Organometallics **2002,** *21,* 2555−2558

Synthesis, Structures, and UV−Visible Absorption Spectra of Tri(9-anthryl)bismuthine Derivatives

Shigehiro Yamaguchi,*,[†,‡] Toshiaki Shirasaka,[†] and Kohei Tamao*,[†]

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan, and PRESTO, Japan Science and Technology Corporation (JST), Uji, Kyoto 611-0011, Japan

Received February 14, 2002

Summary: Tri(9-anthryl)bismuthines **3** *and their difluorobismuth derivatives* **4** *have been synthesized and their UV−visible absorption spectra have been determined. The change from the tricoordinate* **3** *to the pentacoordinate* **4** *causes a subtle blue-shift in the* λ_{0-0} *of the anthryl moieties due to the decreased intramolecular through-space interaction between the anthryl moieties. Among the compounds, tri(9-anthryl)difluorobismuth,* ***4a****, forms unique cocrystals with chloroform that have a porous honeycomb packing structure due to the* π*-stacking of the anthryl moieties.*

In the chemistry of the main group element-containing π-electron systems, the coordination number change of the element represents a new strategy for the control of their photophysical properties, giving rise to new functions such as sensing.[1−5] From this viewpoint, we have so far investigated the coordination number−photophysical property relationships for the tri(9-anthryl) derivatives of boron,[2] silicon,[3] and phosphorus,[4] wherein the structural changes associated with the changes in the coordination number perturb the through-space interaction among the three anthryl groups (Figure 1), leading to significant changes in their photophysical properties. For example, the change from trianthrylfluorosilane **1** to the corresponding difluorosilicate **2** results in about a 10 nm blue-shift of the absorption maxima together with a remarkable enhancement of the fluorescence.[3] In our continuing studies, we have become interested in their bismuth analogues, the trianthrylbismuthines **3** and their difluorobismuth derivatives **4**. We envisioned that the studies of these ultimate trianthryl derivatives of the heaviest main group element with the largest atomic radii would provide decisive information about the through-space interaction among the three anthryl groups (Figure 1). In this contribution, we present the synthesis, structures, and coordination number−photophysical property relationships of the trianthrylbismuth derivatives.[6] The unique packing structure of a cocrystal of tri(9-anthryl)difluorobismuth, **4a**, with chloroform will also be described.

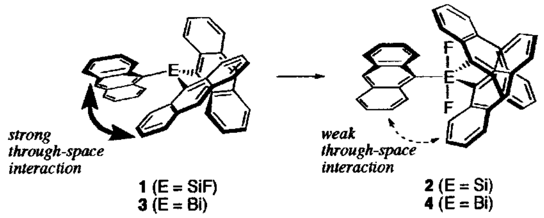
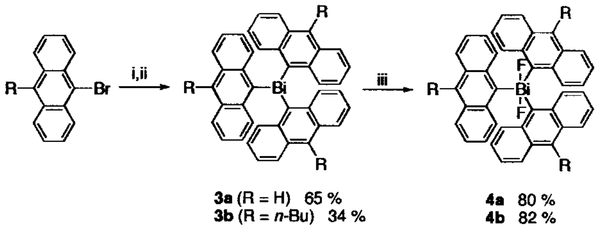


Figure 1. The change in the through-space interaction of anthryl groups in the trianthrylsilicon and -bismuth compounds.

Scheme 1[a]



[a] Reagents and Conditions: (i) *n*-BuLi (1 mol amount), Et_2O, −78 ~0 °C; (ii) $BiCl_3$ (0.33 mol amount), rt; (iii) XeF_2 (1 mol amount), CH_2Cl_2, rt.

Two series of the bismuth compounds, i.e., the tri(9-anthryl)bismuth derivatives and tris(10-*n*-butyl-9-anthryl)bismuth derivatives, have been prepared, as shown in Scheme 1. Thus, the reactions of the anthryllithiums with $BiCl_3$ in ether gave the trianthrylbismuthines **3a** and **3b**, which were further transformed into the corresponding difluorobismuth derivatives **4a** and **4b**, respectively, by treatment with XeF_2. All these compounds are air- and moisture-stable but gradually decompose under ambient light in air.[7] In an inert atmosphere, however, these compounds are stable enough to be handled. Although the unsubstituted derivatives **3a** and **4a** were hard to purify to the analytically pure

---

[†] Institute for Chemical Research, Kyoto University.

[‡] PRESTO, Japan Science and Technology Corporation (JST).

