

# Synthesis and characterization of Group 11 and 12 complexes containing a new thioether-functionalized and pyridine-based bis(phosphine) ligand, 2,6-bis[2-(diphenylphosphino)ethylsulfanylmethyl]pyridine

Shan-Ming Kuang,<sup>a</sup> Zheng-Zhi Zhang<sup>\*.b</sup> and Thomas C. W. Mak<sup>\*.a</sup>

<sup>a</sup> The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

<sup>b</sup> Elemento-Organic Chemistry Laboratory, Nankai University, Tianjin, China

The new ligand 2,6-bis[2-(diphenylphosphino)ethylsulfanylmethyl]pyridine, 2,6-(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N (L<sup>1</sup>), has been synthesized. Reaction of [Cu(MeCN)<sub>4</sub>][CF<sub>3</sub>SO<sub>3</sub>] or AgNO<sub>3</sub> with 1 molar equivalent of L<sup>1</sup> gave [CuL<sup>1</sup>][CF<sub>3</sub>SO<sub>3</sub>] **1** or [AgL<sup>1</sup>][NO<sub>3</sub>] **2**, in good yield. Reaction of equimolar quantities of L<sup>1</sup> and Au<sup>I</sup>, followed by precipitation with AgO<sub>3</sub>SCF<sub>3</sub>, gave [AuL<sup>1</sup>][CF<sub>3</sub>SO<sub>3</sub>] **3**. In the crystal structure of 2·H<sub>2</sub>O, L<sup>1</sup> co-ordinates to Ag via a P<sub>2</sub>S<sub>2</sub> donor set in a distorted tetrahedral geometry. Reaction of M(O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub> (M = Zn or Cd) with 1 molar equivalent of L<sup>1</sup> gave [ML<sup>1</sup>(O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub>] (M = Zn **4** or Cd **5**). Crystal structure analysis of **5** showed that the molecule has symmetry 2, with all five donor atoms of L<sup>1</sup> and a pair of monodentate CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> ligands arranged in an unusual distorted pentagonal bipyramidal co-ordination geometry about the cadmium centre.

Acyclic phosphine ligands are well known to form stable complexes with many metal ions, whereas acyclic thioether complexes tend to be less stable and often hydrolyse readily.<sup>1</sup> As the NS<sub>2</sub> donor set in 2,6-bis(*R*-sulfanylmethyl)pyridine has been found to be good for the stabilization of transition-metal ions,<sup>2</sup> we reasoned that the incorporation of heteroatom donors, such as nitrogen or sulfur, on sites within a diphosphine bridge might result in transition-metal complexes co-ordinated by sulfur (or nitrogen) and the phosphorus centres. We anticipated that, as phosphines are better σ donors compared to thioethers, stabilization of a mixed phosphine–thioether co-ordination complex could be achieved by inhibiting decomplexation of the more weakly bound thioether in solution. In this context, recent reports by Darensbourg and co-workers<sup>3</sup> and Reid and co-workers<sup>4</sup> have demonstrated the development and co-ordination chemistry of dithiobis(phosphine) chelates. We report here the synthesis and characterization of Group 11 and 12 complexes with a new thioether-functionalized and pyridine-based bis(phosphine) ligand, 2,6-bis[2-(diphenylphosphino)ethylsulfanylmethyl]pyridine, 2,6-(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>)<sub>2</sub>-C<sub>5</sub>H<sub>3</sub>N (L<sup>1</sup>), which displays an unusual co-ordination mode toward Cd<sup>2+</sup>.

## Experimental

### General procedure, measurement and materials

All reactions were routinely carried out under a nitrogen atmosphere using Schlenk techniques. The solvents were purified by standard methods. The <sup>1</sup>H and <sup>13</sup>C-<sup>1</sup>H} NMR spectra were recorded on a Bruker-300 spectrometer using SiMe<sub>4</sub> as the external standard and CDCl<sub>3</sub> as solvent, <sup>31</sup>P-<sup>1</sup>H} NMR spectra on a Bruker-500 spectrometer at 202.45 MHz using (PhO)<sub>3</sub>P as the external standard and CDCl<sub>3</sub> as solvent and mass spectra on a Hewlett-Packard 5989B spectrometer. The compounds [Cu(MeCN)<sub>4</sub>][CF<sub>3</sub>SO<sub>3</sub>]<sup>5</sup> and M(O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub> (M = Zn or Cd)<sup>6</sup> were prepared by the literature procedures.

