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

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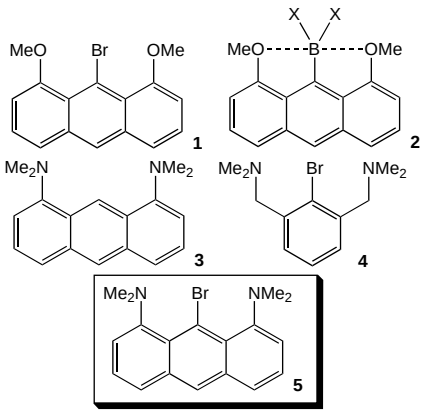
Abstract: A novel potential tridentate ligand, 1,8-bis(dimethylamino)-9-bromoanthracene, was synthesized. The key steps are as follows: 1) dimethylamination of 1,8-dibromo-9-methoxyanthracene by a modified Buchwald's method to afford 1,8-bis(dimethylamino)-9-methoxyanthracene, and 2) reduction of the methoxy group by LDBB (lithium di-*tert*-butylbiphenylide) followed by treatment with $BrCF_2CF_2Br$. 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 one equivalent of *n*BuLi. 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*-catecholateborylanthracene was a symmetrical 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 have unsymmetrical structures with coordination of only one NMe_2 group toward the central boron atom. However, the energy difference between the unsymmetrical and symmeterical structures was found to be very small based on ^1H NMR measurements, in which 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 were observed even at $-80\,^{\circ}C$. 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 $[Pd_2(dba)_3]\cdot CHCl_3$ in THF to give the 9-palladated product. X-ray crystallographic analysis of the Pd compound showed that the square planar palladium atom was coordinated in a symmetrical fashion by both NMe_2 groups (Pd–N bonds are 2.138(5) and 2.146(5) Å).

Keywords: anthracene · boron · N ligands · palladium

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] compound **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 a rigid tridentate anthracene ligand has eagerly been desired, since several bi-[3] and tridentate 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



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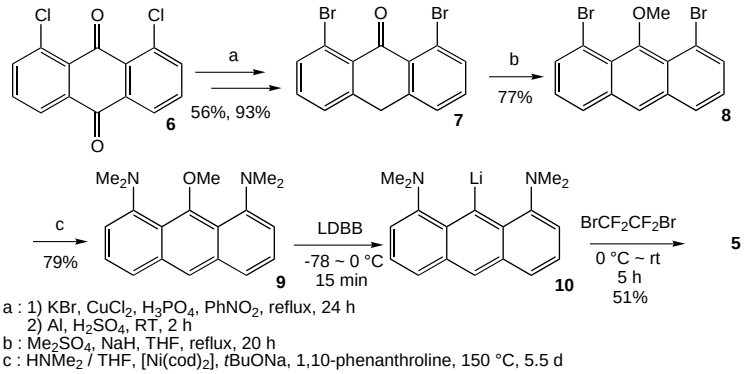
main-group-element compounds,[4] and for transition-metal catalysts of various reactions[5] such as organoplatinum crystals for gas-triggered switches.[6]

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



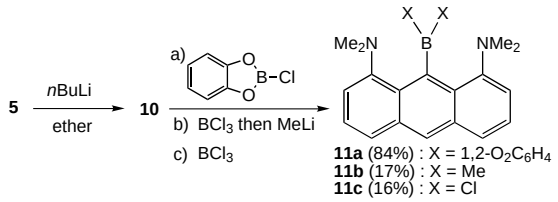
Scheme 1. Synthesis of 1,8-bis(dimethylamino)-9-bromoanthracene (**5**).

Results and Discussion

To prepare **5**, we examined the possibility for direct lithiation of 1,8-bis(dimethylamino)anthracene (**3**)[2] with various bases (*n*BuLi, *s*BuLi, and *t*BuLi) in various solvents (diethyl 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 that is based on our previous synthesis of 1,8-dimethoxy-9-bromoanthracene,[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[7] and reduction[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. The Pd^0-mediated coupling reaction of **8** with various nucleophiles (Bu_3SnNMe_2, Me_3SnNMe_2, $LiNMe_2$ and $HNMe_2$) did not give an expected bis-dimethylaminated compound **9**, instead only the monodimethylaminated 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 solution of **8** in $HNMe_2$/THF up to 150 °C in a pressure-resistant vessel with a Ni^0 catalyst; this is a modified Buchwald's method.[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 $BrCF_2CF_2Br$.

