Synthesis, Structures, and Reactivity of Biphenylylene Complexes of Bismuth(III)

Claire J. Carmalt,[†] Alan H. Cowley,[*,‡] Andreas Decken,[‡,§]
Yvonne G. Lawson,[†] and Nicholas C. Norman[*,†]

Department of Chemistry, The University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU, U.K., and Department of Chemistry & Biochemistry, The University of Texas at Austin, Austin, Texas 78712

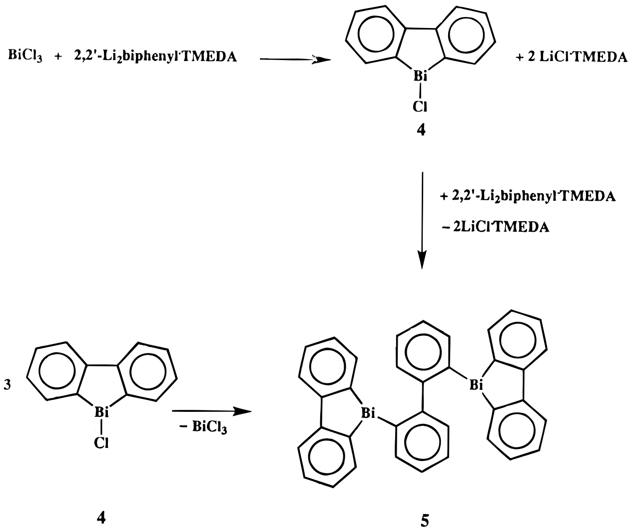
Received September 14, 1995[⊗]

*Summary: The synthesis of [$Bi_2(biph)_3$] (**5**) and [PPN][$BiCl_2(biph)$] (**6**) (biph = 2,2′-biphenylylene, PPN = $Ph_3P{=}N{=}PPh_3$), the first structurally characterized biphenylylene complexes of bismuth (III), are described. Complex **5** crystallizes as a THF (tetrahydrofuran) solvate; each bismuth is three-coordinate with a trigonal pyramidal geometry. The solid state of **6** comprises separated [PPN]$^+$ cations and [$BiCl_2(biph)$]$^-$ anions. The anion adopts a trigonal bipyramidal geometry at the bismuth; the axial sites are occupied by chloride ligands, and two of the three equatorial sites are occupied by ring carbon atoms.*

Introduction

In a recent series of papers[1−4] we have described the results of a number of crystal structure determinations for a range of arylbismuth(III) halides and halogeno anions, from which a number of structural trends have emerged. In contrast to the structures now known for aryl- (mostly phenyl) bismuth compounds, however, there are few structurally characterized examples of linked aryl or heteroaromatic bismuth derivatives. Recently, Suzuki *et al.*[5] reported the structure of 10-((4′-chlorophenyl)ethynyl)phenothiabismin 5,5-dioxide (**1**), in which the bismuth center adopts a three-coordinate, trigonal pyramidal coordination geometry. However, additional interactions are present between the bismuth atom and the sulfonyl oxygen atoms. The structure of a biphenylylene complex of antimony(III), [SbCl(biph)] (**2**), has also been described recently.[6] In compound **2**, the primary coordination environment of the antimony atom is trigonal pyramidal, but additional secondary Sb···Cl interactions are also present resulting in the formation of loosely bound dimers. Biphenylylene complexes of bismuth(III) have not hitherto been structurally characterized, but analytical data have been presented for [BiI(biph)][7] and [PhBi(biph)][8] as well as for the bismuth(V) complex [$Ph_3Bi(biph)$].[9] Herein we report the syntheses of a range of biphenylylene complexes of bismuth(III), two examples of which have been characterized by X-ray crystallography.

