Synthesis of a Novel Potential Tridentate Anthracene Ligand, 1,8-Bis(dimethylamino)-9-bromoanthracene, and its Application as Chelete Ligand for Synthesis of the Corresponding Boron and Palladium Compounds**

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[**] This work was supported by Grant-in-Aid for Scientific Research (Nos. 09239103, 09440218, 11166248, 11304044, 12304044) provided by the Ministry of Education, Culture, Sports, Science and Technology of the Japanese Government and JSPS Research Fellowship (No. 08982) for Young Scientists.
Abstract

A novel potential tridentate ligand, 1,8-bis(dimethylamino)-9-bromoanthracene, was synthesized. Key steps are the following; (i) dimethylamination of 1,8-dibromo-9-methoxyanthracene by a modified Buchwald's method to afford 1,8-bis(dimethylamino)-9-methoxyanthracene, (ii) reduction of the methoxy group by LDBB (lithium di-tert-butylbiphenyliide) followed by treatment with BrCF2CF2Br. The corresponding 1,8-bis(dimethylamino)-9-lithioanthracene, which should be a useful versatile tridentate ligand, could be generated by treatment of the bromide with 1 equiv. of nBuLi. The lithioanthracene reacted with B-chloroborane derivatives to give three 9-boryl derivatives. Although we recently reported that the crystal structure of 1,8-dimethoxy-9-B-catecholatoborylanthracene showed the symmetrical nature of the compound with the almost identical two O--B distances (2.379(2) and 2.441(2)Å), the newly prepared 1,8-bis(dimethylamino)-9-borylanthracene derivatives clearly showed the unsymmetrical structures with coordination of only one NMe2 group toward the central boron atom. But the energy difference between the unsymmetrical structure and the symmetrical one was found to be very small based on the 1H NMR measurement, showing symmetrical anthracene patterns in the aromatic region (two kinds of doublets and a triplet) and a sharp singlet signal of the two NMe2 groups even at -80 °C. 1,8-Bis(dimethylamino)-
9-bromoanthracene itself can be a versatile ligand for transition metal compounds. In fact, direct palladation of the bromide took place by the reaction with Pd₂dba₃·CHCl₃ in THF to give the 9-palladated product. X-ray crystallographic analysis of the Pd compound showed symmetrical tetracoordinate planar palladium atom by coordination of the both NMe₂ groups {Pd-N bonds are 2.138(5) and 2.146(5)Å}.

Introduction

Recently, we reported synthesis of hypervalent pentacoordinate carbon compound bearing a rigid anthracene skeleton, which was prepared from 1,8-dimethoxy-9-trifluoromethanesulfonyloxyanthracene,[1a] and of hypervalent pentacoordinate boron compounds (2) from 1,8-dimethoxy-9-bromoanthracene (1).[1b] Although anthracene bearing only two dimethylamino groups at 1,8-positions (3) has been synthesized in trace amounts by Haenel et al,[2] 3 has not been used as a potential tridentate ligand probably because of the inefficient synthetic method and inertness toward introduction of transition metal compounds. However, such rigid potential tridentate anthracene ligand has eagerly been desired since several bi-[3] and tri-dentate ligands bearing dimethylamino groups, especially van Koten type tridentate ligand such as 2,6-bis(dimethylaminomethyl)phenyl ligand (4), have been effectively applied for stabilization of highly-coordinated main group element compounds,[4] and for transition
metal catalysts of various reactions\textsuperscript{[5]} such as organoplatinum crystals for gas-triggered switches.\textsuperscript{[6]}

**Figure 1**

Here, we report first synthesis of the potential anthracene ligand bearing two dimethylamino groups at 1,8 positions with a Br atom at 9-position (5). The bromide should be a very useful versatile potential tridentate ligand, and in fact, 5 could be easily lithiated with \textit{n}BuLi to introduce a boron atom to the 9-position and could be converted to the corresponding palladium compound.