### Preparations

**2,6-Bis[2-(diphenylphosphino)ethylsulfanylmethyl]pyridine, L<sup>1</sup>.** A solution of LiBu<sup>n</sup> in hexane (1.60 M, 17.0 cm<sup>3</sup>) was added dropwise to a solution of Ph<sub>2</sub>PH (4.65 g, 25 mmol) in tetrahy-

drofuran (thf, 50 cm<sup>3</sup>) at -78 °C. To this mixture, a solution of ethylene sulfide (thiirane) (1.50 cm<sup>3</sup>, 25 mmol) in thf (20 cm<sup>3</sup>) was added. The resulting solution was continuously stirred until 0 °C was reached, and a solution of 2,6-bis(chloromethyl)pyridine (2.20 g, 12.5 mmol) in thf (80 cm<sup>3</sup>) was then added over a period of 3 h with the temperature maintained at 0 °C. After the addition the mixture was stirred at room temperature for 48 h. The thf was removed in vacuum and water (100 cm<sup>3</sup>) added. The water phase was next extracted with diethyl ether (3 × 50 cm<sup>3</sup>) and the organic phase dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> overnight. Most of the diethyl ether was removed in vacuum and hexane (100 cm<sup>3</sup>) was added. Cooling to -30 °C for 8 h yielded a colourless solid. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>–hexane afforded L<sup>1</sup> as an analytically pure product, 5.30 g (71%) (Found: C, 70.24; H, 5.88; N, 2.27. C<sub>35</sub>H<sub>35</sub>NP<sub>2</sub>S requires C, 70.56; H, 5.92; N, 2.35%), m.p. 52–53 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.52 (t, *J* = 3.5, 1 H), 7.36–7.25 (m, 20 H), 7.05 (d, *J* = 2.2 Hz, 2 H), 3.73 (s, 4 H), 2.50 (m, 4 H) and 2.26 (m, 4 H). <sup>13</sup>C-<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 28.73 (d, *J* = 20.3), 28.96 (d, *J* = 14.9 Hz), 38.56 (s) and 121.65–138.57 (m). <sup>31</sup>P-<sup>1</sup>H} NMR: δ -4.54. FAB mass spectrum: *m/z* = 596; Calc. 595 for (Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>-SCH<sub>2</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N.

**[CuL<sup>1</sup>][CF<sub>3</sub>SO<sub>3</sub>] **1**.** To a solution containing compound L<sup>1</sup> (0.30 g, 0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>) was added solid [Cu(MeCN)<sub>4</sub>][CF<sub>3</sub>SO<sub>3</sub>] (0.19 g, 0.5 mmol). The resulting solution was stirred at room temperature for 2 h. Subsequent diffusion of diethyl ether into the concentrated solution gave complex **1** as air-stable colourless crystals (yield 0.34 g, 84%) (Found: C, 53.21; H, 4.71; N, 1.78. C<sub>36</sub>H<sub>35</sub>CuF<sub>3</sub>NO<sub>3</sub>P<sub>2</sub>S<sub>3</sub> requires C, 53.49; H, 4.36; N, 1.73%). <sup>31</sup>P-<sup>1</sup>H} NMR: δ 34.72.

**[AgL<sup>1</sup>][NO<sub>3</sub>] **2**.** The procedure used was similar to that above, except that AgNO<sub>3</sub> (0.09 g, 0.5 mmol) was employed instead of [Cu(MeCN)<sub>4</sub>][CF<sub>3</sub>SO<sub>3</sub>]. Recrystallization of the product from CH<sub>2</sub>Cl<sub>2</sub>–diethyl ether afforded complex 2·H<sub>2</sub>O as colourless crystals. Yield: 0.29 g (76%) (Found: C, 54.99; H, 4.61; N, 3.55. C<sub>35</sub>H<sub>35</sub>AgN<sub>2</sub>O<sub>3</sub>P<sub>2</sub>S<sub>2</sub>·H<sub>2</sub>O requires C, 54.86; H, 4.72; N, 3.57%). <sup>31</sup>P-<sup>1</sup>H} NMR: δ 43.14.

