ORGANOMETALLICS

Synthesis of a Tin(II) 1,3-Benzobis(thiophosphinoyl)methanediide Complex and Its Reactions with Aluminum Compounds

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Supporting Information



ABSTRACT: The synthesis of a tin(II) 1,3-benzobis(thiophosphinoyl)methanediide complex and its reactions with aluminum compounds are reported. The reaction of the 1,3-benzodiphosphole disulfide $[1,3-C_6H_4(PhP=S)_2CH_2]$ (4) with $[Sn{N(SiMe_3)_2}_2]$ in refluxing toluene afforded the tin(II) 1,3-benzobis(thiophosphinoyl)methanediide $[{\mu-1,3-C_6H_4(PhP=S)_2C}]$ (5). The X-ray crystal structure of 5 shows that it has a 1,3-dimetallacyclobutane structure. The reaction of 5 with 1 equiv of AlCl_3 in CH_2Cl_2 afforded $[1,3-C_6H_4(PhP=S)_2C(Sn){Sn(S=PPh)_2C(AlCl_3)-1,3-C_6H_4}]$ (6). The reaction proceeds via an insertion of a AlCl_3 molecule into one of the Sn-C bonds in 5. The reaction of 5 with 2 equiv of AlCl_3 in CH_2Cl_2 afforded $[1,3-C_6H_4(PhP=S)_2C(Sn){Sn(S=PPh)_2C(AlCl_3)-1,3-C_6H_4}]$ (6), which then undergoes an insertion with another AlCl_3 molecule to form compound 7. The transmetalation reaction of 5 with 2 equiv of AlMe_3 in CH_2Cl_2 afforded $[1,3-C_6H_4(PhP=S)_2CAIMe]_2$ (8), which contains a terminal $C_{methanediide}$ –Al bond.

INTRODUCTION

Low-valent group 14 metal bis(phosphinoyl)methanediide complexes of composition $[:MC(PPh_2=E)_2]_2$ (M = Ge, Sn, Pb, $E = NSiMe_3$, S) have attracted much attention in the past decade.¹ Moreover, the pyridine- and lutidene-functionalized low-valent group 14 metal phosphinoylmethanediide complexes have been reported.² They have either a metallavinylidene structure (A and B, Scheme 1) or a 1,3-dimetallacyclobutane structure (C-F). The reactivity of low-valent group 14 metallavinylidene derivatives has been well studied. Leung et al. reported that the bis(germavinylidene) $[(Me_3SiN=PPh_2)_2C=Ge:]_2$ (A) acts as a Lewis base or undergoes an 1,2-addition or cycloaddition toward various transition-metal complexes and organic and inorganic substrates.³ We have also reported the synthesis of the tin(II) (iminophosphinoyl)(thiophosphinoyl)methanediide [(PPh₂= NSiMe₃)(PPh₂=S)CSn:]₂ (**B**)^{1b} and its reactions with sulfur, isocyanates, and [RhCl(cod)]₂.⁴ In contrast, the reactivity of low-valent group 14 1,3-dimetallacyclobutane has been less studied. Only one example was reported. Leung et al. showed that the reaction of $[Pb{\mu-C(PPh_2=S)_2}]_2$ with sulfur formed $[PbS{C (PPh_2=S)_2$], in which the sulfur atom is inserted into the C_{methanediide}-Pb bond.^{1c} Since the group 14 elements in a low-valent group 14 1,3-dimetallacyclobutane contain a lone pair of electrons, we are highly interested in exploring their reactivities with Lewis acids such as aluminum compounds. In this paper, we report (i) the synthesis of the 1,3-benzodiphosphole disulfide [1,3- $C_6H_4(PhP=S)_2CH_2$ (4) from $[CH_2(PPh_2=S)_2]$, (ii) the synthesis of the tin(II) 1,3-benzobis(thiophosphinoyl)methanediide

complex $[\{\mu\text{-}1,3\text{-}C_6H_4(PhP=S)_2C\}Sn]_2$ (5), and (iii) the reactions of compound 5 with AlMe_3 and AlCl_3.

RESULTS AND DISCUSSION

Synthesis of the 1,3-Benzodiphosphole Disulfide [1,3- $C_6H_4(PhP=S)_2CH_2$]. The reaction of $[CH_2(PPh_2=S)_2]$ (1) with 1 equiv of BuⁿLi in THF, followed by treatment with 1 equiv of Bu^tOK in THF afforded [(PPh₂=S)₂CHK] (2; Scheme 2). Moreover, the reaction of 1 with 1 equiv of Bu^tOK and 1.2 equiv of BuⁿLi in refluxing THF afforded the potassium 1,3-benzobis(thiophosphinoyl)methanide $[1,3-C_6H_4(PhP=$ S_2 CHK·3THF] (3). Furthermore, treatment of 2 with PhLi or BuⁿLi in refluxing THF afforded compound 3, which has been confirmed by NMR spectroscopy. In contrast, there is no reaction between 2 and Bu^tOLi. According to these results, the reaction of 1 with Bu^tOK/BuⁿLi in refluxing THF probably proceeds via the formation of 2. Consequently, the ortho position of the phenyl ring is lithiated by BuⁿLi, followed by an intramolecular displacement of a PhLi molecule to form 3 (Scheme 3). The PhLi molecule then is involved in the lithiation of the ortho position of the phenyl ring. As a result, a slight excess of BuⁿLi (1.2 equiv) is enough to initiate the ortho metalation of the phenyl ring. Similar ortho metalation of the PPh₂ moiety of the bis(iminophosphinoyl)methanediide and (iminophosphinoyl)(trimethylsilyl)methanide ligands has been reported.5

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Scheme 1. Low-Valent Metallavinylidene Derivatives (A and B) and 1,3-Dimetallacyclobutane Derivatives (C-F)

Scheme 2. Synthesis of 2-4



3 was then hydrolyzed by water in THF to form $[1,3-C_6H_4(PhP=S)_2CH_2]$ (4). It is noteworthy that the P=S moieties are cis to each other in solution and in the solid state (see below).