**Results and Discussion**
In order to prepare 5, we examined the possibility for direct lithiation of 1,8-bis(dimethylamino)anthracene (3)\textsuperscript{[2]} with various base (nBuLi, sBuLi and tBuLi) in various solvents (ether, THF and hexane) with or without addition of TMEDA, but the lithiation at the 9 position did not take place at all. In addition, a strategy to use 1,8-bis(dimethylamino)anthrone as a synthetic intermediate which is based on our previous synthesis of 1,8-dimethoxy-9-bromoanthracene,\textsuperscript{[1b]} did not work because reduction of 1,8-bis(dimethylamino)anthraquinone to the corresponding anthrone was not successful.

Finally, 5 could be prepared by a completely new route as illustrated in Scheme 1. Bromine substitution\textsuperscript{[7]} and reduction\textsuperscript{[8]} of commercially available dichloroanthraquinone 6 afforded dibromoanthrone (7) in good yield. Deprotonation of 7 followed by methylation gave 1,8-dibromo-9-methoxyanthracene (8) in 77 % yield. Pd(0) mediated coupling reaction of 8 with various nucleophiles (Bu\textsubscript{3}SnNMe\textsubscript{2}, Me\textsubscript{3}SnNMe\textsubscript{2}, LiNMe\textsubscript{2} and HNMe\textsubscript{2}) did not give an expected bis-dimethylamminated compound (9), instead only mono-dimethylamminated product was obtained in most cases and reduction of the C-Br bonds took place in some cases. However, dibromoanthracene 8 could be converted to desired 1,8-bis(dimethyamino)-9-methoxyanthracene 9 in 79 % yield by heating a HNMe\textsubscript{2}-THF solution of 8 up to 150 °C in a pressure-resistant vessel with Ni(0)-catalyst, which is a modified Buchwald’s method.\textsuperscript{[9]} To our knowledge, this is the first example for direct dimethylamination of aryl bromides.

LDBB (lithium di-tert-butylbiphenylide) reduction of the
methoxy group at the 9-position\[^{1b,10}\] worked well for 9 to afford the novel anthracene ligand 5 in 51% yield after reaction with BrCF\(_2\)CF\(_2\)Br.

Scheme 1

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{O} & \quad \text{O} \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{O} \\
6 & \quad \text{a} \quad 56\%, 93\% \\
\text{Br} & \quad \text{Br} \\
\end{align*}
\]

\[
\begin{align*}
\text{Me}_2\text{N} & \quad \text{OMe} \\
\text{NMe}_2 & \quad \text{NMe}_2 \\
9 & \quad \text{b} \quad 77\% \\
\text{Li} & \quad \text{NMe}_2 \\
\text{BrCF}_2\text{CF}_2\text{Br} & \quad \text{c} \quad 79\% \\
\end{align*}
\]

\[
\begin{align*}
\text{C} \quad \text{C} \\
\text{O} \quad \text{O} \\
\text{Li} & \quad \text{NMe}_2 \\
\text{BrCF}_2\text{CF}_2\text{Br} & \quad \text{LDBB} \quad 0{\degree}\text{C} \to {\degree}\text{C} \\
10 & \quad 51\% \\
\end{align*}
\]

\text{a: 1) KBr, CuCl}_2, \text{H}_3\text{PO}_4, \text{PhNO}_2, \text{reflux, 24 h} \\
2) \text{Al, H}_2\text{SO}_4, \text{rt, 2 h} \\
\text{b: Me}_2\text{SO}_4, \text{NaH, THF, reflux, 20 h} \\
\text{c: HNMe}_2/\text{THF, Ni(COD)}_2, \text{BuONa, 1,10-phenanthroline, 150 }{\degree}\text{C, 5.5 d} \\
\text{LDBB = lithium di-tert-butylbiphenylide}