**[AuL<sup>1</sup>][CF<sub>3</sub>SO<sub>3</sub>] **3**.** The complex K[AuCl<sub>4</sub>]·2H<sub>2</sub>O (0.10 g, 0.25 mmol) was reduced to Au<sup>I</sup> by 2,2'-thiodiethanol (0.06 g, 0.5

mmol) in methanol (20 cm<sup>3</sup>) for 30 min. Compound L<sup>1</sup> (0.15 g, 0.25 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) was added and stirred for 10 min, and then AgO<sub>3</sub>SCF<sub>3</sub> (0.26 g, 1.0 mmol) in methanol (20 cm<sup>3</sup>) was added to the mixture and stirred for 30 min. Filtration followed by solvent removal and subsequent recrystallization from CH<sub>2</sub>Cl<sub>2</sub>–hexane afforded complex **3** as colourless crystals. Yield: 0.15 g (81%) (Found: C, 45.78; H, 3.77; N, 1.41. C<sub>36</sub>H<sub>35</sub>AuF<sub>3</sub>NO<sub>3</sub>P<sub>2</sub>S<sub>3</sub> requires C, 45.91; H, 3.75; N, 1.49%). <sup>31</sup>P-<sup>1</sup>H} NMR: δ 42.91.

[ZnL<sup>1</sup>][CF<sub>3</sub>SO<sub>3</sub>]<sub>2</sub> **4**. To a solution containing compound L<sup>1</sup> (0.30 g, 0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>) was added solid Zn(O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub> (0.18 g, 0.5 mmol). The resulting solution was stirred at room temperature for 2 h. Subsequent diffusion of diethyl ether into the concentrated solution gave complex **4** as air-stable colourless crystals (yield 0.40 g, 77%) (Found: C, 43.95; H, 3.67; N, 1.33. C<sub>37</sub>H<sub>35</sub>F<sub>6</sub>NO<sub>3</sub>P<sub>2</sub>S<sub>4</sub>Zn·CH<sub>2</sub>Cl<sub>2</sub> requires C, 43.71; H, 3.57; N, 1.34%). <sup>31</sup>P-<sup>1</sup>H} NMR: δ 56.53.

[CdL<sup>1</sup>(O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub>] **5**. The procedure used was similar to that above, except that Cd(O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub> (0.21 g, 0.5 mmol) was used instead of Zn(O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub>. Recrystallization of the product from CH<sub>2</sub>Cl<sub>2</sub>–hexane afforded complex **5** as colourless crystals. Yield: 0.32 g (64%) (Found: C, 43.37; H, 3.49; N, 1.34. C<sub>37</sub>H<sub>35</sub>CdF<sub>6</sub>NO<sub>3</sub>P<sub>2</sub>S<sub>4</sub> requires C, 44.16; H, 3.51; N, 1.39%). <sup>31</sup>P-<sup>1</sup>H} NMR: δ 55.09.

### X-Ray crystallography

Intensity data for complexes **2**·H<sub>2</sub>O and **5** were collected at 294 K in the variable ω-scan mode on a four-circle diffractometer (Siemens R3m/V) using Mo-Kα radiation (λ = 0.710 73 Å, 50 kV, 25 mA; 2θ<sub>min</sub> = 3, 2θ<sub>max</sub> = 55°). Empirical absorption corrections were applied by fitting a pseudo-ellipsoid to the ψ-scan data of 25 selected strong reflections over a range of 2θ angles.<sup>7a</sup>

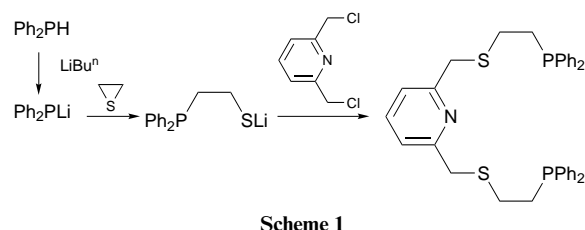
Structure solution by the direct method yielded the positions of all non-hydrogen atoms, which were refined using anisotropic thermal parameters. Hydrogen atoms were all generated geometrically (C–H bond lengths fixed at 0.96 Å), assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All the H atoms were held stationary and included in the structure-factor calculation in the final stage of full-matrix least-squares refinement. All computations were performed on an IBM-compatible 486 personal computer with the SHELTX PC, version 5.03, program package.<sup>7b</sup>

Information concerning X-ray data collection and structure refinement of all compounds is summarized in Table 1.