(1) A mini-review: Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Organomet. Chem.*, in press.

(2) (a) Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2000**, *122*, 6335. (b) Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2001**, *123*, 11372.

(3) Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2000**, *122*, 6793.

(4) Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Organomet. Chem.* **2002**, *646*, 277.

(5) Properties control based on the changes in the valence states of the main group elements: (a) Barbarella, G.; Favaretto, L.; Zambianchi, M.; Pudova, O.; Arbizzani, C.; Bongini, A.; Mastragostino, M. *Adv. Mater.* **1998**, *10*, 551. (b) Barbarella, G.; Favaretto, L.; Sotgiu, G.; Zambianchi, M.; Bongini, A.; Arbizzani, C.; Mastragostino, M.; Anni, M.; Gigli, G.; Cingolani, R. *J. Am. Chem. Soc.* **2000**, *122*, 11971. (c) Barbarella, G.; Favaretto, L.; Sotgiu, G.; Zambianchi, M.; Antolini, L.; Marseglia, E. A.; Tedesco, E.; Gigli, G.; Cingolani, R. *Synth. Met.* **2000**, *115*, 47. (d) Jiang B.; Tilley, T. D. *J. Am. Chem. Soc.* **1999**, *121*, 9744. (e) Suh, M. C.; Jiang, B.; Tilley, T. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 2870. (f) Hay, C.; Vilain, D. L.; Deborde, V.; Toupet, L.; Réau, R. *Chem. Commun.* **1999**, 345. (g) Hay, C.; Fischmeister, C.; Hissler, M.; Toupet, L.; Réau, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 2870. (h) Hay, C.: Hissler, M.; Fischmeister, C.; Rault-Berthelot, J.; Toupet, L.; Nyulaszi, L.; Reau, R. *Chem. Eur. J.* **2001**, *7*, 4222.

(6) Through this paper, the discussion is made from a viewpoint of the changes in the coordination number rather than the changes in the valence state in order to compare the present results to the previous silicon case.

10.1021/om020124f CCC: $22.00
Publication on Web 05/14/2002

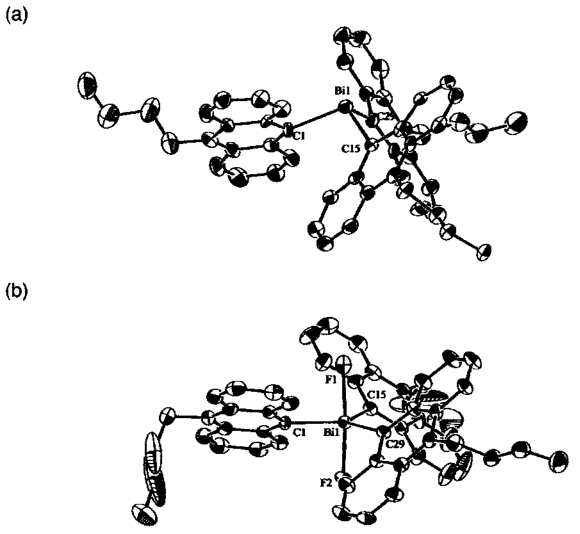


Figure 2. ORTEP drawings of (a) **3b** and (b) **4b** (50% probability for thermal ellipsoids). Selected bond lengths (Å) and bond angles (deg): **3b**: Bi1−C1 2.296(6), Bi1−C15 2.282(6), Bi1−C29 2.293(6), C1−Bi1−C15 101.1(2), C1−Bi1−C29 105.3(2), C15−Bi1−C29 105.8(2); **4b**: Bi1−C1 2.214(4), Bi1−C15 2.214(4), Bi1−C29 2.207(5), Bi1−F1 2.202(4), Bi1−F2 2.144(3), C1−Bi1−C15 120.2(2), C1−Bi1−C29 124.5(2), C15−Bi1−C29 115.3(2), F1−Bi1−F2 176.5(1).

form due to their limited solubility and high photoreactivity, the butyl derivatives **3b** and **4b** have good solubilities to the common solvents such as THF and benzene and the purification by recrystallization readily afforded the analytically pure products.