After regeneration of the lithium derivative **10** by the reaction of **5** with *n*BuLi in diethyl ether, compound **10** was treated with various boron reagents to give 9-boryl derivatives (**11a–c**) (Scheme 2). Compounds **11a–c** were air and moisture stable and the single crystals suitable for X-ray analysis were obtained from



Scheme 2. Synthesis of 1,8-bis(dimethylamino)-9-borylanthracene (**11**).

a solution of the compounds in CH_2Cl_2/hexane. X-ray crystallographic analysis of **11a–c** (Figure 1) showed the unsymmetrical structures with coordination of only one NMe_2 group toward the central boron atom. The shorter N–B bond lengths are 1.809(2), 1.739(2), and 1.664(3) Å and the longer N–B bond lengths are 2.941(2), 3.124(3), and 3.129(3) Å in **11a**, **11b**, and **11c**, respectively. The results are somewhat surprising because almost symmetrical structures were observed in the corresponding boron compounds **2**, which bear an OMe group at the 1,8-positions,[1b] although similar unsymmetrical structure was recently observed by us in the corresponding boron compound with phosphorus donors (i.e., $P(iPr)_2$) at 1,8-position of the anthracene skeleton.[10] The reason why compounds **11** have unsymmetrical structures in contrast to **2** with oxygen donors is not clear yet, but these unsymmetrical structures observed in **11** may be related to the stronger N–B bonding energy in comparison with the

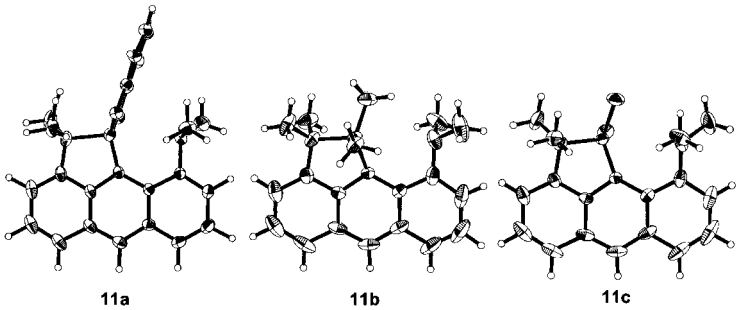


Figure 1. Crystal structures (30% thermal ellipsoids) of **11a–c**.

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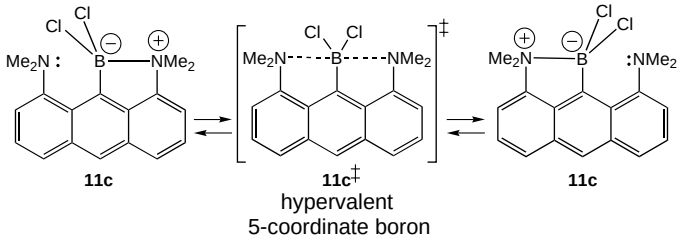
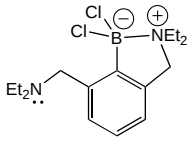
corresponding O–B energy as was reported for F_3B–NMe_3 (26.6 kcal mol^{-1}) and F_3B–OEt_2 (13.9 kcal mol^{-1}).[11] However the energy difference between the unsymmetrical and symmetrical structures should be very small (vide infra).

In the ^{1}H NMR spectra ($CDCl_3$ or CD_2Cl_2) of **11a–c**, 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 were observed at room temperature. The peaks kept their sharpness and symmetrical pattern at $-80\,^\circ$C even for the most unsymmetrical dichloro compound **11c** (CD_2Cl_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 the "bell-clapper" mechanism,[12] must be very small (Scheme 3). The result is in

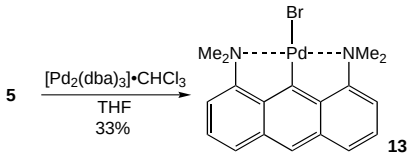


Scheme 3. Very rapid N–B bond-switching equilibrium in **11c**.

contrast to the relatively high energy barrier of the similar S_N2 type reaction of $BCl_2[2,6\text{-}(NEt_2CH_2)_2C_6H_3]$ (**12**),[13a] which showed two kinds of NEt_2 groups in C_6D_6 or [D_8]THF at 25 °C.