CCDC reference number 186/780.

### Results and Discussion

The synthesis of a new thioether-functionalized and pyridine-based bis(phosphine) ligand, namely 2,6-bis[2-(diphenylphosphino)ethylsulfanyl]methylpyridine (L<sup>1</sup>), was accomplished in two steps in good yield, as outlined in Scheme 1. Reaction of Ph<sub>2</sub>PLi (prepared *in situ* from Ph<sub>2</sub>PH and LiBu<sup>n</sup>) with ethylene sulfide at low temperature gave the lithium 2-diphenylphosphinoethanethiolate salt, which then reacted with 2,6-bis-(chloromethyl)pyridine to give the designed phosphine ligand. The structure of 2,6-(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N, L<sup>1</sup>, was confirmed by elemental analysis and <sup>1</sup>H, <sup>13</sup>C-<sup>1</sup>H}, <sup>31</sup>P-<sup>1</sup>H} NMR spectroscopy and FAB mass spectrometry. In the <sup>1</sup>H NMR spectrum the SCH<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N methylene protons appeared as a singlet at δ 3.73 and two groups of signals attributed to the SCH<sub>2</sub>CP and SCCH<sub>2</sub>P methylene protons coupled with the phosphorus atoms were observed at δ 2.50 and 2.26. In the <sup>13</sup>C-<sup>1</sup>H} NMR spectrum the SCC<sub>5</sub>H<sub>3</sub>N carbon atom appeared as a singlet at δ 38.56, whereas the SCCP carbon atoms appeared as



Scheme 1

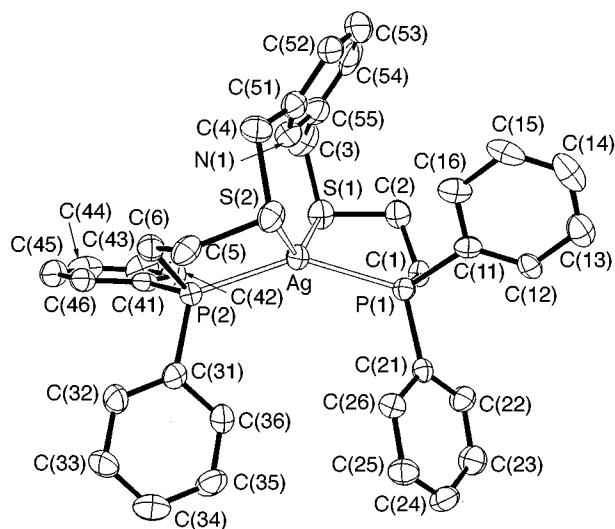


Fig. 1 Perspective view of the cation in [Ag{(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>)<sub>2</sub>-C<sub>5</sub>H<sub>3</sub>N}][NO<sub>3</sub>]·H<sub>2</sub>O, 2·H<sub>2</sub>O. The atoms are shown as 35% thermal ellipsoids

a pair of doublets centred at δ 28.73 (*J* = 20.3) and 28.96 (*J* = 14.9 Hz). On the basis of literature data for P–C coupling constants<sup>8</sup> and the observed chemical shifts for related phosphine-containing ligands, we assigned the first and second doublets to the carbon atoms located in the α and β positions, respectively, with respect to the phosphorus atom. The FAB mass spectrum showed the molecular ion at *m/z* = 596, and the <sup>31</sup>P-<sup>1</sup>H} NMR spectrum exhibited a singlet at δ –4.54.

Reaction of [Cu(MeCN)<sub>4</sub>][CF<sub>3</sub>SO<sub>3</sub>] or AgNO<sub>3</sub> with 1 molar equivalent of L<sup>1</sup> in degassed dichloromethane, followed by precipitation with diethyl ether, gave [CuL<sup>1</sup>][CF<sub>3</sub>SO<sub>3</sub>] **1** or [AgL<sup>1</sup>][NO<sub>3</sub>] **2**, as white solids in good yield. Reaction of equimolar amounts of L<sup>1</sup> and Au<sup>I</sup>, generated *in situ* by the reduction of K[AuCl<sub>4</sub>] with 2,2'-thiodiethanol in methanol, gave a colourless solution at room temperature. Addition of AgO<sub>3</sub>SCF<sub>3</sub> to the solution precipitated [AuL<sup>1</sup>][CF<sub>3</sub>SO<sub>3</sub>] **3**, as a white solid.