Scheme 1



Results and Discussion

The reaction between $BiCl_3$ and 1 equiv of 2,2′-dilithiobiphenyl·TMEDA[10] (**3**) (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine) in Et_2O solution afforded, after workup, a cream colored crystalline solid, analytical data for which (Table 1) were consistent not with the expected formula [BiCl(biph)] (**4**) (biph = 2,2′-biphenylylene) but with the formula [$Bi_2(biph)_3$] (**5**). As indicated in Scheme 1, **5** presumably results either from the reaction of **4** with **3** or via a redistribution reaction of **4**. Redistribution reactions of this type have been found to be characteristic of arylbismuth halide compounds in solution.[1−4] However, it is also of interest to note (ref 7) that analytical data have been presented for the related antimony complex, [$Sb_2(biph)_3$], which results from the reaction of [SbI(biph)] with Li_2(biphenyl). Moreover, compound **5** was obtained in higher yield from the stoichiometrically correct reaction between 2 equiv of $BiCl_3$ and 3 equiv of **3** in Et_2O solution.

[†] The University of Newcastle upon Tyne.

[‡] The University of Texas at Austin.

[§] Present address: Chemistry Department, University of New Brunswick, Bag Service 45222, Fredericton, New Brunswick, Canada E3B 6E2.

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1995.

(1) Clegg, W.; Errington, R. J.; Fisher, G. A.; Hockless, D. C. R.; Norman, N. C.; Orpen, A. G.; Stratford, S. E. *J. Chem. Soc., Dalton Trans.* **1992**, 1967.

(2) Clegg, W.; Errington, R. J.; Fisher, G. A.; Flynn, R. J.; Norman, N. C. *J. Chem. Soc., Dalton Trans.* **1993**, 637.

(3) Clegg, W.; Elsegood, M. R. J.; Errington, R. J.; Fisher, G. A.; Norman, N. C. *J. Mater. Chem.* **1994**, *4*, 891.

(4) Carmalt, C. J.; Cowley, A. H.; Decken, A.; Norman, N. C. *J. Organomet. Chem.* **1995**, *496*, 59.

(5) Suzuki, H.; Murafuji, T.; Azuma, N. *J. Chem. Soc., Perkin Trans.* **1992**, 1593.

(6) Millington, P. L.; Sowerby, D. B. *J. Organomet. Chem.* **1994**, *480*, 227.

(7) Hellwinkel, D.; Bach, M. *J. Organomet. Chem.* **1969**, *17*, 389.

(8) Wittig, G.; Hellwinkel, D. *Chem. Ber.* **1964**, *97*, 789.

(9) Hellwinkel, D.; Bach, M. *Liebigs Ann. Chem.* **1968**, *720*, 198.

(10) Neugebauer, W.; Kos, A. J.; Schleyer, P. v. R. *J. Organomet. Chem.* **1982**, *228*, 107.

0276-7333/96/2315-0887$12.00/0

Table 1. NMR and Analytical Data

compd	$\delta(^1H)^b$	$\delta(^{13}C\{^1H\})^b$	elemental anal.[a] C	H	N
5	8.19 (m, 2H), 8.14 (m, 2H), 7.95 (m, 2H), 7.87 (m, 2H), 7.62−7.71 (m, 8H), 7.53−7.61 (m, 6H), 7.39 (m, 2H)	C−H carbons, 139.1, 138.9, 138.8, 131.5, 131.4, 129.6, 129.4, 129.2, 129.0, 128.8, 127.8, 127.7; C−C and C−Bi carbons, 160.0, 159.6, 153.0	50.10 (50.40)	3.30 (3.40)	
product of the reacn of **5** with $BiCl_3$	8.36 (d, 2H, *J* = 7.2 Hz), 8.25 (d, 2H, *J* = 7.8Hz), 7.73 (t, 2H, *J* = 7.2 Hz), 7.61 (t, 2H, *J* = 7.5 Hz)	C−H carbons, 140.7, 133.0, 132.2, 130.8; C−C and C−Bi carbons; 197.6, 165.4	25.60 (28.70)	2.10 (1.60)	
7	8.23 (d, 2H, *J* = 7.1 Hz), 8.18 (d, 2H, *J* = 7.7 Hz), 7.81 (m, 6H, *p*-C_6H_5), 7.62−7.72 (m, 26H, *o,m*-C_6H_5, and 2H, biph), 7.54 (t, 2H, *J* = 7.4 Hz)	C−H carbons (biph), 140.5, 132.7, 131.7, 130.7; C−C or C−Bi carbons (biph), 195.4, 165.3; 137.7 (s, *p*-C_6H_5, PPN), 136.0 (m, *o*/*m*-C_6H_5, PPN), 133.5 (m, *o*/*m*-C_6H_5, PPN), 130.8 (d, *i*-C_6H_5, PPN, J_{PC} = 108 Hz)	59.10 (59.40)	3.90 (3.95)	1.50 (1.45)