Compound 2 has been synthesized in situ for the preparation of vinylidene phosphine sulfide.⁶ However, its isolation and characterization were not reported. Compound 2 was isolated as a highly air- and moisture-sensitive pale yellow crystalline

Scheme 3. Proposed Mechanism for the Formation of 3



solid which is soluble in Et₂O and THF. It is stable in the solid state at room temperature under an inert atmosphere. The ¹H NMR spectrum of **2** shows a triplet at δ 1.48 ppm (²*J*_{P-H} = 2.32 Hz) for the proton on the C_{methanide} atom. The ¹³C{¹H} NMR spectrum shows a triplet at δ 20.12 ppm (*J*_{P-C} = 107.3 Hz) for the C_{methanide} atom. The ³¹P{¹H} NMR spectrum displays a singlet at δ 38.03 ppm for the equivalent P nuclei.

The molecular structure of compound 2 is shown in Figure 1. Selected bond lengths and angles of 2 are given in Table 1.



Figure 1. Molecular structure of compound **2**: (a) perspective view of the molecule (50% thermal ellipsoids); (b) its polymeric form (15% thermal ellipsoids). Hydrogen atoms are omitted for clarity.

Compound 2 has a polymeric structure by the electrostatic interaction of the K(1) atoms with the thiophosphinoyl substituents of the adjacent molecules. The coordination sphere on the K(1) atoms is further supplemented by an η^3 interaction with the phenyl substituents (K(1)…C(15) = 3.453(8) Å,

 $\hat{S} \bigoplus_{K} \hat{S}$ $K(1) \cdots C(16) = 3.336(8) \text{ Å}, K(1) \cdots C(17) = 3.432(8) \text{ Å}).^7$ In the monomeric form, the K(1) atom is coordinated with the S(1) and S(2) atoms of the thiophosphinoyl substituents to form a twisted six-membered metallacycle. The C(1) \cdots K(1) distance (4.807(7) Å) is significantly longer than that in $[(PPh_2 = 1)]$

average 1.829 Å).¹⁰ Compound **3** was isolated as a highly air- and moisturesensitive orange crystalline solid which is soluble only in THF. It is stable in the solid state at room temperature under an inert atmosphere. The ¹H NMR spectrum of **3** shows a triplet at δ 1.35 ppm (²J_{P-H} = 11.2 Hz) for the proton on the C_{methanide} atom. The ¹³C{¹H} NMR spectrum shows a triplet at δ 26.0 ppm (J_{P-C} = 101.1 Hz) for the C_{methanide} atom. The ³¹P{¹H} NMR spectrum displays a singlet at δ 44.12 ppm for the equivalent P nuclei.

NSiMe₃)₂CHK(THF)₂] (4.145(2) Å),⁸ which indicates that

there is no contact between the C(1) and K(1) atoms. The

K(1)-S(1) (3.187(3) Å) and K(1)-S(2) bonds (3.234(3) Å)

are comparable with those in the potassium bis(thiophosphinoyl)amide $[KN(PPh_2=S)_2]$ (3.203(1), 3.279(1) Å).⁹ The P–S bonds (1.982(2), 1.997(2) Å) are lengthened and the C–P bonds (1.696(7), 1.718(7) Å) are shortened compared with those in $[CH_2(PPh_2=S)_2]$ (P–S, average 1.945 Å; P–C,

The molecular structure of compound 3 (Figure 2, with selected bond lengths and angles in Table 1) shows that the K(1) atom is coordinated with the C(1), S(1), and S(2) atoms of the ligand to form a couchlike conformation. The dihedral angle between the C(8)C(13)P(2)C(1)P(1) and P(1)S(1)-S(2)P(2) least-squares planes is 80.41°. The K(1)S(1)P(1)-C(1)P(2)S(2) metallacycle adopts a pseudo-boat conformation in which the C(1) and K(1) atoms are displaced from the P(1)S(1)S(2)P(2) least-squares plane by 0.897 and 0.637 Å, respectively. The coordination sphere on the K(1) atom is further supplemented by coordinating with three THF molecules. The K(1)-C(1) bond (3.196(6) Å) is comparable to that in $[(PPh_2=NSiMe_3)(PPh_2)CHK]_n$ (3.166(7) Å),¹¹ which suggests that there is a contact between the C(1) and K(1) atoms. The K(1)-S(1) (3.2667(18) Å) and K(1)-S(2)bonds (3.3622(19) Å) are comparable with those in 2.

Compound 4 was isolated as a pale yellow crystalline solid which is soluble in toluene and THF. Its molecular structure is shown in Figure 3. The P=S moieties are cis to each other. The result is in contrast to the X-ray crystal structure of $[CH_2(PPh_2=S)_2]$, in which the P=S moieties are on opposite sides.¹⁰ The C-P bonds (1.8229(14), 1.8373(14) Å) are lengthened and the P-S bonds (1.9463(5), 1.9498(5) Å) are shortened compared with those in 3 (C-P = 1.698(5), 1.721(5) Å; P-S = 1.9846(19), 1.987(2) Å).

Compound 4 also retains its solid-state structure in solution. The ¹H NMR spectrum displays a quartet at δ 3.26 (² J_{P-H} = 15.9 Hz) and a multiplet at δ 3.61 ppm for two nonequivalent $-PCH_2P-$ protons. The ¹³C{¹H} NMR spectrum shows a