The structures of the butyl derivatives **3b** and **4b** have been determined by X-ray crystallography, as shown in Figure 2. The tricoordinate **3b** has a trigonal pyramidal structure with the sum of the C_{ipso}−Bi−C_{ipso} angles being 312.2°. This is a rather large value relative to those of the other triarylbismuthanes,[8] probably due to the steric repulsion among the anthryl groups. The pentacoordinate **4b** has a nearly ideal trigonal bipyramidal structure; the sum of the C_{ipso}−Bi−C_{ipso} angle is 360° and the F−Bi−F angle is 176.5(1)°. As an index to estimate the distance between the anthryl groups in **3b** and **4b**,[3] their nonbonded C_{ipso}- - -C_{ipso} distances are compared to each other, revealing that the change from the tricoordinate **3b** (av 3.61 Å) to the pentacoordinate **4b** (av 3.83 Å) elongates the distance by about 0.2 Å.[6] In addition, the arrangement of the three anthracene rings around the central Bi atom is changed from trigonal pyramidal in **3b** to trigonal planar in **4b**.

The UV−visible absorption spectra of the butyl derivatives **3b** and **4b** have been determined to elucidate the effect of the coordination number on their absorption properties.[9,10] The measurements were carried out using the THF solutions of their analytically pure samples under an argon atmosphere. Their spectra are shown in Figure 3, and the data are summarized in Table 1 together with those for anthrylditolylbismuthine, **3c**,[11] and anthrylditolyldifluorobismuth, **4c**, for comparison. While **3b** has the λ_{0-0} band of the anthryl moieties at 412 nm, the λ_{0-0} of **4b** appeared at 407 nm with an extinction coefficient comparable with that of **3b**. Thus, the change from tricoordinate to pentacoordinate causes a blue-shift of the λ_{0-0} by 5 nm.[6] A similar solvent effect on the λ_{0-0} was also observed in benzene: **3b**, 414 nm; **4b**, 409 nm. Considering the identical λ_{0-0} values between the monoanthryl derivatives **3c** and **4c**, the blue-shift observed for the trianthryl series is attributed not to the change in the electronic effect of the bismuth moiety,[9] but to the decreased through-space interaction among the three anthryl groups.[12]

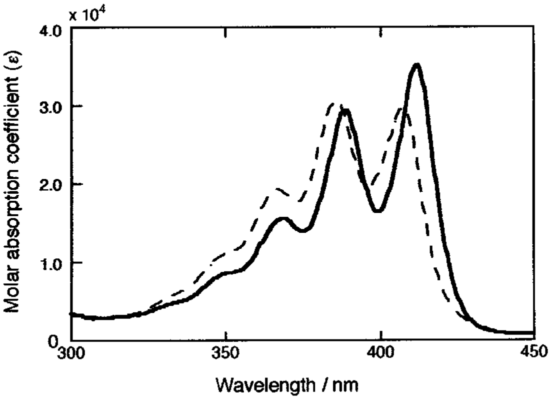
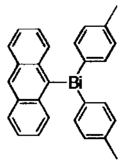


Figure 3. UV−visible absorption spectra of tris(9-butylanthryl)bismuthine, **3b** (solid line), and tris(9-butylanthryl)difluorobismuth, **4b** (broken line), in THF.

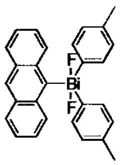
Table 1. UV−Visible Absorption Spectral Data for Anthrylbismuth Derivatives[a]

compound	λ_{0-0} (nm)	log ϵ
3b	412	4.55
4b	407	4.47
3c	392	3.98
4c	392	3.71

[a] In THF.



3c



4c

The comparison of the present results with the previously reported observations for the trianthrylsilane series **1** and **2**[3] provides notable insights into the through-space interaction. Thus, the *tricoordinate* **3b**

---

(7) For example, **3b** completely decomposed into 9-butylanthracene, 10,10′-dibutyl-9,9′-bianthryl, and other unidentified compounds upon standing in a benzene solution under an oxygen atmosphere for 6 h under ambient light. The photoreactivity of triarylbismuthines, see: (a) Matano, Y.; Ikegami, T. *Organobismuth Chemistry*; Matano, Y., Suzuki, H., Eds.; Elsevier Science: Amsterdam, 2001; pp 21−246. (b) Alberti, A.; Hudson, A. *J. Organomet. Chem.* **1979**, *182*, C49.

(8) Ogawa, T. *Organobismuth Chemistry*; Matano, Y., Suzuki, H. Eds.; Elsevier Science: Amsterdam, 2001; pp 441−546.

(9) UV−visible absorption spectra of triarylbismuthines: (a) Rao, C. N. R.; Ramachandran, J.; Balasubramanian, A. *Can. J. Chem.* **1961**, *39*, 171. (b) Zohn, H.; Schindlbauer, H.; Hammer, D. *Monatsh. Chem.* **1967**, *98*, 731. (c) Matano, Y.; Kurata, H.; Murafuji, T.; Azuma, N.; Suzuki, H. *Organometallics* **1998**, *17*, 4049.