The <sup>31</sup>P-<sup>1</sup>H} NMR spectra of complexes **1** and **2** at 298 K showed a singlet at δ 34.72 and 43.14, respectively, and no Ag–P coupling was observed for **2**. For complex **3** the <sup>31</sup>P-<sup>1</sup>H} NMR spectrum displayed a high-frequency shift of 47.4 ppm relative to the free phosphine. This shift is similar to those of the complexes [Au{(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>)<sub>2</sub>}][PF<sub>6</sub>] (49.2 ppm) and [Au{(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>}][PF<sub>6</sub>] (46.1 ppm),<sup>4b</sup> both of which involve averaged P<sub>2</sub> co-ordination in solution. In view of the similarity of these species, we expect that in the solid state **3** also adopts a similar primary P<sub>2</sub> co-ordination about Au<sup>I</sup> and a distorted linear geometry.

Crystals of [AgL<sup>1</sup>][NO<sub>3</sub>]·H<sub>2</sub>O suitable for single-crystal X-ray study were obtained by layering a solution of the complex in CH<sub>2</sub>Cl<sub>2</sub> at ca. –20 °C with toluene. The structure of the molecular cation with the atom numbering scheme is depicted in Fig. 1. The co-ordination geometry around silver(I) may be described as a very distorted tetrahedron with a P–Ag–P angle of 144.4(1)° (Table 2), far higher than the idealized value of 109.5°. This is certainly caused by the repulsion between two phenyl rings [C(26)⋯C(36) 3.690 Å] which has the further consequence of narrowing the S–Ag–P bond angles to 80.2(1) and 81.3(1)°. A similar effect has been reported in [Ag(Ph<sub>2</sub>P-

**Table 1** Crystal and structural data for complexes **2**·H<sub>2</sub>O and **5**

Formula	C <sub>35</sub> H <sub>35</sub> AgN <sub>2</sub> O <sub>3</sub> P <sub>2</sub> S <sub>2</sub> ·H <sub>2</sub> O <b>2</b> ·H <sub>2</sub> O	C <sub>37</sub> H <sub>35</sub> CdF <sub>6</sub> NO <sub>6</sub> P <sub>2</sub> S <sub>4</sub> <b>5</b>
<i>M</i>	783.6	1006.2
Crystal system	Orthorhombic	Trigonal
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 3 <sub>2</sub> 21
<i>a</i> /Å	9.875(1)	18.072(3)
<i>b</i> /Å	12.585(5)	18.072(3)
<i>c</i> /Å	28.362(3)	12.099(2)
<i>U</i> /Å <sup>3</sup>	3524.7(12)	3425(2)
<i>Z</i>	4	3
<i>F</i> (000)	1608	1524
<i>D</i> <sub>c</sub> /g cm <sup>-3</sup>	1.477	1.464
<i>μ</i> /cm <sup>-1</sup>	0.821	0.797
Goodness of fit	1.22	1.10
No. unique reflections ( <i>R</i> <sub>int</sub> )	4909 (0.027)	4876 (0.030)
No. observed reflections [ <i> F</i>   ≥ 4σ( <i>F</i> )]	3183	4561
No. variables, <i>p</i>	410	263
<i>R</i> <sub>F</sub> <sup>a</sup>	0.053	0.049
<i>R</i> <sub>F</sub> <sup>2b</sup>	0.087	0.052

<sup>a</sup> Σ(|*F*<sub>o</sub>| - |*F*<sub>c</sub>|)/Σ|*F*<sub>o</sub>|. <sup>b</sup> {w[Σ(|*F*<sub>o</sub>| - |*F*<sub>c</sub>|)<sup>2</sup>]/Σ|*F*<sub>o</sub>|<sup>2</sup>]<sup>1/2</sup>.