Fable 1. Selected Bond Ler	gths (A) and Angl	les (deg) for C	2–8 compounds
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$[(PPh_2=S)_2CHK]$ (2)							
K(1) - S(1)	3.187(3)	K(1) - S(2)	3.234(3)				
K(1) - S(1C)	3.137(3)	K(1) - S(2B)	3.117(2)				
C(1) - P(1)	1.696(7)	C(1) - P(2)	1.718(7)				
P(1) - S(1)	1.997(2)	P(2) - S(2)	1.982(2)				
K(1) - C(15)	3.453(8)	K(1) - C(16)	3.336(8)				
K(1) - C(17)	3.432(8)	$C(1) \cdots K(1)$	4.807(8)				
S(1)-K(1)-S(2)	81.34(6)	K(1)-S(1)-P(1)	103.65(9)				
S(1) - P(1) - C(1)	119.7(2)	P(1)-C(1)-P(2)	124.8(4)				
C(1)-P(2)-S(2)	116.6(2)						
[1,	$3-C_6H_4(PhP=S)$	$_{2}$ CHK·3THF] (3)					
K(1) - C(1)	3.196(6)	K(1) - S(1)	3.2667(18)				
K(1) - S(2)	3.3622(19)	C(1) - P(1)	1.698(5)				
C(1) - P(2)	1.721(5)	P(1)-S(1)	1.9846(19)				
P(2) - S(2)	1.987(2)	K(1) - O(1)	2.714(4)				
K(1) - O(2)	2.662(5)	K(1)-O(3)	2.742(6)				
K(1) - C(5)	3.362(6)						
C(1)-K(1)-S(1)	59.02(10)	C(1)-K(1)-S(2)	58.35(10)				
S(1)-K(1)-S(2)	110.44(5)	K(1)-S(1)-P(1)	83.66(6)				
S(1) - P(1) - C(1)	119.50(19)	P(1)-C(1)-K(1)	90.4(2)				
K(1)-S(2)-P(2)	83.25(6)	S(2) - P(2) - C(1)	119.2(2)				
P(2)-C(1)-K(1)	92.6(2)	P(1)-C(1)-P(2)	116.0(3)				
$[1,3-C_6H_4(PhP=S)_2CH_2]$ (4)							
C(1) - P(2)	1.8229(14)) C(1)-P(1)	1.8373(14)				
P(1) - S(1)	1.9463(5)	P(2)-S(2)	1.9498(5)				
P(1)-C(1)-P(2)	110.41(7)						
$[{\mu-1,3-C_6H_4(PhP=S)_2C}Sn]_2$ (5)							
C(1) - Sn(1)	2.334(2)	C(1)-Sn(1A)	2.301(2)				
Sn(1) - S(1)	2.7174(6)	C(1) - P(1)	1.750(2)				
C(1) - P(2)	1.766(2)	P(1) - S(1)	2.0111(8)				
P(2) - S(2)	1.9618(8)						
C(1)-Sn(1)-C(1A)	84.13(8)	Sn(1)-C(1)-Sn(1A)	95.88(8)				
P(1)-C(1)-P(2)	110.28(12)	P(1)-C(1)-Sn(1)	96.71(10)				
P(1)-C(1)-Sn(1A)	113.55(11)	P(2)-C(1)-Sn(1)	106.36(11)				
P(2)-C(1)-Sn(1A)	127.50(11)	C(1) - P(1) - S(1)	106.13(8)				
P(1)-S(1)-Sn(1)	79.63(2)	S(1)-Sn(1)-C(1)	72.71(6)				
C(1)-P(2)-S(2)	114.43(8)						
$[1,3-C_6H_4(PhP=S)_2C(Sn){Sn(S=PPh)_2C(AlCl_3)-1,3-C_6H_4}]$ (6)							
C(1) - Al(1)	1.923(4)	Sn(1) - S(1)	2.685(8)				
Sn(1) - S(2)	2.7094(11)	C(1) - P(1)	1.724(8)				

triplet at δ 41.62 ppm (J_{P-C} = 40.0 Hz) for the C_{PCP} atom. The ³¹P{¹H} displays a singlet at δ 45.80 ppm for the P nuclei.

Synthesis of the Tin(II) 1,3-Benzobis(thiophosphinoyl)methanediide [$\{\mu$ -1,3-C₆H₄(PhP=S)₂C}Sn]₂. The reaction of compound 4 with [Sn{N(SiMe₃)₂}₂] in refluxing toluene afforded [$\{\mu$ -1,3-C₆H₄(PhP=S)₂C}Sn]₂ (5; Scheme 4). The X-ray crystal structure of 5 shows that it has a 1,3dimetallacyclobutane structure (see below). Similar tin(II) and lead(II) bis(phosphinoyl)methanediide complexes [M{ μ -C(PPh₂=E)₂}]₂ (M = Sn, Pb; E = S, NSiMe₃) with a 1,3dimetallacyclobutane structure have been reported by Leung et al.^{1a,c}

Compound **5** was isolated as an air- and moisture-sensitive yellow crystalline solid which is soluble in CH₂Cl₂. The ¹H NMR spectrum displays resonances for the phenyl protons. It is noteworthy that the ¹³C NMR signal for the C_{methanediide} atom in **5** is not observed. Similarly, there is no ¹³C NMR resonance for the C_{methanediide} atom in [Sn{ μ -C(PPh₂=E)_2]₂ (E = S, NSiMe₃).^{1a,c} The ³¹P{¹H} NMR spectrum displays a singlet with satellites due to coupling to ^{117/119}Sn at δ 54.91 ppm

$[1,3-C_{6}H_{4}(PhP=S)_{2}C(Sn)\{Sn(S=PPh)_{2}C(AlCl_{3})-1,3-C_{6}H_{4}\}] (6)$					
C(1) - P(2)	1.670(15)	P(1)-S(1)	2.059(8)		
P(2)-S(2)	2.036(16)	C(20) - Sn(1)	2.310(4)		
C(20) - Sn(2)	2.297(4)	Sn(2) - S(3)	2.8152(11)		
Sn(2) - S(4)	2.8055(11)	C(20) - P(3)	1.763(4)		
C(20) - P(4)	1.753(4)	P(3) - S(3)	2.0091(15)		
P(4) - S(4)	2.0087(14)				
P(1)-C(1)-Al(1)	123.1(3)	P(2)-C(1)-Al(1)	128.9(3)		
P(1)-C(1)-P(2)	107.4(4)	C(20)-Sn(1)-S(1)	81.7(3)		
C(20)-Sn(1)-S(2)	81.34(10)	S(1) - Sn(1) - S(2)	101.8(2)		
Sn(1)-S(1)-P(1)	89.4(3)	S(1) - P(1) - C(1)	117.8(4)		
P(2)-S(2)-Sn(1)	89.2(3)	C(1)-P(2)-S(2)	118.3(6)		
C(20)-Sn(2)-S(4)	73.18(10)	C(20)-Sn(2)-S(3)	73.18(9)		
Sn(2)-S(3)-P(3)	78.44(4)	S(3) - Sn(2) - S(4)	100.08(3)		
P(3)-C(20)-Sn(2)	99.33(17)	S(3) - P(3) - C(20)	109.05(14)		
P(3)-C(20)-P(4)	107.0(2)	P(3)-C(20)-Sn(1)	121.96(19)		
Sn(2)-C(20)-P(4)	99.21(16)	Sn(2)-C(20)-Sn(1)	100.38(14)		
P(4)-S(4)-Sn(2)	78.38(4)	C(20)-P(4)-S(4)	109.14(13)		
$[1,3-C_6H_4(PhP=S)_2C(Sn)(AlCl_3)]$ (7)					
C(1) - Al(1)	1.963(3)	C(1) - Sn(1)	2.392(3)		
Sn(1) - S(1)	2.6435(9)	Sn(1) - S(2)	2.6364(9)		
C(1) - P(1)	1.758(3)	C(1)-P(2)	1.756(3)		
P(1)-S(1)	2.0191(11)	P(2)-S(2)	2.0164(11)		
S(1)-Sn(1)-C(1)	74.22(8)	S(2)-Sn(1)-C(1)	74.57(8)		
S(1)-Sn(1)-S(2)	100.29(3)	Sn(1)-C(1)-Al(1)	102.33(13)		
Al(1)-C(1)-P(1)	123.27(18)	Al(1)-C(1)-P(2)	124.45(18)		
Sn(1)-S(1)-P(1)	82.59(4)	S(1) - P(1) - C(1)	107.22(11)		
P(1)-C(1)-P(2)	106.27(17)	C(1)-P(2)-S(2)	107.81(11)		
P(2)-S(2)-Sn(1)	82.26(4)				
$[1,3-C_6H_4(PhP=S)_2CAlMe]_2$ (8)					
C(1) - Al(1)	1.9469(17)	C(2)-Al(1)	1.9547(18)		
Al(1A)-S(1)	2.3331(7)	Al(1A)-S(2)	2.3312(6)		
C(1) - P(1)	1.7111(16)	C(1) - P(2)	1.7102(16)		
P(1) - S(1)	2.0616(6)	P(2) - S(2)	2.0596(6)		
C(1)-Al(1)-S(1A)	108.07(5)	C(1)-Al(1)-S(2A)	109.94(5)		
S(1A)-Al(1)-S(2A)	113.44(2)	C(2) - Al(1) - C(1)	116.56(8)		
Al(1)-C(1)-P(1)	125.68(9)	Al(1)-C(1)-P(2)	127.19(9)		
Al(1A) - S(1) - P(1)	98.41(2)	S(1) - P(1) - C(1)	115.75(6)		
P(1)-C(1)-P(2)	104.37(9)	C(1)-P(2)-S(2)	117.59(6)		
P(2)-S(2)-Al(1A)	97.12(2)				