[a] Calculated values in parentheses. [b] Referenced to TMS (Me_4Si), with positive values to high frequency. All spectra were obtained in DMSO-d_6 (dimethyl-d_6 sulfoxide).

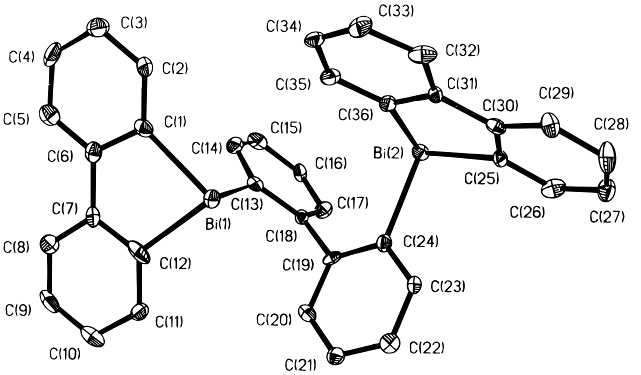


Figure 1. View of the molecular structure of **5** showing the atom-numbering scheme.

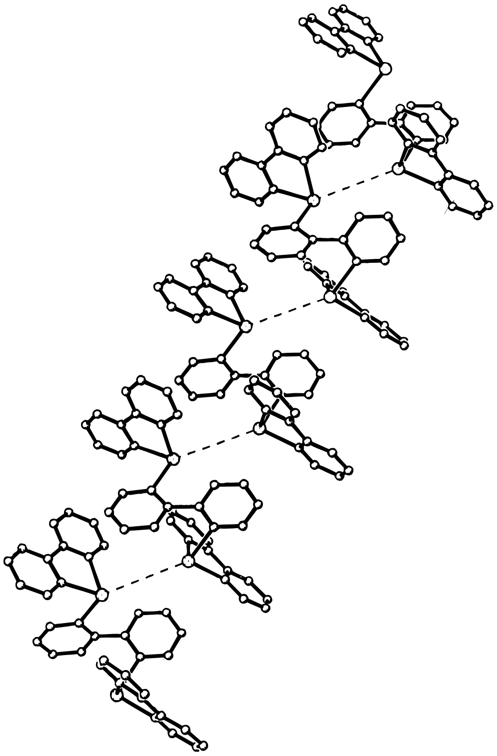


Figure 2. View of part of the crystal structure of **5** showing the Bi···Bi contacts.

Table 2. Selected Bond Lengths and Angles for 5

Bond Lengths (Å)[a]			
Bi(1)−C(1)	2.272(12)	Bi(1)−C(12)	2.225(12)
Bi(1)−C(13)	2.284(9)	Bi(2)−C(25)	2.233(12)
Bi(2)−C(36)	2.227(10)	Bi(2)−C(36)	2.279(10)
Bond Angles (deg)[a]			
C(1)−Bi(1)−C(12)	78.2(5)	C(1)−Bi(1)−C(13)	92.6(4)
C(12)−Bi(1)−C(13)	90.9(4)	C(25)−Bi(2)−C(36)	77.6(4)
C(25)−Bi(2)−C(24)	93.9(4)	C(36)−Bi(2)−C(24)	95.5(4)
C(11)−C(12)−Bi(1)	124.9(11)	C(7)−C(12)−Bi(1)	112.1(9)
C(14)−C(13)−Bi(1)	122.3(8)	C(18)−C(13)−Bi(1)	118.6(7)
C(6)−C(1)−Bi(1)	112.6(8)	C(2)−C(1)−Bi(1)	129.1(10)
C(19)−C(24)−Bi(2)	117.7(7)	C(23)−C(24)−Bi(2)	122.8(8)
C(35)−C(36)−Bi(2)	127.4(9)	C(31)−C(36)−Bi(2)	112.4(8)
C(30)−C(25)−Bi(2)	113.4(8)	C(26)−C(25)−Bi(2)	125.2(8)