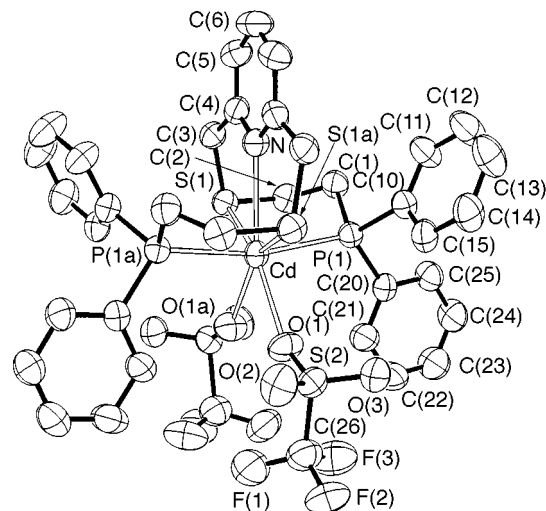
**Table 2** Selected bond lengths (Å) and angles (°) of complexes **2**·H<sub>2</sub>O and **5**

<b>2</b> ·H <sub>2</sub> O			
Ag–P(1)	2.455(3)	Ag–P(2)	2.448(3)
Ag–S(1)	2.869(3)	Ag–S(2)	2.846(3)
P(1)–Ag–P(2)	144.4(1)	P(1)–Ag–S(1)	80.2(1)
P(1)–Ag–S(2)	110.5(1)	P(2)–Ag–S(1)	111.2(1)
S(1)–Ag–S(2)	142.7(1)	P(2)–Ag–S(2)	81.3(1)
<b>5</b>			
Cd–P(1)	2.590(1)	Cd–S(1)	2.821(1)
Cd–O(1)	2.455(2)	Cd–N(1)	2.695(3)
P(1)–Cd–S(1)	79.9(1)	P(1)–Cd–O(1)	97.1(1)
S(1)–Cd–O(1)	75.8(1)	P(1)–Cd–N(1)	83.4(1)
S(1)–Cd–N(1)	70.1(1)	O(1)–Cd–N(1)	145.2(1)
P(1)–Cd–P(1a)	166.8(1)	S(1)–Cd–S(1a)	140.1(1)
O(1)–Cd–O(1a)	69.5(2)	P(1)–Cd–S(1a)	95.6(1)
P(1)–Cd–O(1a)	93.8(1)	S(1)–Cd–O(1a)	143.7(1)

CH<sub>2</sub>CH<sub>2</sub>SEt<sub>2</sub>][ClO<sub>4</sub>] with a P–Ag–P angle of 148.9(1)°.<sup>9</sup> The Ag(1)···N(1) distance of 2.689 Å, much longer than the corresponding distance of 2.368(6) Å in [AgL<sup>2</sup>][PF<sub>6</sub>] [L<sup>2</sup> = 6,9,12-trioxa-3,15-dithia-21-azabicyclo[15.3.1]henicosa-1(21),17,19-triene],<sup>10</sup> indicates that the Ag···N interaction is very feeble, which is consistent with the fact that the nitrogen lone pair does not point directly toward the silver atom (Fig. 1). The Ag–P distances of 2.455(3) and 2.448(3) Å are within the expected range for silver tertiary phosphine complexes. The Ag–S distances of 2.869(3) and 2.846(3) Å, which are longer than 2.694(2) Å in [Ag(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>SEt<sub>2</sub>)]<sub>2</sub>[ClO<sub>4</sub>]<sup>9</sup> and 2.589(2) Å (average) in [Ag<sub>n</sub>(PhSCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SPh)<sub>2n</sub>][BF<sub>4</sub>]<sub>n</sub>·0.5*n*H<sub>2</sub>O,<sup>11</sup> suggest that the silver ion is weakly bound to the sulfur atoms.

Reactions of M(O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub> (M = Zn or Cd) with 1 molar equivalent of L<sup>1</sup> in dichloromethane at room temperature gave a colourless solution which on addition of diethyl ether gave [ML<sup>1</sup>(O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub>] (M = Zn **4** or Cd **5**). The <sup>31</sup>P-{<sup>1</sup>H} NMR spectra of **4** and **5** at 298 K showed a singlet at δ 56.53 and 55.09, respectively, and no Cd–P coupling was observed for **5**.