To show the versatility of the newly prepared potential ligand, direct palladation of **5** was examined. Although the reaction with $[Pd(PPh_3)_4]$ gave a complicated mixture, reaction of **5** with $[Pd_2(dba)_3]\cdot CHCl_3$ in THF gave the expected 9-palladated product **13** in 33% yield (Scheme 4). Although **13** was not stable under air in



Scheme 4. Synthesis of palladium derivative **13**.

solution and decomposed during purification with silica gel, it could be purified by recycling HPLC (Japan Analytical Industry). Single crystals of **13** suitable for X-ray analysis were obtained from CH_2Cl_2/hexane. An ORTEP drawing of **13** is illustrated in Figure 2, showing symmetrical square planar palladium atom coordinated by both NMe_2 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

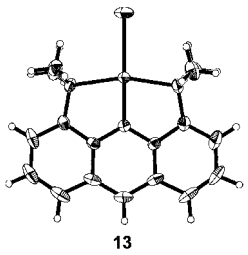


Figure 2. Crystal structure (30% thermal ellipsoids) of **13**.

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(sp^2) (2.06 Å),[15] Pt–N(sp^3) (2.08–2.11 Å),[5a, 6c, 16] although we did not find examples for N(sp^3)-Pd-N(sp^3) 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. Investigations of possible catalytic activity are under way.

Experimental Section

General: Diethyl 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 were used for column chromatography and preparative TLC. LC908-C60 and LC-918 (Japan Analytical Industry, JAIGEL-2H, $ClCH_2CH_2Cl$) and LC908 (Japan Analytical Industry, JAIGEL-ODS-AP, CH_3CN/THF = 9:1) were used for HPLC purification. Melting points were taken on a Yanagimoto micro melting point apparatus. ^{1}H NMR (400 MHz), ^{11}B NMR (127 MHz), and ^{13}C 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 $CHCl_3$ for ^{1}H ($\delta = 7.26$) or from external $BF_3\cdot OEt_2$ for ^{11}B ($\delta = 0.0$) or from internal $CDCl_3$ for ^{13}C ($\delta = 77.0$). Elemental analysis was performed on Perkin–Elmer 2400CHN elemental analyzer.

Synthesis of 9: A mixture of **8**[10] (9.15 g, 25 mmol), $[Ni(cod)_2]$ (687 mg, 2.5 mmol), *t*BuONa (9.60 g, 100 mmol), 1,10-phenanthroline (905 mg, 5.0 mmol) and $HNMe_2$ (in THF: 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 (CH_2Cl_2) to give yellow-orange powder of **9** (5.8 g, 79%). M.p. 98–100 °C (decomp); ^{1}H NMR (400MHz, $CDCl_3$, 25 °C, $CHCl_3$): $\delta = 2.94$ (s, 12H; NMe_2), 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); ^{13}C NMR (99 MHz, $CDCl_3$, 25 °C, $CDCl_3$): $\delta = 45.4$, 62.8, 111.0, 120.6, 121.5, 122.5, 125.2, 134.9, 150.2, 154.3; MS (FAB$^+$): *m*/*z*: 294 [M^++1]; elemental analysis calcd (%) for $C_{19}H_{22}N_2O$: 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 a lithium di-*tert*-butylbiphenylide (LDBB) solution. The LDBB solution was added to a solution of **9** (5.49 g, 19 mmol) in THF (100 mL) at $-78\,^\circ$C over a period of 5 min. The reaction mixture was quickly allowed to warm to 0 °C and was stirred for 15 min at 0 °C. Then, $BrCF_2CF_2Br$ (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 a further 5 h at RT. The product was purified by column chromatography (CH_2Cl_2/hexane = 1:5) to give red-orange powder of pure **5** (3.3 g, 51%). M.p. 142–144 °C (decomp); ^{1}H NMR (400MHz, $CDCl_3$, 25 °C, $CHCl_3$): $\delta = 2.93$ (s, 12H; NMe_2), 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); ^{13}C NMR (99 MHz, $CDCl_3$, 25 °C, $CDCl_3$): $\delta = 43.8$, 113.3, 115.8, 121.3, 125.3, 127.0, 127.2, 134.3, 150.3; MS (FAB$^+$): *m*/*z*: 342/344 [M^+];

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elemental analysis calcd (%) for $C_{18}H_{19}BrN_2$: 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 *n*BuLi in *n*hexane (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. A boron reagent [*B*-chlorocatecholborane (85.3 mg, 0.55 mmol) in THF (2 mL) for **11a**; a solution of BCl_3 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 diethyl 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** (CH_2Cl_2/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 %). Single crystals of **11a–c** suitable for X-ray analysis were obtained from CH_2Cl_2/hexane under Ar.