[a] Esd's given in parentheses.

The structure of **5** was established by X-ray crystallography, the results of which are shown in Figures 1 and 2. Selected bond lengths and angles are given in Table 2. As well as confirming the proposed formula for **5**, the X-ray study revealed that this compound crystallizes as a THF solvate with one molecule of **5** and one of THF per asymmetric unit. Both bismuth centers adopt a three-coordinate, trigonal pyramidal coordination geometry (sums of angles at Bi(1) and Bi(2) = 261.7(5) and 267.4(4)°, respectively). The Bi−C distances [average 2.253(12) Å] fall within the range reported for other Bi(III) aryl derivatives.[1−4] The C−Bi−C angles fall into two distinct ranges, namely 78.2(5)−77.6(4) and 90.9(4)−95.9(4)°. The smaller values relate to the endocyclic angles and result from the constraints of the chelating biph ligand. The C_4Bi rings are both planar within experimental error, and the largest deviations from the mean plane were found to be 0.025 Å for Bi(1) and 0.046 Å for Bi(2). Both values are similar to that reported for **2** (0.03 Å). The longer, exocyclic C−Bi−C bond angles in **5** are comparable to those reported for $BiPh_3$ which span the range 92−96°.[11] The torsion angle about the C(18)−C(19) bond, in the central biph ligand, is 80.0(13)° thus indicating a large degree of twist about this bond. The intermolecular Bi···Bi contacts in **5** are 4.7 Å (Figure 2).

As a further point of discussion, we note that molecules of **5** possess approximate C_2 symmetry and are therefore chiral. As in the case of other substituted biphenyl compounds with bulky substituents at the 2 and 2′ positions, this structural feature arises because of the inhibition of free rotation about the central biphenyl C−C bond.[12] The chirality of **5** is also evident in the ^1H and $^{13}C\{^1H\}$ NMR spectra (Table 1). Note that 12 C−H resonances are observed as a consequence of the inequivalence of the terminal biphenylylene groups.

---

[11] Hawley, D. M.; Ferguson, G. *J. Chem. Soc. A* **1968**, 2059.

[12] For a further discussion of this matter, see: March, J. *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, 2nd ed.; McGraw-Hill: Kogakusha, Tokyo, 1977; pp 92−94.

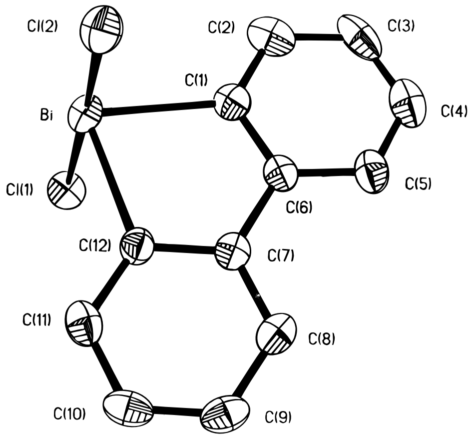


Figure 3. View of the molecular structure of **6**$^-$ showing the atom-numbering scheme.