 $({}^{2}J_{\text{Sn-P}} = 47.7, 160.4 \text{ Hz})$. The results are not consistent with the solid-state structure. It is suggested that the thiophosphinoyl substituents are fluxional in solution. Similar observations can be found in $[\text{Sn}\{\mu\text{-C}(\text{PPh}_2\text{=-S})_2\}]_2$.^{1c} The ¹¹⁹Sn $^{1}\text{H}\}$ NMR spectrum shows a triplet at δ 26.28 ppm $({}^{2}J_{\text{Sn-P}} = 50.2 \text{ Hz})$. On comparison of the ¹¹⁹Sn NMR signal of **5** with those of $[(\text{PPh}_2\text{=-NSiMe}_3)(\text{PPh}_2\text{=-S})\text{CSn:}]_2$ (δ 132.1 ppm)^{1b} and the 6-stannapentafulvene $[(\text{Tbt})(\text{Mes})\text{Sn=-CR}_2]$ (Tbt = 2,4,6-{CH}(\text{SiMe}_3)_2}_3C_6H_2, Mes = 2,4,6-Me₃C₆H₂, CR₂ = fluorenylidene) (δ 270 ppm),¹² it is suggested that compound **5** does not have a vinylidene structure in solution.

The molecular structure of **5** (Figure 4, with selected bond lengths and angles in Table 1) is comparable to that of $[Sn{\mu-C(PPh_2=S)_2}]_2$.^{1c} It has a 1,3-dimetallacyclobutane structure in which the Sn(1) and Sn(1A) atoms are coordinated with two $C_{\text{methanediide}}$ atoms (C(1), C(1A)). The Sn(1) and Sn(1A) atoms are also coordinated with one of the thiophosphinoyl substituents of the ligand and display a distorted-trigonalpyramidal geometry (sum of bond angles 254.02°). The results illustrate that the Sn atoms possess a high-s-character lone pair.



Figure 2. Molecular structure of **3** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and the disordered THF molecule are omitted for clarity.



Figure 3. Molecular structure of 4 with thermal ellipsoids at the 50% probability level.

Scheme 4. Synthesis of 5-8

The C(1)–Sn(1) (2.334(2) Å) and C(1A)–Sn(1) bonds (2.301(2) Å) in **5** are longer than the C_{methanediide}–Sn bond in $[(PPh_2=NSiMe_3)(PPh_2=S)CSn:]_2$ (2.2094(9) Å).^{1b} The difference between the C–Sn bond lengths in **5** (0.033 Å) is significantly smaller than that in $[Sn{\mu-C(PPh_2=S)_2}]_2$ (2.327(3), 2.514(3) Å; $\Delta = 0.187$ Å).^{1c} It is noteworthy that the P=S moieties are cis to each other. The result is in contrast to the X-ray crystal structure of $[Sn{\mu-C(PPh_2=S)_2}]_2$, in which the P=S moieties are on opposite sides.^{1c}

Reactivity of $[\{\mu-1,3-C_6H_4(PhP=S)_2C\}Sn]_2$ (5) toward Aluminum Compounds. The reaction of 5 with 1 equiv of AlCl₃ in CH₂Cl₂ afforded $[1,3-C_6H_4(PhP=S)_2C(Sn)\{Sn(S=PPh)_2C(AlCl_3)-1,3-C_6H_4\}]$ (6). The results show that the lowvalent Sn atoms in 5 do not form any adduct with AlCl₃. Instead, the reaction appears to proceed via an insertion of AlCl₃ into one of the Sn-C bonds in 5 to form the intermediate **G**. The C-Sn bond is then cleaved in order to release the steric congestion between two 1,3-benzobis-(thiophosphinoyl)methanediide ligands. The results illustrate that the C_{methanediide}-Sn bonds in 5 are polar and the C_{methanediide} atom is nucleophilic. Hence, the lone pair electrons on the tin atoms are less favorable for bond formation.