After regeneration of the lithium derivative 10 by the reaction of 5 with nBuLi in ether, 10 was reacted with various boron reagents to give 9-boryl derivatives (11a-c) (Scheme 2). These boryl derivatives (11a-c) were air and moisture stable and the single crystals of 11a-c suitable for X-ray analysis were obtained from CH\(_2\)Cl\(_2\)-hexane solution. X-ray crystallographic analysis of 11a-c (Figure 2) showed the unsymmetrical structures with coordination of only one NMe\(_2\) group toward the central boron atom. Shorter N-B bond lengths are 1.809(2) Å in 11a, 1.739(2) Å in 11b, and 1.664(3) Å in 11c, and the longer N-B bonds are 2.941(2) Å in 11a, 3.124(3) Å in
11b, and 3.129(3) Å in 11c, respectively. The results are somewhat surprising because almost symmetrical structures were observed in the corresponding boron compounds (2) bearing the OMe group at 1,8-positions,[1b] although similar unsymmetrical structure was recently observed by us in the corresponding boron compound with phosphorus donors {P(iPr)$_2$} at 1,8-position of the anthracene skeleton.[10] The reason why 11 showed unsymmetrical structures in contrast to 2 with oxygen donors is not clear yet, but the unsymmetrical structures observed in 11 may be related to the stronger N-B bonding energy in comparison with the corresponding O-B energy as was reported for F$_3$B-NMe$_3$ (26.6 kcalmol$^{-1}$) and F$_3$B-OEt$_2$ (13.9 kcalmol$^{-1}$).[11] But the energy difference between the unsymmetrical structure and the symmetrical one should be very small (vide infra).
In $^1$H NMR (CDCl$_3$ or CD$_2$Cl$_2$), 11a-c showed symmetrical anthracene patterns in the aromatic region (two kinds of doublets and a triplet) and a sharp singlet signal of the two NMe$_2$ groups at room temperature. The peaks kept its sharpness and symmetrical pattern even at -80 °C even in the most unsymmetrical dichloro compound 11c (CD$_2$Cl$_2$). Since the energy barrier of the N-B bond switching process in 11c was too small to measure by coalescence method, the energy difference between the unsymmetrical tetracoordinate dichloroboron 11c and the pentacoordinate one 11c$^+$, which should be the transition state of the bond switching process named as _bell-clapper_ mechanism$^{[12]}$, must be very small (Scheme 3). The result is in contrast to the relatively high energy barrier of the similar $S_N2$ type reaction of BCl$_2[2,6-(NEt_2CH_2)_2C_6H_3]$ (12$^{[13a]}$), which showed two kinds of NEt$_2$ groups in C$_6$D$_6$ or THF-d$_8$ solvents at 25 °C.
In order to show the versatility of the newly prepared potential ligand (5), direct palladation of 5 was examined. Although the reaction with Pd(PPh₃)₄ gave a complicated mixture, reaction of 5 with Pd₂dba₃·CHCl₃ in THF gave the expected 9-palladated product 13 in 33 % yield (Scheme 4). Although 13 was not stable under air in solution and decomposed during purification with silica gel, it could be purified by recycle HPLC (Japan Analytical Industry). The single crystals of 13 suitable for X-ray analysis were obtained from CH₂Cl₂-hexane. ORTEP drawing of 13 is illustrated in Figure 3, showing symmetrical tetracoordinate planar palladium atom by coordination of the both NMe₂ groups. The bond lengths of the two Pd-N bonds are 2.138(5) and 2.146(5) Å. These lengths are slightly longer than a sum of the covalent radii (1.98 Å),[14] and are also longer than the reported Pd-N (or Pt-N) bond lengths in NCN pincer type tridentate compounds, for
example, Pd-N(sp²) (2.06 Å),[15] Pt-N(sp³) (2.08-2.11 Å)[5a,6c,16] although we did not find examples for N(sp³)-Pd-N(sp³) type compounds. The longer Pd-N length may be due to the strain of the anthracene skeleton, and efficient reactivities of 13 as catalysts may be anticipated. The investigation toward the direction is under way.