*Compound **11a***: Yellow-green solid; m.p. 194–196 °C (decomp); ^{1}H NMR (400MHz, $CDCl_3$, 25 °C, $CHCl_3$): $\delta = 2.65$ (s, 12H, NMe_2), 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); ^{11}B NMR (127 MHz, $CDCl_3$, 25 °C, $BF_3 \cdot Et_2O$): $\delta = 17–20$ (br).

*Compound **11b***: Yellow solid; m.p. 186–187 °C (decomp); ^{1}H NMR (400MHz, $CDCl_3$, 25 °C): $\delta = 0.19$ (s, 6H, BMe_2), 2.83 (s, 12H, NMe_2), 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); ^{11}B NMR (127 MHz, $CDCl_3$, 25 °C, $BF_3 \cdot Et_2O$): $\delta = 8–14$ (br).

*Compound **11c***: Yellow solid, m.p. 132–134 °C (decomp); ^{1}H NMR (400MHz, $CDCl_3$, 25 °C, $CHCl_3$): $\delta = 3.04$ (s, 12H, NMe_2), 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); ^{11}B NMR (127 MHz, $CDCl_3$, 25 °C, $BF_3 \cdot Et_2O$): $\delta = 12–15$ (br).

Synthesis of 13: THF (1 mL) was added to a mixture of **5** (34 mg, 0.1 mmol) and $[Pd_2(dba)_3] \cdot CHCl_3$ (78 mg, 0.75 mmol) at RT under Ar. After the reaction mixture was stirred at 75 °C for 1 h, it was filtered. The solid was purified by HPLC (LC908 and LC918) to afford **13** (14.4 mg, 33 %) as a yellow solid. Single crystals suitable for X-ray analysis were obtained from CH_2Cl_2/hexane. M.p. 154–162 °C (decomp); ^{1}H NMR (400MHz, $CDCl_3$, 25 °C, $CHCl_3$): $\delta = 3.55$ (s, 12H; NMe_2), 7.26 (d, $^3J(H,H) = 8$ Hz, 2H; aromatic CH), 7.45 (t, $^3J(H,H) = 8$ Hz, 2H; aromatic CH), 7.77 (d, $^3J(H,H) = 8$ Hz, 2H; aromatic CH), 8.03 (s, 1H; aromatic CH); ^{13}C NMR (99 MHz, $CDCl_3$, 25 °C, $CDCl_3$): $\delta = 54.5$, 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: CCDC-176315, CCDC-176316, CCDC-176317, and CCDC-176318 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

Data were collected at 298 K on a Mac Science DIP2030 imaging plate equipped with graphite-monochromated $Mo_{K\alpha}$ 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 ϕ. Data were processed by using SCALEPACK. The structures were solved by using the teXsan system and refined by full-matrix least-squares.

*Crystal data for **11a***: monoclinic, space group $P2_1/n$ (no. 14), $a = 16.3780(6)$, $b = 7.4670(2)$, $c = 16.9660(6)$ Å, $\beta = 105.007(2)°$, $V = 2004.1(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.267$ g cm^{-3}. $R = 0.0661$ ($Rw = 0.1247$) for 4022 observed reflections (262 parameters) with $I > 2\sigma(I)$. Goodness of fit = 1.308.

*Crystal data for **11b***: monoclinic, space group $P2_1/n$ (no. 14), $a = 10.7260(4)$, $b = 12.5420(4)$, $c = 13.0800(4)$ Å, $\beta = 91.437(2)°$, $V = 1759.04(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.149$ g cm^{-3}. $R = 0.0699$ ($Rw = 0.1271$) for 3321 observed reflections (208 parameters) with $I > 2\sigma(I)$. Goodness of fit = 1.584.

*Crystal data for **11c***: monoclinic, space group $P2_1/n$ (no. 14), $a = 12.7770(4)$, $b = 12.5510(6)$, $c = 10.7200(4)$ Å, $\beta = 90.546(3)°$, $V = 1719.0(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.333$ g cm^{-3}. $R = 0.0667$ ($Rw = 0.1344$) for 3323 observed reflections (208 parameters) with $I > 2\sigma(I)$. Goodness of fit = 1.516.

*Crystal data for **13***: tetragonal, space group $P4_1$ (no. 76), $a = b = 10.3490(2)$, $c = 16.1520(4)$ Å, $V = 1729.91(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.726$ g cm^{-3}. $R = 0.0426$ ($Rw = 0.0668$) 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.

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