Compound **6** was isolated as a highly air- and moisturesensitive yellow crystalline solid which is soluble only in CH₂Cl₂. The ¹H NMR spectrum displays resonances for the phenyl protons. The ¹³C{¹H} NMR signal for the C_{methanediide} atom in **6** cannot be observed. The ³¹P{¹H} NMR spectrum displays two singlets with satellites due to coupling to the Sn nuclei at δ 55.05 (²J_{Sn-P} = 47.7 Hz, ²J_{Sn-P} = 160.4 Hz) for the *PCP* nuclei and δ 58.45 ppm (²J_{Sn-P} = 164.7 Hz) for the *PC*(AlCl₃)*P* nuclei. The ¹¹⁹Sn{¹H} NMR spectrum displays two triplets at δ 22.15 (²J_{Sn-P} = 48.1 Hz) for the Sn(2) atom (see Figure 5 for the numbering scheme) and δ –160.40 ppm (²J_{Sn-P} = 164.3 Hz) for the Sn(1) atom, which show a upfield shift compared with those of **5**. These indicate that the Sn atoms have a positive charge.

The molecular structure of **6** is shown in Figure 5. Selected bond lengths and angles of **6** are given in Table 1. The Sn(1)S(1)P(1)C(1)P(2)S(2) and Sn(2)S(3)P(3)C(20)P(4)S(4)





Figure 4. Molecular structure of 5 with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

metallacycles adopt a pseudo-boat conformation. The C(20)atom is coordinated with the Sn(1) and Sn(2) atoms. The C(20)-Sn(1) (2.310(4) Å) and C(20)-Sn(2) bond lengths (2.297(4) Å) are comparable with those in 5. Each tin atom is also coordinated with two thiophosphinoyl substituents and adopts a distorted-trigonal-pyramidal geometry (Sn(1),264.84°; Sn(2), 246.44°). These indicate that the tin atoms possess a high-s-character lone pair. The C(1)...Sn(1) distance (3.065(4) Å) is significantly longer than the C-Sn bond in base-stabilized stannylenes such as [{C₅H₄N-2-C(SiMe₃)₂}Sn- $\{N(SiMe_3)_2\}$ (2.356(8) Å) and $[\{2,6-(CH_2NMe_2)_2C_6H_3\}$ -SnCl] (2.158(8) Å),¹³ but it is shorter than the sum of van der Waals radii (ca. 3.87 Å). The results suggest that there is a weak interaction between the C(1) and Sn(1) atoms. The C(1)-Al(1) bond (1.923(4) Å) is slightly shorter than the Al-C_{methanediide} bonds in the aluminum (iminophosphinoyl)-(thiophosphinoyl)methanediide complex $[(PPh_2=S)(PPh_2=NSiMe_3)CAIMe]_2$ (1.976(1) Å).¹⁴ Moreover, the C(1)–P bonds (1.670(15), 1.724(8) Å) are significantly shorter than the C(20)-P bonds (1.753(4), 1.763(4) Å), while the P(1)-S(1) (2.059(8) Å) and P(2)-S(2) (2.036(16) Å) bonds are longer than the P(3)-S(3) (2.0091(15) Å) and P(4)-S(4) bonds (2.0087(14) Å). On the basis of the theoretical studies of the dilithium bis(thiophosphinoyl)methanediide complex,¹⁵ it is suggested that the C(1) atom contains two lone pairs of electrons (LP), as illustrated in Scheme 5. One of the LPs

Scheme 5. Resonance Structure of the 1,3-Benzobis(thiophosphinoyl)methanediide Ligand



donates to the vacant p orbital of the Al(1) atom. Another LP is stabilized by the negative hyperconjugation with the P-C_{Ph} and P-S σ^* orbitals, which results in shortening the C(1)-P bonds and lengthening the P(1)-S(1) and P(2)-S(2) bonds.



Figure 5. Molecular structure of **6** with thermal ellipsoids at the 30% probability level. Hydrogen atoms, disordered phenyl substituents, P(1A), P(2A), and S(1A) atoms, and solvent molecules are omitted for clarity.

Similarly, the reaction of **5** with 2 equiv of $AlCl_3$ in CH_2Cl_2 afforded $[1,3-C_6H_4(PhP=S)_2C(Sn)(AlCl_3)]$ (7). The reaction appears to proceed via the formation of compound **6**, which then undergoes an insertion with another $AlCl_3$ molecule to form compound 7.

Compound 7 was isolated as a highly air- and moisturesensitive colorless crystalline solid, which is soluble only in CH₂Cl₂. The ¹H NMR spectrum displays resonances for the phenyl protons. The ¹³C{¹H} NMR signal for the C_{methanediide} atom in 7 cannot be observed. The ³¹P{¹H} spectrum shows a singlet with satellites due to coupling to the Sn nuclei at δ 58.54 ppm (²J_{Sn-P} = 164.7 Hz). The ¹¹⁹Sn{¹H} NMR spectrum displays a triplet at δ –140.25 ppm (²J_{Sn-P} = 170.8 Hz), which is comparable with that in the tin(II) β -diketiminate cation [HC(CMeNAr)₂Sn(OEt₂)][MeB(C₆F₅)₃] (Ar = 2,6-Pri₂C₆H₃, δ –139.50 ppm).¹⁶

The molecular structure of 7 (Figure 6, with selected bond lengths and angles in Table 1) shows that the Sn(1) atom is



Figure 6. Molecular structure of 7 with thermal ellipsoids at the 50% probability level.

coordinated with the thiophosphinoyl substituents and the $C_{methanediide}$ atom. The Sn(1)S(1)P(1)C(1)P(2)S(2) metallacycle adopts a pseudo-boat conformation in which the C(1) and Sn(1) atoms are displaced from the P(1)S(1)S(2)P(2) least-squares plane by 1.049 and 1.667 Å, respectively. Moreover, the geometry around the Sn(1) atom is distorted

Scheme 6. Proposed Mechanism for the Formation of 8



trigonal pyramidal (sum of bond angles 249.08°). This geometry indicates that the Sn(1) atom possesses a high-scharacter lone pair. The C(1)–Sn(1) bond (2.392(3) Å) is comparable with those in **5** and **6**. The C(1)–Al(1) bond (1.963(3) Å) is longer than that in **6**.