![Diagram](image)

**Figure 3**

**Experimental Section**

**General**

Ether and tetrahydrofuran were freshly distilled from sodium-benzophenone and other solvents were distilled from calcium hydride under argon atmosphere. Merck silica gel 9385
and 7730 was used for column chromatography and preparative TLC. LC908-C60 and LC-918 (Japan Analytical Industry, JAIGEL-2H, ClCH₂CH₂Cl) and LC908 (Japan Analytical Industry, JAIGEL-ODS-AP, CH₃CN/THF = 9/1) were used for HPLC purification. Melting points were taken on a Yanagimoto micro melting point apparatus. ¹H NMR (400 MHz), ⁱ¹B NMR (127 MHz) and ¹³C NMR (99 MHz) spectra were recorded on a JEOL EX-400 and AL-400 spectrometer. Chemical shifts (δ) are reported as parts per million from internal CHCl₃ for ¹H (δ 7.26) or from external BF₃·OEt₂ for ¹¹B (δ 0.0) or from internal CDCl₃ for ¹³C (δ 77.0). Elemental analysis was performed on Perkin-Elmer 2400CHN elemental analyzer.

Synthesis of 9: A mixture of 8[¹⁰] (9.15 g, 25 mmol) and Ni(COD)₂ (687 mg, 2.5 mmol) and tBuONa (9.60 g, 100 mmol) and 1,10-phenanthroline (905 mg, 5.0 mmol) and THF solution of HNMe₂ (100 mL, 2.0 M, 200 mmol) was stirred for 5.5 d at 150 °C in a pressure-resistant vessel under Ar. The crude product was purified by column chromatography (CH₂Cl₂) to give yellow-orange powder of 9 (5.8 g, 79%); m.p. 98-100 °C (dec.); ¹H NMR (400 MHz, CDCl₃, 25 °C, CDCl₃) δ 2.94 (s, 12H; NMe₂), 3.59 (s, 3H; OMe), 6.90 (d, 3J (H, H) = 8 Hz, 2H; aromatic CH), 7.30 (t, 3J (H, H) = 8 Hz, 2H; aromatic CH), 7.49 (d, 3J (H, H) = 8 Hz, 2H; aromatic CH), 8.07 (s, 1H; aromatic CH); ¹³C NMR (99 MHz, CDCl₃, 25 °C, CDCl₃) δ 45.4, 62.8, 111.0, 120.6, 121.5, 122.5, 125.2, 134.9, 150.2, 154.3; MS (FAB⁺): m/z : 294 [M⁺]; elemental analysis calcd for C₁₉H₂₂N₂O: C 77.52, H 7.53, N 9.52; found: C 77.82, H 7.61, N 9.44.
**Synthesis of 5**: THF (100 mL) was added to a mixture of Li (278 mg, 40 mmol) and di-tert-butylbiphenyl (DTBB; 10.7 g, 40 mmol) at 0 °C under Ar. The mixture was stirred for 6 h at 0 °C to give lithium di-tert-butylbiphenyliide (LDBB) solution. The LDBB solution was added to a solution of 9 (5.49 g, 19 mmol) in THF (100 mL) at -78 °C within 5 min. The reaction mixture was quickly allowed to warm to 0 °C and was stirred for 15 min at 0 °C. Then, BrCF₂CF₂Br (3.6 mL, 30 mmol) was added dropwise to the reaction mixture at 0 (°C. The reaction mixture was allowed to warm to rt and was stirred for 5 h at rt. The product was purified by column chromatography (CH₂Cl₂ : hexane = 1 : 5) to give red-orange powder of pure 5 (3.3 g, 51%); m.p. 142-144 °C (dec.); ¹H NMR (400 MHz, CDCl₃, 25 °C, CHCl₃) δ 2.93 (s, 12H; NMe₂), 7.03 (d, 3J (H, H) = 8 Hz, 2H; aromatic CH), 7.36 (t, 3J (H, H) = 8 Hz, 2H; aromatic CH), 7.54 (d, 3J (H, H) = 8 Hz, 2H; aromatic CH), 8.26 (s, 1H; aromatic CH); ¹³C NMR (99 MHz, CDCl₃, 25 °C, CDCl₃) δ 43.8, 113.3, 115.8, 121.3, 125.3, 127.0, 127.2, 134.3, 150.3; MS (FAB⁺): m/z : 342/344 [M⁺]; elemental analysis calcd for C₁₈H₁₉BrN₂: C 62.98, H 5.58; N 8.16; found: C 62.95, H 5.31, N 8.03.

