (d, 2H, *J* = 8 Hz), 7.90 (d, 2H, *J* = 8 Hz), 8.22 (s, 1H); ^{31}P NMR (99 MHz, $CDCl_3$, 25 °C) δ 17.4.

7 THF (20 mL) was added to a mixture of 39.8 mg (5.0 mmol) of Li and 0.758 g (5.0 mmol) of di-*tert*-butylbiphenyl (DTBB) at 0 °C under Ar. The mixture was stirred for 5 h at 0 °C to give lithium di-*tert*-butylbiphenylide (LDBB) solution. A cooled (–78 °C) THF solution of 0.887 g (2 mmol) of **9** was added to the LDBB solution at –78 °C within 15 min. The reaction mixture was stirred for 15 min at –78 °C and for 12 h at 0 °C. Then, 1.1 mL (5.0 mmol) of $BrCF_2CF_2Br$ was added dropwise to the solution at 0 °C. The reaction mixture was stirred for 5 h at 0 °C. The crude product was purified by column chromatography (CH_2Cl_2) to give 0.504 g (51%) of **5**; mp 198–200 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 0.92 (d, 6H, *J* = 8 Hz), 0.95 (d, 6H, *J* = 8 Hz), 1.16 (d, 6H, *J* = 8 Hz), 1.18 (d, 6H, *J* = 8 Hz), 2.20–2.32 (m, 4H), 7.36 (dd, 2H, *J* = 8 Hz, 8 Hz), 7.84 (d, 2H, *J* = 8 Hz), 7.88 (d, 2H, *J* = 8 Hz), 8.30 (s, 1H); ^{31}P NMR (99 MHz, $CDCl_3$, 25 °C) δ 4.54 ; MS (FAB$^+$) M$^+$ = 489, 491.

8 *n*-BuLi (0.40 mL, 0.59 mmol) was added dropwise to a solution of 0.247 g (0.5 mmol) of **5** in 15 mL of THF at –78 °C under Ar. The reaction mixture was stirred for 2 h at –78 °C and added to 83.1 mg (0.53 mmol) of *B*-chlorocatecholborane in 5 mL of THF at –78 °C. The reaction mixture was stirred for 3 h at –78 °C and for 1 h at room temperature. The crude product was purified by preparative TLC (CH_2Cl_2:hexane = 10:1) to give 32.2 mg (12%) of **12**; mp 218–220 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 0.85–1.56 (m, 24H), 2.08–2.12 (m, 4H), 6.85–6.89 (m, 4H), 7.48 (dd, 2H, *J* = 8 Hz, 8 Hz), 7.72 (d, 2H, *J* = 8 Hz), 8.10 (d, 2H, *J* = 8 Hz), 8.52 (s, 1H); ^{31}P NMR (99 MHz, $CDCl_3$, 25 °C) δ 0.97; ^{11}B NMR (127 MHz, $CDCl_3$, 25 °C) δ 15.0–20.5 (br).

9 Data were collected at 298 K on a Mac Science DIP2030 imaging plate equipped with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Unit cell parameters were determined by autoindexing several images in each data set separately with program DENZO. For each data set, rotation images were collected in 3° increments with a total rotation of 180° about ϕ. Data were processed by using SCALEPACK. The structure was solved using the teXsan system and refined by full-matrix least-squares. Crystal data for **12**: monoclinic system, space group $P2_1/a$ (no. 14), a = 10.440(1) Å, b = 12.4310(8) Å, c = 23.664(3) Å, β = 90.462(4)°, V = 3071.0(5) Å^3, Z = 4, ρ_{calc} = 1.143 g cm^{-3}. R = 0.0716 (R_w = 0.1202) for 4029 observed reflections (244 parameters) with $I > 3\sigma(I)$. Goodness of fit = 1.320

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