The transmetalation reaction of 5 with 2 equiv of AlMe₃ in CH_2Cl_2 afforded $[1,3-C_6H_4(PhP=S)_2CAlMe]_2$ (8). The byproducts are SnMe₄ and Me₃Sn-SnMe₃, which were confirmed by ¹¹⁹Sn{¹H} NMR spectroscopy. The reaction appears to proceed through the formation of $[1,3-C_6H_4(PhP=S)_2C(Sn)AlMe_3]$ (Scheme 6). The methyl groups are then transferred from the Al atom to the Sn atom, which leads to the formation of 8 and SnMe₂. Subsequently, the reactive SnMe₂ intermediate may decompose to form SnMe₄ and Me₃Sn-SnMe₃. The mechanism is similar to that proposed for the transmetalation reactions of transition-metal bis(thiophosphinoyl)methanediide complexes.¹ The X-ray crystal structure shows that compound 8 has a terminal C_{methanediide}-Al bond (see below), which is comparable with those of other aluminum bis(phosphinoyl)methanediide complexes such as $[(PPh_2=NSiMe_3)(PPh_2=S)CAIMe]_2^{14}$ and $[(PPh_2=S)CAIMe]_2^{14}$ $[(PPh_2=S)_2CAlCl]_2$

Compound 8 was isolated as a highly air- and moisturesensitive colorless crystalline solid, which is soluble only in CH₂Cl₂. The ¹H NMR spectrum shows signals for the Me substituent and phenyl protons. It is noteworthy that the ¹³C NMR signal for the C_{methanediide} atom cannot be observed. The ³¹P{¹H} spectrum displays a singlet at δ 52.43 ppm, which shows a downfield shift compared with that of [(PPh₂=S)₂CAlCl]₂ (δ 32.24 ppm).¹⁸

The molecular structure of **8** is comparable to that of $[(PPh_2=S)_2CAlCl]_2$ (Figure 7, with selected bond lengths and



Figure 7. Molecular structure of 8 with thermal ellipsoids at the 50% probability level. One of the two independent molecules in the asymmetric unit is shown. Solvent molecules are omitted for clarity.

angles in Table 1).¹⁸ The Al(1) atom is bonded to the $C_{methanediide}$ atom, the methyl substituent, and the thiophosphinoyl substituent of the adjacent ligand, which adopts a tetrahedral geometry. The C(1)–Al(1) bond (1.9469(17) Å) is slightly shorter than that in [(PPh₂=NSiMe₃)(PPh₂=S)-CAIMe]₂ (1.976(1) Å)¹⁴ and [(PPh₂=S)₂CAICl]₂ (1.975(2) Å).¹⁸ In addition, the C_{methanediide}–Al bond in 8 is slightly shorter than the C_{Me}–Al bond (1.9547(18) Å). According to the theoretical studies of [(PPh₂=NSiMe₃)(PPh₂=S)CAIMe]₂,¹⁴ it is suggested that the C_{methanediide}–Al bond in 8 is highly ionic and has

In conclusion, the tin(II) 1,3-benzobis(thiophosphinoyl)methanediide $[\{\mu-1,3-C_6H_4(PhP=S)_2C\}Sn]_2$ (5) undergoes an insertion reaction with AlCl₃ to form $[1,3-C_6H_4(PhP=S)_2C(Sn)\{Sn(S=PPh)_2C(AlCl_3)-1,3-C_6H_4\}]$ (6) and $[1,3-C_6H_4(PhP=S)_2C(Sn)(AlCl_3)]$ (7). Compound 5 also undergoes a transmetalation reaction with 2 equiv of AlMe₃ in CH₂Cl₂ to afford $[1,3-C_6H_4(PhP=S)_2CAlMe]_2$ (8).

EXPERIMENTAL SECTION

weak covalent binding.

All manipulations were carried out under an inert atmosphere of nitrogen gas using standard Schlenk techniques. Et₂O, THF, and toluene were dried over and distilled over Na/K alloy prior to use. CH₂Cl₂ was dried over and distilled over CaH₂ prior to use. **1** was prepared as described in the literature.¹⁵ The ¹H, ¹³C, ³¹P, and ¹¹⁹Sn NMR spectra were recorded on a JEOL ECA 400 spectrometer. The chemical shifts δ are relative to SiMe₄ for ¹H and ¹³C, SnMe₄ for ¹¹⁹Sn, and 85% H₃PO₄ for ³¹P. Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

[(PPh2=S)2CHK] (2). BunLi (1.8 mL, 3.6 mmol, 2 M solution in cyclohexane) was added slowly to a solution of 1 (1.57 g, 3.5 mmol) in THF (20 mL) at -78 °C. The yellow solution was warmed to ambient temperature and stirred overnight. The resulting solution was then added dropwise to a solution of Bu^tOK (0.39 g, 3.5 mmol) in THF (5 mL) at -78 °C. The yellow solution was warmed to ambient temperature and stirred for 24 h. Volatiles were removed under reduced pressure. After washing with hexane, the residue was extracted by Et₂O/THF (1:1, 30 mL). The insoluble precipitate was filtered. The filtrate was concentrated to give compound 2 as pale yellow crystals. Yield: 1.24 g (73%). Mp: 305 °C. Anal. Calcd for C₂₅H₂₁KP₂S₂: C, 61.71; H, 4.35. Found: C, 61.51; H 4.35. ¹H NMR (399.5 MHz, THF- d_{8} , 21.5 °C): δ 1.48 (t, ${}^{2}J_{P-H}$ = 2.32 Hz, 1H, PCHP), 7.18-7.21 (m, 12H, Ph), 8.00-8.05 ppm (m, 8H, Ph). ¹³C{¹H} NMR (100.5 MHz, THF- d_{8} , 21.5 °C): δ 20.12 (t, PCP, J_{P-C} = 107.3 Hz), 126.73 (t, ${}^{3}J_{P-C}$ = 5.75 Hz, C_{meta} of Ph), 128.24 (s, C_{para} of Ph), 131.47 (t, ${}^{2}J_{C-P}$ = 5.76 Hz, C_{ortho} of Ph), 142.97 ppm (dd, J_{P-C} = 96.9 Hz, ${}^{3}J_{\mathrm{P'-C}}$ = 2.87 Hz, C_{ipso} of Ph). ${}^{31}\mathrm{P}\{{}^{1}\mathrm{H}\}$ NMR (161.7 MHz, THF- d_{g} , 21.7 °C): δ 38.03 ppm.

[1,3-C₆H₄(PhP=S)₂CHK·3THF] (3). Method A. BuⁿLi (1.8 mL, 3.6 mmol, 2 M solution in cyclohexane) was added slowly to a solution of 1 (1.34 g, 3.0 mmol) and Bu^tOK (0.34 g, 3.0 mmol) in THF (20 mL) at ambient temperature. The orange solution was refluxed at 70 °C overnight to give a reddish brown solution. Volatiles were removed under vacuum, and Et₂O was added to the residue to afford a

red solid after 16 h. The red solid was then recrystallized in THF to give compound 3 as orange crystals. Yield: 0.88 g (47%).