Scheme 2

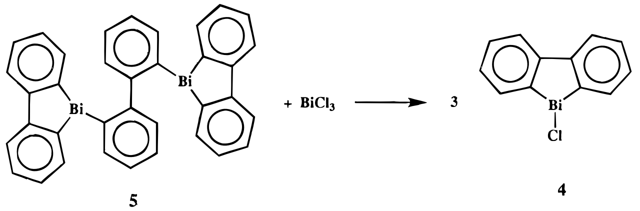


Table 3. Selected Bond Lengths and Angles for 6

	Bond Lengths (Å)[a]		
Bi–Cl(1)	2.702(2)	Bi–Cl(2)	2.743(2)
Bi–C(1)	2.256(8)	Bi–C(12)	2.230(8)
	Bond Angles (deg)[a]		
Cl(1)–Bi–Cl(2)	175.10(7)	C(1)–Bi–C(12)	77.6(3)
C(1)–Bi–Cl(1)	92.2(2)	C(1)–Bi–Cl(2)	90.4(2)
C(12)–Bi–Cl(1)	89.5(2)	C(12)–Bi–Cl(2)	87.0(2)
C(2)–C(1)–Bi	126.5(7)	C(6)–C(1)–Bi	111.7(5)
C(7)–C(12)–Bi	112.7(5)	C(11)–C(12)–Bi	126.6(6)

[a] Esd's given in parentheses.

In an effort to intercept and isolate the desired benzannelated chlorobismole **4**, complex **5** was treated with an equimolar quantity of BiCl$_3$ in Et$_2$O solution (Scheme 2). The ^{1}H and ^{13}C{^{1}H} NMR data for the resulting cream colored solid (Table 1) indicated that a pure product was formed and were supportive of the proposed formulation, [BiCl(biph)] (**4**). However, the analytical data for this product were low for both carbon and hydrogen indicating that pure **4** is not formed possibly because it is contaminated with BiCl$_3$. Attempts to isolate pure **4** were unsuccessful even under high-dilution conditions. Further treatment of this mixture with an excess of [PPN]Cl (PPN = Ph$_3$P=N=PPh$_3$) afforded, after recrystallization from MeCN/Et$_2$O mixtures, colorless crystals of the salt [PPN][BiCl$_2$(biph)] (**6**). The proposed formulation for **6** was consistent with pertinent analytical and spectroscopic data (Table 1). However, in order to confirm the structure, it was necessary to appeal to X-ray crystallography. The solid state of **6** consists of [PPN]$^+$ cations and [BiCl$_2$(biph)]$^-$ anions (henceforth referred to as **6**$^-$) and there are no unusually short interionic contacts. The structure of **6**$^-$ is illustrated in Figure 3, and selected bond distances and angles are given in Table 3. A view of the packing of the anions and cations in **6** is presented in Figure 4. The structure of **6**$^-$ comprises a four-coordinate bismuth center with an equatorially vacant, trigonal bipyramidal or disphenoidal coordination environment. The chloride ligands adopt axial sites, and the Bi–Cl(1) and Bi–Cl(2) bond distances are 2.702(2) and 2.743(2) Å, respectively. The Cl(1)–Bi–Cl(2) bond angle is 175.10(7)°. Although this is a small departure from linearity, it is interesting to note that contrary to VSEPR arguments the chloride ligands point away from rather than toward the biph ligand.[13] The biph ligand occupies two equatorial positions, and the Bi–C bond distances [Bi–C(4a) 2.256 Å and Bi–C(5a) 2.230 Å] fall within the usual range.[1–4] The fact that the C(1)–Bi–C(12) bond angle [77.6(3)°] is appreciably less than the ideal value of 120° is attributable to the chelating nature of the biph ligand; comparable acute angles are also evident in **5**. The C$_4$Bi ring is planar within experimental error, the mean deviation being 0.024 Å. In the related complex [PPh$_4$][BiBr$_2$Ph$_2$],[1] the bismuth center in the anion adopts a similar structure, the only significant difference being the larger unconstrained angle between the equatorial carbon atoms [95.9(1)°].