**Synthesis of 11a-c**: A solution of nBuLi in nhexane (0.35 mL, 0.55 mmol) was added dropwise to a solution of 5 (172 mg, 0.5 mmol) in THF (10 mL) at -78 °C under Ar. The reaction mixture was stirred for 1.5 h at -78 °C and 10 was generated in situ. Boron reagent [B-chlorocatecholborane (85.3 mg, 0.55 mmol) in THF (2 mL) for 11a; a solution of BCl₃ in heptane (0.5 mL, 0.5 mmol) for 11b and 11c] was added dropwise to the solution of
10. The reaction mixture was stirred for 2 h at -78 °C [followed by an addition of a solution of MeLi in ether (1.3 mL, 1.5 mmol) for 11b] and for 3 h at rt. Solvents were removed from the reaction mixture under reduced pressure. The crude products were purified [by HPLC (LC908-C60) for 11a (RT = 64 min), by preparative TLC for 11b (CH2Cl2 : hexane = 1 : 3 eluent), and by HPLC for 11c (RT = 69 min)] to give 11a (84 mg, 49%), 11b (36 mg, 17%) and 11c (28 mg, 16%). The single crystals of 11a-c suitable for X-ray analysis were obtained from their CH2Cl2/hexane solution under Ar; 11a; yellow-green solid, m.p. 194-196 °C (dec.); 1H NMR (400MHz, CDCl3, 25 °C, CHCl3) δ 2.65 (s, 12H, NMe2), 6.82 (dd, 3J (H, H) = 6 Hz, 4J (H, H) = 3 Hz, 2H; catechol CH), 6.92 (dd, 3J (H, H) = 6 Hz, 4J (H, H) = 3 Hz, 2H; catechol CH), 7.28 (d, 3J (H, H) = 8 Hz, 2H; aromatic CH), 7.45 (t, 3J (H, H) = 8 Hz, 2H; aromatic CH), 7.87 (d, 3J (H, H) = 8 Hz, 2H; aromatic CH), 8.44 (s, 1H; aromatic CH); 13C NMR (127 MHz, CDCl3, 25 °C, BF3·Et2O) δ 17-20 (br); 11b; yellow solid, m.p. 186-187 °C (dec.); 1H NMR (400MHz, CDCl3, 25 °C) δ 0.19 (s, 6H, BMe2), 2.83 (s, 12H, NMe2), 7.21 (d, 3J (H, H) = 8 Hz, 2H; aromatic CH), 7.39 (t, 3J (H, H) = 8 Hz, 2H; aromatic CH), 7.80 (d, 3J (H, H) = 8 Hz, 2H; aromatic CH), 8.17 (s, 1H); 13C NMR (127 MHz, CDCl3, 25 °C, BF3·Et2O) δ 8-14 (br); 11c; yellow solid, m.p. 132-134 °C (dec.); 1H NMR (400MHz, CDCl3, 25 °C, CHCl3) δ 3.04 (s, 12H, NMe2), 7.38 (d, 3J (H, H) = 8 Hz, 2H; aromatic CH), 7.47 (t, 3J (H, H) = 8 Hz, 2H; aromatic CH), 7.87 (d, 3J (H, H) = 8 Hz, 2H; aromatic CH), 8.38 (s, 1H; aromatic CH); 13C NMR (127 MHz, CDCl3, 25 °C, BF3·Et2O) δ 12-15 (br).
Synthesis of 13: THF (1 mL) was added to a mixture of 5 (34 mg, 0.1 mmol) and Pd\textsubscript{2}dba\textsubscript{3}·CHCl\textsubscript{3} (78 mg, 0.75 mmol) at rt under Ar. After the reaction mixture was stirred at 75 °C for 1 h, the mixture was filtered. The solid was purified by HPLC (LC908 and LC918) to afford yellow solids of 13 (14.4 mg, 33%). Single crystals suitable for X-ray analysis were obtained from CH\textsubscript{2}Cl\textsubscript{2}-hexane; m.p. 154-162 °C (dec.); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, 25 °C, CHCl\textsubscript{3}) δ 3.55 (s, 12H; NMe\textsubscript{2}), 7.26 (d, \textsuperscript{3}J (H, H) = 8 Hz, 2H; aromatic CH), 7.45 (t, \textsuperscript{3}J (H, H) = 8 Hz, 2H; aromatic CH), 7.77 (d, \textsuperscript{3}J (H, H) = 8 Hz, 2H; aromatic CH), 8.03 (s, 1H; aromatic CH); \textsuperscript{13}C NMR (99 MHz, CDCl\textsubscript{3}, 25 °C, CDCl\textsubscript{3}) δ 54.5, 114.6, 116.3, 126.7, 126.9, 132.7, 134.6, 156.8, 158.7.