Method B. PhLi (0.5 mL, 1.0 mmol, 2 M solution in dibutyl ether) was added slowly to a solution of 2 (0.48 g, 1.0 mmol) in THF (10 mL) at ambient temperature. The orange solution was refluxed at 70 °C overnight to give a reddish brown solution. Volatiles were removed under vacuum, and the residue was extracted by Et_2O . After filtration, a red crystalline solid was obtained in the filtrate. The red solid was then recrystallized in THF to give compound 3 as orange crystals. Yield: 0.17 g (27%).

Mp: 274 °C dec. Anal. Calcd for C₃₁H₃₉KO₃P₂S₂: C, 59.59; H, 6.30. Found: C, 59.54; H, 6.31. ¹H NMR (399.5 MHz, THF- d_8 , 21.5 °C): δ 1.35 (t, ²J_{P-H} = 11.2 Hz, 1H, PCHP), 7.22–7.33 (m, 8H, Ph and C₆H₄), 7.52–7.58 (m, 2H, Ph and C₆H₄), 8.00–8.06 ppm (m, 4H, Ph and C₆H₄). ¹³C{¹H} NMR (100.5 MHz, THF- d_8 , 21.5 °C): δ 26.0 (t, J_{P-C} = 101.1 Hz, PCP), 127.76 (t, ³J_{P-C} = 6.71 Hz, C_{meta} of Ph), 128.90 (t, ²J_{P-C} = 11.5 Hz, C₆H₄), 129.68 (s, C_{para} of Ph), 130.14 (t, ³J_{P-C} = 3.83 Hz, C₆H₄), 131.94 (t, ²J_{P-C} = 4.79 Hz, C_{ortho} of Ph), 143.61 (t, J_{P-C} = 44.1 Hz, C_{ipso} of Ph/C₆H₄), 144.63 ppm (t, J_{P-C} = 52.7 Hz, C_{ipso} of Ph/C₆H₄). ³¹P{¹H} NMR (161.7 MHz, THF- d_8 , 21.9 °C): δ 44.12 ppm.

[1,3-C₆H₄(PhP=S)₂CH₂] (4). Excess degassed H₂O was added to a solution of 3 (1.87 g, 3.0 mmol) in THF (20 mL) at room temperature. The resulting pale yellow suspension was stirred at room temperature for 1 h. Volatiles were removed under reduced pressure. The residue was washed with 10 mL of toluene. The pale yellow residue was then extracted by CH₂Cl₂/hexane (1/1). After filtration and concentration of the filtrate, compound 4 was obtained as pale yellow crystals. Yield: 0.93 g (84%). Mp: 172 °C. Anal. Calcd for C₁₉H₁₆P₂S₂: C, 61.62; H, 4.36. Found: C, 61.29; H, 4.29. ¹H NMR (395.9 MHz, CDCl₃, 21.6 °C): δ 3.26 (quartet, ²J_{P-H} = 15.9 Hz, 1H, PCH₂P), 3.61 (m, 1H, PCH₂P), 7.12–7.18 (m, 4H, Ph and C₆H₄), 7.27–7.32 (m, 6H, Ph and C₆H₄), 7.37–7.79 (m, 2H, Ph and C₆H₄), 7.91–7.99 ppm (m, 2H, Ph and C₆H₄). ¹³C{¹H} NMR (100.5 MHz, THF-d₈, 21.7 °C): δ 41.62 (t, J_{P-C} = 40.0 Hz, PCP), 129.41 (d, ³J_{P-C} = 6.71 Hz, C_{meta} of Ph), 131.49 (d, ²J_{P-C} = 11.4 Hz, C₆H₄), 131.70 (t, ³J_{P-C} = 10.5 Hz, C₆H₄), 132.43 (s, C_{para} of Ph), 134.38 (d, ²J_{P-C} = 11.4 Hz, C_{ortho} of Ph), 135.60 (d, J_{P-C} = 5.7 Hz, C₆H₄), 140.17 ppm (dd, J_{P-C} = 86.8 Hz, ³J_{P'-C} = 15.3 Hz, C_{ipso} of Ph). ³¹P{¹H} NMR (160.2 MHz, CDCl₃, 21.8 °C): δ 45.80 ppm.

[{µ-1,3-C₆H₄(PhP=S)₂C}Sn]₂ (5). Toluene (30 mL) was added to a mixture of 4 (1.11 g, 3.0 mmol) and $Sn[N(SiMe_3)_2]_2$ (1.40 g, 3.2 mmol) at ambient temperature. The orange suspension was then refluxed at 140 °C overnight. After filtration, the residue was then extracted by CH₂Cl₂. After filtration and concentration of the filtrate, 5 was isolated as yellow crystals. Yield: 1.42 g (83%). Mp: 230 °C dec. Anal. Calcd for C38H28P4S4Sn2: C, 46.85; H, 2.90. Found: C, 46.79; H, 2.87. ¹H NMR (395.9 MHz, CDCl₃, 23.2 °C): δ 7.37-7.43 (m, 8H, Ph and C₆H₄), 7.47–7.51 (m, 4H, Ph and C₆H₄), 7.61–7.73 ppm (m, 16H, Ph and C₆H₄). ¹³C{¹H} NMR (99.5 MHz, CD₂Cl₂, 21.4 °C): δ 129.17 (m, C_{meta} of Ph and C_6H_4), 130.84 (d, ${}^2J_{C-P}$ = 12.4 Hz, C_6H_4), 132.26 (s, C_{para} of Ph), 137.11 (d, J_{C-P} = 80.11 Hz, C_6H_4), 143.18 ppm (dd, $J_{P-C} = 75.3 \text{ Hz}$, ${}^{3}J_{P'-C} = 23.8 \text{ Hz}$, C_{ipso} of Ph). ${}^{31}P{}^{1}H{}$ NMR (161.7 MHz, CDCl₃, 23.4 °C): δ 54.91 ppm (² $J_{\text{Sn-P}}$ = 47.7, 160.4 Hz). ¹¹⁹Sn{¹H} NMR (147.6 MHz, CDCl₃, 23.2 °C): δ 26.28 ppm (t, ${}^{2}J_{\mathrm{Sn-P}} = 50.2 \mathrm{~Hz}$).