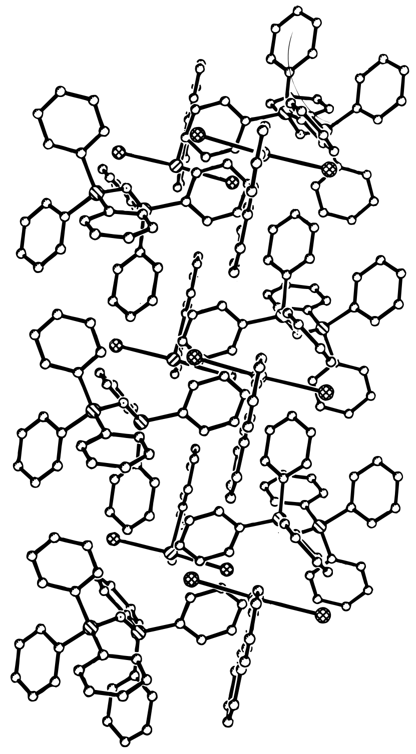


Figure 4. View of the packing of the cations and anions in **6**.

Experimental Section

General Procedures. All reactions were performed using standard Schlenk techniques under an atmosphere of dry, oxygen-free dinitrogen. All solvents were distilled from appropriate drying agents immediately prior to use (sodium–benzophenone for Et$_2$O and THF, CaH$_2$ for CH$_2$Cl$_2$, and sodium for hexanes). The halides, BiBr$_3$ (99%+), BiCl$_3$ (99%+), [PPN]Cl, and [Ph$_4$P]Br were procured commercially and used without further purification; 2,2′-dilithiobiphenyl·2TMEDA[10] (**3**) was prepared according to the literature method. Microanalytical data were obtained at The University of Newcastle upon Tyne. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded

---

(13) For other cases where VSEPR arguments are not in accord with all structural details, see: (a) Hall, M.; Sowerby, D. B. *J. Organomet. Chem.* **1988**, *347*, 59. (b) Calderazzo, F.; Marchetti, F.; Ungari, F.; Wieber, M. *Gazz. Chim. Ital.* **1991**, *121*, 93.

Table 4. Crystallographic and Structure Solution Data for Compounds 5 and 6

	5	**6**
compd formula	$C_{36}H_{24}Bi_2{\cdot}C_4H_8O$	$C_{48}H_{38}BiCl_2NP_2$
M_r	946.62	970.6
space group	$P2_1/c$	$C2/c$
cryst system	monoclinic	monoclinic
a/Å	13.861(2)	35.430(5)
b/Å	17.059(2)	8.962(1)
c/Å	14.681(1)	27.321(3)
β/deg	115.098(8)	93.07(1)
V/Å^3	3143.6(6)	8663(3)
Z	4	8
D_{calc}/g cm^{-3}	2.000	1.488
F(000)	1784	3840
μ(Mo Kα)/cm^{-1}	112.12	43.01
T/K	183(2)	293(2)
scan mode	ω	$\theta/2\theta$
θ range/deg	$2.01 < \theta < 27.50$	$2.30 < \theta < 24.97$
cryst size/mm	0.191 × 0.27 × 0.50	0.18 × 0.19 × 0.67
range of transm coeff	0.113−0.453	0.299−0.724
no. of data collcd	14 430	17 353
no. of unique data	7222	7617
hkl range	$-18 \rightarrow 18, 0 \rightarrow 22, -19 \rightarrow 19$	$-42 \rightarrow 42, -10 \rightarrow 1, -32 \rightarrow 32$
no. of refined params	391	489
Final R	0.0567	0.0483
Final $R_w{}^2$	0.1313	0.1246
goodness of fit, S	1.021	1.115
largest remaining feature in electron density map[a]/e Å^{-3}	+2.891 (max), −2.725 (min)	+2.221 (max), −0.867 (min)
shift/esd in last cycle	0.001 (max), 0.000 (av)	0.001 (max), 0.000 (av)

[a] Found near Bi atoms.

on Bruker WP200 and WM500 spectrometers, and ^{31}P NMR spectra were measured on a JEOL FX90Q spectrometer.