X-ray structural analysis of 11a-c and 13. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-176315, 176316, 176317, and 176318. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). Data were collected at 298K on a Mac Science DIP2030 imaging plate equipped with graphite-monochromated Mo-K\textsubscript{α} radiation (\(\lambda = 0.71073\) 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 \(\phi\). Data were processed by using SCALEPACK. The structure was solved using the teXsan system and refined
by full-matrix least-squares. Crystal data for **11a**: monoclinic system, space group P2\(_1\)/n (no. 14), \(a = 16.3780(6) \text{ Å}, b = 7.4670(2) \text{ Å}, c = 16.9660(6) \text{ Å}, \beta = 105.007(2)°, V = 2004.1(1) \text{ Å}^3, Z = 4, \rho_{\text{calc}} = 1.267 \text{ g cm}^{-3}, R = 0.0661 (R_w = 0.1247)\) for 4022 observed reflections (262 parameters) with \(I>2\sigma(I)\). Goodness of fit = 1.308; Crystal data for **11b**: monoclinic system, space group P2\(_1\)/n (no. 14), \(a = 10.7260(4) \text{ Å}, b = 12.5420(4) \text{ Å}, c = 13.0800(4) \text{ Å}, \beta = 91.437(2)°, V = 1759.04(9) \text{ Å}^3, Z = 4, \rho_{\text{calc}} = 1.149 \text{ g cm}^{-3}, R = 0.0699 (R_w = 0.1271)\) for 3321 observed reflections (208 parameters) with \(I>2\sigma(I)\). Goodness of fit = 1.584; Crystal data for **11c**: monoclinic system, space group P2\(_1\)/n (no. 14), \(a = 12.7770(4) \text{ Å}, b = 12.5510(6) \text{ Å}, c = 10.7200(4) \text{ Å}, \beta = 90.546(3)°, V = 1719.0(1) \text{ Å}^3, Z = 4, \rho_{\text{calc}} = 1.333 \text{ g cm}^{-3}, R = 0.0667 (R_w = 0.1344)\) for 3323 observed reflections (208 parameters) with \(I>2\sigma(I)\). Goodness of fit = 1.516; Crystal data for **13**: tetragonal system, space group P4\(_1\) (no. 76), \(a = 10.3490(2) \text{ Å}, c = 16.1520(4) \text{ Å}, V = 1729.91(5) \text{ Å}^3, Z = 4, \rho_{\text{calc}} = 1.726 \text{ g cm}^{-3}, R = 0.0426 (R_w = 0.0668)\) for 2081 observed reflections (200 parameters) with \(I>3\sigma(I)\). Goodness of fit = 1.054. The programs (DENZO and SCALEPACK) are available from Mac Science Co. Z. Otwinowski, University of Texas, Southwestern Medical Center. The program texsan is available from Rigaku Co.

**References and Notes**

39, 4055-4058.