Diffraction-quality crystals of [CdL<sup>1</sup>(O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub>] **5** were obtained by vapour diffusion of diethyl ether into a solution of the complex in CH<sub>2</sub>Cl<sub>2</sub> at room temperature. A perspective view of the molecular structure of **5**, which possesses a crystallographically imposed two-fold axis passing through Cd, N and C(6), is illustrated in Fig. 2. The co-ordination geometry about the cadmium centre is a distorted pentagonal bipyramid, with

**Fig. 2** An ORTEP<sup>12</sup> view of the [Cd{(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>N}-(O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub>] molecule, **5**. The atoms are shown as 35% thermal ellipsoids. Note that a two-fold symmetry axis passes through the Cd, N and C(6) atoms

coplanar O(1), S(1), N, S(1a) and O(1a) atoms at the equatorial sites, and P(1) and P(1a) occupying the axial positions. The seven-co-ordinate geometry observed in this complex is largely a result of the constraints imposed by the pentadentate ligand. Since there is no ligand-field stabilization effect in Cd<sup>2+</sup>, the stereochemistry of its complexes is in general determined by ionic size, electrostatics, and covalent bonding energies.<sup>13</sup> Owing to its size, Cd<sup>2+</sup> commonly has a co-ordination number of six as in CdCl<sub>2</sub>, [CdCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>], [CdCl(OH)], K<sub>4</sub>[CdCl<sub>4</sub>], CdI<sub>2</sub> and Cd(OH)<sub>2</sub>.<sup>14</sup> However, a seven-co-ordinate, distorted pentagonal bipyramidal complex of Cd<sup>2+</sup> containing a thioether ligand is known, namely [Cd([15]aneS<sub>3</sub>)]<sub>2</sub>[ClO<sub>4</sub>]<sub>2</sub>·H<sub>2</sub>O ([15]aneS<sub>3</sub> = 1,4,7,10,13-pentathiacyclopentadecane).<sup>15</sup>

The P(1)–Cd–S(1) and P(1)–Cd–N angles are somewhat acute [79.9(1) and 83.4(1)°, respectively], while P(1)–Cd–S(1a) and P(1)–Cd–O(1) are somewhat obtuse [95.6(1) and 97.1(1)°]. This distortion is attributable to the geometrical constraints imposed by the ligand, as the ethylene bridges between S and P atoms do not allow P(1) and P(1a) to pull away far enough from each other. The P(1)–Cd–P(1a) angle of 166.8(1)° is accordingly less than the ideal value of 180°.

The P–Cd bond length of 2.590(1) Å is close to the sum of covalent radii of cadmium and phosphorus (1.48 + 1.10 = 2.58 Å)<sup>16</sup> and also comparable to 2.602(2) Å found in [Cd{P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>}<sub>2</sub>][NO<sub>3</sub>]<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>.<sup>17</sup> The Cd–S bond length of 2.821(1) Å is comparable to those of [Cd([15]aneS<sub>3</sub>)]<sub>2</sub>[ClO<sub>4</sub>]<sub>2</sub>·H<sub>2</sub>O (Cd–S<sub>av</sub> 2.76 Å)<sup>15</sup> and significantly longer than 2.703(1) Å in the six-co-ordinate complex [{CdL<sup>2</sup>Cl<sub>2</sub>·H<sub>2</sub>O}<sub>2</sub>] [L<sup>2</sup> = 2,6-bis(ethylsulfanylmethyl)pyridine]<sup>18</sup> and four-co-ordinate complex [Cd([16]aneS<sub>4</sub>)]<sub>2</sub>[ClO<sub>4</sub>]<sub>2</sub> (Cd–S<sub>av</sub> 2.65 Å) ([16]aneS<sub>4</sub> = 1,5,9,13-tetrathiacyclohexadecane).<sup>19</sup> It has been observed that in mercury(II) thioether complexes<sup>20</sup> the metal–sulfur bond lengths are a function of the number of donor atoms. As the co-ordination number of the metal centre goes up, its bonds to sulfur are lengthened. Hence it is not surprising that the seven-co-ordinate complex **5** has such long Cd–S bonds compared to those of an analogous six- or four-co-ordinate complex. The Cd–N bond distance of 2.695(3) Å is also longer than 2.380(3) Å in the six-co-ordinate, dimeric complex [{CdL<sup>2</sup>Cl<sub>2</sub>·H<sub>2</sub>O}<sub>2</sub>].<sup>18</sup>

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