(10) Although we have attempted to evaluate the fluorescence properties, the present trianthrylbismuth compounds gradually decomposed under the fluorescence measurement condition.

(11) Rahman, M. M.; Matano, Y.; Suzuki, H. *Organometallics* **1997**, *16*, 3565.

(12) The difference between **4b** and **4c** ($\Delta\lambda_{0-0}$, 15 nm) is comparable to that between 9-butylanthracene (λ_{0-0}, 389 nm) and anthracene (λ_{0-0}, 376 nm), suggesting that the longer λ_{0-0} of **4b** relative to that of **4c** is attributed to the electronic effect of the butyl groups.

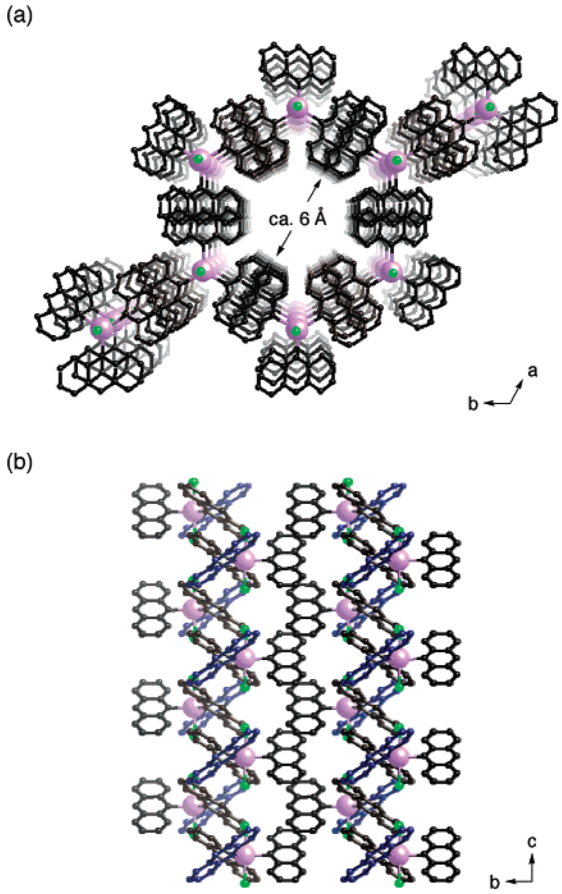


Figure 4. Crystal packing structure of **4a**: (a) a view down the *c*-axis and (b) a view of the *bc*-plane. Chloroform molecules inside of the channels are omitted for clarity. The Bi atoms are purple and the F atoms are green.

has longer nonbonded C_{ipso}- - -C_{ipso} distances (av 3.61 Å) than those in the *pentacoordinate* **2** (3.28−3.45 Å), which has no significant through-space interaction. Nevertheless, in compound **3b** the through-space interaction among the anthryl groups indeed occurs, suggesting that not the distance but the arrangement of the three anthryl groups is crucial to producing the through-space interaction. However, it is also true that the distance between the anthryl groups affects the degree of the through-space interaction, in light of the fact that the blue-shift observed for the present bismuth series is smaller than that for the silicon series.

During the course of the study on the crystal structures, we also found that the unsubstituted trianthryldifluorobismuth, **4a**, forms unique cocrystals with chloroform in a 1:1 ratio, which crystallizes in trigonal space group $P\bar{3}1c$ with a porous honeycomb packing structure, as shown in Figure 4. The intermolecular offset face-to-face π-stacking of the anthryl moieties of the present C_{3v} symmetry molecule (intermolecular anthracene−anthracene distance, ∼3.4 Å) results in the formation of large hexagonal linear channels extending along the *c*-axis with the mean diameter of about 6 Å, which are filled with disordered chloroforms. Notably, this honeycomb motif is unique for the present bismuth case. Other C_{3v} symmetry trianthryl analogues, trianthrylborane,[2] trianthryldifluorosilicate,[3] and trianthryldifluorophosphorane,[4] which we have already prepared, never form this type of packing structure. The longer Bi−C bond distance may allow the hexagonal channels to form, which can accommodate chloroform as the guest molecules.