[1,3-C₆H₄(PhP=S)₂C(Sn){Sn(S=PPh)₂C(AlCl₃)-1,3-C₆H₄] (6). A solution of 5 (0.57 g, 0.6 mmol) in CH₂Cl₂ (30 mL) was added to a suspension of AlCl₃ (0.06 g, 0.5 mmol) in CH₂Cl₂ (10 mL) at ambient temperature. The resulting yellow suspension was stirred overnight to give a clear yellow solution. After filtration, the filtrate was concentrated to give compound 6 as yellow crystals. Yield: 0.31 g (56%). Mp 225 °C dec. Anal. Calcd for C₃₈H₂₈AlCl₃P₄S₄Sn₂: C, 41.20; H, 2.55. Found: C, 41.13; H, 2.46. ¹H NMR (395.9 MHz, CDCl₃, 21.6 °C): δ 7.34-7.94 ppm (m, 28H, Ph and C₆H₄). ¹³C{¹H} NMR (99.5 MHz, CDCl₃, 21.8 °C): δ 128.6-129.0 (m, Ph and C₆H₄), 130.3-130.4 (m, C_{ortho} of Ph and C₆H₄), 131.68 (s, C_{para} of Ph), 132.24-132.37 (m, C₆H₄), 133.81-134.09 ppm (m, C_{ipso} of Ph). ³¹P{¹H} NMR (160.3 MHz, CDCl₃, 22.2 °C): δ 55.05 (²J_{Sn-P} = 47.7 Hz, ${}^{2}J_{\text{Sn}^{-P}} = 160.4 \text{ Hz}, PCP)$ and 58.45 ppm (${}^{2}J_{\text{Sn}^{-P}} = 164.7 \text{ Hz}, PC(\text{AlCl}_{3})P$). ${}^{119}\text{Sn}{}^{1}\text{H}$ NMR (147.6 MHz, CD₂Cl₂, 23.2 °C): δ 22.15 (t, ${}^{2}J_{\text{Sn}^{-P}} = 48.1 \text{ Hz}$), -160.40 ppm (t, ${}^{2}J_{\text{Sn}^{-P}} = 164.3 \text{ Hz}$).

 $[1,3-C_6H_4(PhP=S)_2C(Sn)(AlCl_3)]$ (7). A solution of 5 (0.57 g, 0.6 mmol) in CH₂Cl₂ (30 mL) was added to a suspension of AlCl₃ (0.13 g, 1.0 mmol) in CH₂Cl₂ (10 mL) at ambient temperature. The resulting yellow suspension was stirred overnight to give a clear yellow solution. After filtration, the filtrate was concentrated to give compound 7 as colorless crystals. Yield: 0.39 g (63%). Mp 257 °C dec. Anal. Calcd for C₁₉H₁₄AlCl₃P₂S₂Sn: C, 36.77; H, 2.28. Found: C, 36.64; H, 2.17. ¹H NMR (395.9 MHz, CDCl₃, 22.7 °C): δ 7.51–7.63 (m, 6H, Ph and C₆H₄), 7.69–7.76 (m, 4H, Ph and C₆H₄), 7.88–7.94 ppm (m, 4H, Ph and C_6H_4). ¹³C{¹H} NMR (99.5 MHz, CDCl₃, 21.8 °C): δ 128.64–129.06 (m, $C_{\rm meta}$ of Ph and $C_{6}{\rm H_{4}}),$ 132.19–132.41 (m, C_{ortho} of Ph and C_6H_4), 133.85–133.93 (m, C_6H_4), 134.01 (s, C_{para} of Ph), 142.46 ppm (dd, J_{P-C} = 80.11 Hz, $J_{P'-C}$ = 21.93 Hz, C_{ipso} of Ph). ³¹P{¹H} NMR (160.3 MHz, CDCl₃, 14.6 °C): δ 58.54 ppm (² J_{Sn-P} = 164.7 Hz). ¹¹⁹Sn{¹H} NMR (147.6 MHz, CDCl₃, 23.2 °C): δ –140.25 ppm $({}^{2}J_{\text{Sn-P}} = 170.8 \text{ Hz}).$

[1,3-C₆H₄(PhP=S)₂CAIMe]₂ (8). AlMe₃ (0.5 mL, 1.0 mmol, 2 M solution in toluene) was added to a solution of **5** (0.57 g, 0.5 mmol) in CH₂Cl₂ (30 mL) at 0 °C. The resulting orange solution was stirred overnight. After filtration, the orange filtrate was concentrated to give compound **8** as yellow crystals. Yield: 0.21 g (51%). Mp: 266 °C dec. Anal. Calcd for C₄₀H₃₄Al₂P₄S₄: C, 58.54; H, 4.18. Found: C, 58.21; H, 3.95. ¹H NMR (399.5 MHz, CDCl₃): δ –1.03 (s, 6H, AlMe), 7.45–7.61 (m, 20H, Ph and C₆H₄), 7.92–7.97 ppm (m, 8H, Ph and C₆H₄). ¹³C{¹H} NMR (100.5 MHz, CDCl₃, 22.7 °C): δ 1.18 (s, AlMe), 127.90 (t, ³J_{P-C} = 11.5 Hz, C_{meta} of Ph), 128.43–128.57 (m, C₆H₄), 133.74 (dd, J_{P-C} = 84.8 Hz, ³J_{P'-C} = 4.79 Hz, C₆H₄), 143.41 ppm (dd, J_{P-C} = 83.87 Hz, ³J_{P'-C} = 23.0 Hz, C_{ipso} of Ph). ³¹P{¹H} NMR (161.7 MHz, CDCl₃): δ 52.43 ppm.

X-ray Data Collection and Structural Refinement. Intensity data for compounds 2–8 were collected using a Bruker APEX II diffractometer. The crystals of 2–8 were measured at 103(2) K. The structures were solved by direct phase determination (SHELXS-97) and refined for all data by full-matrix least-squares methods on $F^{2,19}$ All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotopic thermal parameters and included in the structure factor calculations. The X-ray crystallographic data of 2–8 are summarized in Table S1 (see the Supporting Information).

ASSOCIATED CONTENT

S Supporting Information

CIF files giving X-ray data for 2-8 and a table giving crystallographic data of 2-8. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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