Synthesis of $[Bi_2(biph)_3]$ (5). An orange solution of **3** (3.426 g, 8.57 mmol) in Et_2O (40 mL) was added to a stirred solution of $BiCl_3$ (2.697 g, 8.55 mmol) in Et_2O (30 mL) at −78 °C. A precipitate formed immediately, and after being stirred for 30 min, the reaction mixture was allowed to warm to room temperature. The mixture was stirred overnight and then filtered through Celite. The volume of the resulting pale yellow solution was reduced to about half, and after a period of days at −22 °C, 0.801 g of cream colored crystalline **5** was isolated (20% yield based on bismuth).

Compound **5** was also made in higher yield by treatment of 2 equiv of $BiCl_3$ with 3 equiv of **3**. For example, the reaction between $BiCl_3$ (0.222 g, 0.704 mmol) and **3** (0.422 g, 1.054 mmol) was carried out as above and afforded 0.335 g of **5** after workup (50% yield based on bismuth).

Reaction of 5 with $BiCl_3$. A solution of $BiCl_3$ (0.143 g, 0.452 mmol) in Et_2O (6 mL) was added to a stirred solution of **5** (0.300 g, 0.452 mmol) in Et_2O (10 mL) at room temperature resulting in the formation of a pale yellow precipitate. After stirring of the reaction mixture for approximately 30 min, the supernatant liquid was removed by syringe. Removal of the solvent and volatiles under vacuum left 0.315 g of cream colored solid. Analytical and NMR data for this product are summarized in Table 1.

Synthesis of $[PPN][BiCl_2(biph)]$ (6). A sample of the product obtained in the previous reaction (0.104 g) and [PPN]-Cl (0.168 g, 0.292 mmol) were dissolved in THF (15 mL), and the resulting mixture was stirred for 24 h, after which time the reaction flask contained a cloudy white solution. The solvent and volatiles were removed under reduced pressure, the resulting white solid was dissolved in hot CH_3CN (7 mL), and Et_2O (20 mL) was added as an overlayer after allowing the CH_3CN solution to cool to room temperature. Solvent diffusion over a period of days at room temperature afforded colorless crystals of **6** (0.097 g, 70%), one of which was used for X-ray crystallography.

X-ray Crystallography. Crystallographic data and details of the data collection procedures and structure refinement for **5** and **6** are presented in Table 4. The following section deals with the structure of **5** with details for the structure of **6**, where different, given in brackets. Data were collected on an Enraf-Nonius CAD4 diffractometer [Nicolet P3 for **6**] with graphite-monochromated X-radiation ($\lambda = 0.710\ 73$ Å). Accurate unit cell parameters were determined by recentering 25 optimal high-angle reflections. Three standard reflections were measured every 1 h [four in every 96 reflections for **6**] during data collection, and no decrease in intensities was noted. Corrections were applied for Lorentz−polarization and absorption effects. The structure was solved for the heavy atoms by direct methods (SHELXL PLUS).[14] Subsequent difference syntheses gave all other non-hydrogen atomic positions. All non-hydrogen atoms were allowed anisotropic thermal motion. Hydrogen atoms were included at calculated positions (C−H 0.96 Å) and were refined using a riding model and a general isotropic thermal parameter. Refinement was by full-matrix least squares on F^2.

Acknowledgment. We thank the SERC for a studentship (C.J.C.) and NATO for an International Collaborative Research Grant. N.C.N. also thanks the Royal Society for additional supporting funds. A.H.C. thanks the National Science Foundation and the Robert A. Welch Foundation for financial support.

Supporting Information Available: Table of X-ray parameters, atom coordinates, thermal parameters, and bond distances and angles and ORTEP diagrams (18 pages). Ordering information is given on any current masthead page.

OM950734Y

---

[14] Sheldrick, G. M. SHEXTL-PLUS, Siemens Analytical X-ray Instruments, Inc. Göttingen, 1990.