Experimental Section

General Procedures. ^{1}H, ^{13}C, and ^{19}F NMR spectra were measured with a Varian Mercury 300 spectrometer for ^{1}H (300 MHz) and with a JEOL EX-270 spectrometer for ^{13}C (67.8 MHz) and ^{19}F (254 MHz), respectively. UV−visible absorption spectra were measured with a Shimadzu UV-3100PC spectrometer using a degassed spectral grade THF. Compound **3c** was prepared according to the method reported by Suzuki and co-workers.[11]

Tris(10-butyl-9-anthryl)bismuthine (3b). To a Et_2O (50 mL) solution of 9-bromo-10-butylanthracene (1.45 g, 4.21 mmol) was added a hexane solution of *n*-BuLi (1.6 M, 2.6 mL, 4.21 mmol) at −78 °C. The reaction mixture was warmed to 0 °C and stirred for 1 h. The resulting solution was added to a Et_2O (20 mL) solution of $BiCl_3$ (441 mg, 1.40 mmol) at −78 °C. The mixture was allowed to warm to room temperature and stirred for 14 h. After usual aqueous workup, recrystallization from a benzene−MeOH mixed solvent afforded analytically pure **3b** (440 mg, 0.484 mmol) in 34% yield as yellow crystals: mp 208 °C (dec). ^{1}H NMR (C_6D_6): δ 0.87 (t, $J = 7.5$ Hz, 9H), 1.38 (sex, $J = 7.5$ Hz, 6H), 1.65 (m, 6H), 3.40 (m, 6H), 6.87 (m, 6H), 7.12 (m, 6H), 8.22 (d, $J = 8.4$ Hz, 6H), 9.04 (d, $J = 8.1$ Hz, 6H). ^{13}C NMR (C_6D_6): δ 14.15, 23.58, 28.41, 33.59, 125.31, 125.54, 125.86, 131.58, 135.42, 137.29, 139.07, 163.11. Anal. Calcd for $C_{54}H_{51}Bi$: C, 71.35; H, 5.66. Found: C, 70.96; H, 5.58.

Tris(10-butyl-9-anthryl)difluorobismuth (4b). To a CH_2Cl_2 (20 mL) solution of **3b** (430 mg, 0.47 mmol) was added a CH_2Cl_2 (4 mL) solution of XeF_2 (82 mg, 0.47 mmol) at room temperature. After stirring for 10 min, the reaction mixture was concentrated under reduced pressure. The resulting mixture was recrystallized from a benzene−MeOH mixed solvent to afford **4b** (469 mg, 0.495 mmol) in 82% yield as red crystals: mp 198 °C (dec). ^{1}H NMR ($CDCl_3$): δ 0.99 (t, $J = 7.5$ Hz, 9H), 1.49 (sex, $J = 7.5$ Hz, 6H), 1.78 (m, 6H), 3.54 (t, $J = 8.1$ Hz, 6H), 6.81 (m, 6H), 7.10 (m, 6H), 8.29 (d, $J = 8.7$ Hz, 6H), 9.59 (d, $J = 8.7$ Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 14.17, 23.64, 28.95, 33.66, 125.00, 125.46, 127.12, 128.67, 131.19, 134.40, 141.85, 142.38. ^{19}F NMR ($CDCl_3$): δ −84.2. Anal. Calcd for $C_{54}H_{51}BiF_2$: C, 68.49; H, 5.43. Found: C, 68.41; H, 5.50.

Tri(9-anthryl)bismuthine (3a). This compound was prepared essentially in the same manner described for **3b** and was characterized by means of ^{1}H NMR spectroscopy and mass spectrometry: mp >300 °C. ^{1}H NMR ($CDCl_3$): δ 6.94 (m, 6H), 7.26 (m, 6H), 7.98 (d, $J = 8.1$ Hz, 6H), 8.42 (s, 3H), 8.49 (d, $J = 8.7$ Hz, 6H). MS (FAB) *m/e* (relative intensity): 740 (M^+, 10), 562 (100).

Tri(9-anthryl)difluorobismuth (4a). This compound was prepared essentially in the same manner described for **4b** and was characterized by means of ^{1}H and ^{19}F NMR spectroscopy and X-ray crystallography: mp 165 °C (dec). ^{1}H NMR ($CDCl_3$): δ 7.01−7.12 (m, 6H), 7.37−7.44 (m, 6H), 8.16 (d, $J = 8.4$ Hz, 6H), 8.53−8.84 (m, 9H). ^{19}F NMR ($CDCl_3$): δ −60.0 (br). For compounds **3a** and **4a**, the ^{13}C NMR spectra could not be measured due to their low solubility to organic solvents, and the elemental analyses failed even using their crystals obtained by the recrystallization.

(9-Anthryl)di(*p*-tolyl)difluorobismuth (4c). This compound was prepared essentially in the same manner desribed for **4b**: mp 225 °C (dec). ^{1}H NMR ($CDCl_3$): δ 2.45 (s, 6H), 7.42−7.49 (m, 4H), 7.53 (d, $J = 8.4$ Hz, 4H), 8.04−8.10 (m, 2H), 8.31 (d, $J = 8.4$ Hz, 4H), 8.46−8.52 (m, 2H), 8.62 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 21.48, 125.43, 126.88, 128.03, 129.15, 131.91, 132.14, 132.88, 133.47, 133.54, 135.05, 142.10, 153.85. ^{19}F NMR ($CDCl_3$): δ −141.0. Anal. Calcd for $C_{28}H_{23}BiF_2$: C, 55.45; H, 3.82. Found: C, 55.47; H, 3.83.

Table 2. Crystallographic Data for Compounds 3b, 4a, and 4b

	3b	**4a**·$CHCl_3$	**4b**·$0.5C_6H_6$
formula	$C_{54}H_{51}Bi$	$C_{43}H_{28}BiF_2Cl_3$	$C_{57}H_{54}BiF_2$
mol wt	908.98	898.03	986.03
cryst color, habit	colorless, prismatic	red, prismatic	orange, prismatic
cryst dimens, mm	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.20	0.20 × 0.20 × 0.10
cryst syst	triclinic	trigonal	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{3}1c$ (No. 163)	$P\bar{1}$ (No. 2)
cell const			
a, Å	9.8404(5)	15.5590(4)	13.7108(4)
b, Å	22.298(2)		17.1509(6)
c, Å	9.7168(7)	8.5586(3)	9.5357(3)
α, deg	95.712(2)		94.909(2)
β, deg	104.838(5)		90.606(2)
γ, deg	93.981(4)		103.523(2)
V, Å^3	2040.7(2)	1794.31(8)	2171.1(1)
Z	2	2	2
D_{calcd}, g cm^{-3}	1.479	1.662	1.508
temp, °C	−100	−120	−100
μ(Mo Kα), cm^{-1}	43.49	51.68	41.01
$2\theta_{max}$, deg	55.2	55.0	55.1
no. of unique reflns	7289 ($I > 3\sigma(I)$)	1176 ($I > 3\sigma(I)$)	8035 ($I > 3\sigma(I)$)
reflns/param ratio	14.67	15.47	14.82
R^a	0.057	0.048	0.037
$R_w{}^b$	0.080	0.062	0.056
GOF	1.25	1.18	1.02

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$.

X-ray Crystal Structure Analysis. Single crystals of **3b**, **4a**, and **4b** suitable for the X-ray crystallography were obtained by recrystallization from a $CHCl_3$−hexane mixed solvent for **4a** and a benzene−MeOH mixed solvent for **3b** and **4b**, respectively. Intensity data were collected on a Rigaku RAXIS-IV imaging plate area detector with graphite-monochromated Mo Kα radiation to a maximum 2θ value of 55°. The data were corrected for Lorentz and polarization effects and secondary extinction. The crystal structures were solved by direct methods in SIR92[13] for **3b** and **4a** and by the heavy-atom Patterson methods[14] for **4b**, and full-matrix least squares refinements were carried out for all non-hydrogen atoms. Hydrogen atoms were included except for those of solvent molecules in the crystals of **4a** and **4b**, but not refined. All the calculations were performed using the teXsan crystallographic package from Molecular Structure Corp. The crystallographic data for these compounds are summarized in Table 2.

Acknowledgment. We acknowledge the financial support from the Ministry of Education, Culture, Sports, Science and Technology, Japan, for the Grant-in-Aids for the COE Research on Elements Science, No. 12CE2005, and S.Y. thanks PRESTO, Japan Science and Technology Corporation (JST).

Supporting Information Available: Crystal structure data for **3b**, **4a**, and **4b**, including tables of atomic coordinates, anisotropic displacement parameters, bond distances, and bond angles. This material is available free of charge via Internet at http://pubs.acs.org.

OM020124F

---

[13] Altomore, A.; Burla, M. C.; Camalli, M.; Cascarano, M. Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Crystallogr.* **1994**, *27*, 435.

[14] Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF program system*; Techincal Report of the Crystallography Laboratory; University of Nijimegen: The Netherlands, 1992.