

# Co-ordination chemistry of tridentate phosphinothiolates; syntheses and structures of $[\text{Li}_4\{\text{PhP}(\text{C}_6\text{H}_3\text{S}-2-\text{SiMe}_3)_2\}_2(\text{MeOCH}_2\text{CH}_2\text{OMe})_2]$ , $[\text{Sn}_2\{\text{PhP}(\text{C}_6\text{H}_3\text{S}-2-\text{SiMe}_3)_2\}_2]$ and $[\text{NHEt}_3][\text{Sm}\{\text{PhP}(\text{C}_6\text{H}_3\text{S}-2-\text{R}-3)_2\}_2(\text{py})_2]\cdot 2\text{py}$ ( $\text{R} = \text{H}$ or $\text{SiMe}_3$ , $\text{py} = \text{C}_5\text{H}_5\text{N}$ )

Nikolaus Froelich,<sup>a</sup> Peter B. Hitchcock,<sup>a</sup> Jin Hu,<sup>a</sup> Michael F. Lappert<sup>\*a</sup> and Jonathan R. Dilworth<sup>b</sup>

<sup>a</sup> School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK

<sup>b</sup> Department of Chemistry and Biological Chemistry, University of Essex, Wivenhoe Park, Colchester CO4 3SQ, UK

Treatment of  $\text{PhP}[\text{C}_6\text{H}_3(\text{SH}-2)\text{R}-3]_2$  ( $\text{R} = \text{H}$ ,  $\text{H}_2\text{L}^1$ , or  $\text{SiMe}_3$ ,  $\text{H}_2\text{L}^2$ , with  $\text{SmI}_3$  and  $\text{NEt}_3$  and then recrystallisation from pyridine (py) yielded  $[\text{NHEt}_3][\text{SmL}_2(\text{py})_2]\cdot 2\text{py}$  ( $\text{L} = \text{L}^1$  **3** or  $\text{L}^2$  **4**), while  $\text{H}_2\text{L}^2$  and  $\text{LiBu}^n$  or  $[\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2]$  afforded  $[\{\text{Li}_2\text{L}^2(\text{dme})\}_2]$  **1** (after addition of dme) or  $[\{\text{SnL}^2\}_2]$  **2**, respectively ( $\text{dme} = \text{MeOCH}_2\text{CH}_2\text{OMe}$ ). Compounds **1–4** have been characterised by microanalysis, NMR spectra and single-crystal X-ray diffraction.

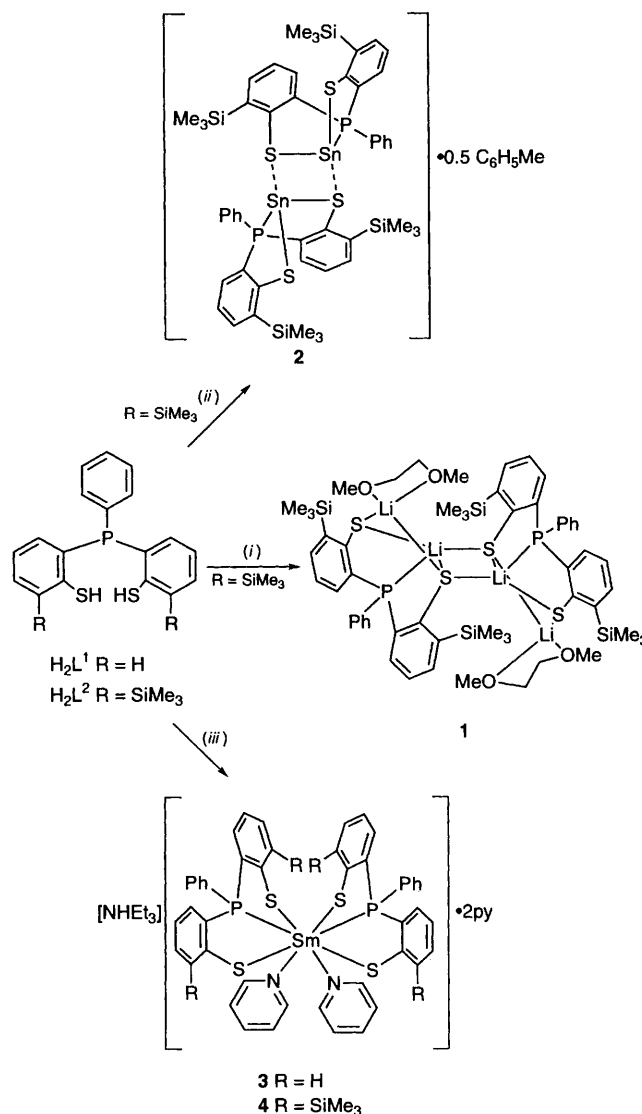
There have been extensive studies of transition-metal thiolato complexes, in part because of their possible relevance to the structure, bonding and function of biologically active reactive centres in metalloproteins such as ferredoxins, nitrogenase, blue copper proteins, and metallothioneins. The chemistry of metal complexes of both simple<sup>1</sup> and bulky<sup>2</sup> thiolate ligands has been well documented. Recently attention has also increasingly been paid to the co-ordination chemistry of polydentate compounds incorporating both thiolato and tertiary phosphine donor sites, as their combination was likely to confer unusual structures and reactivities on derived metal complexes. Most such studies have hitherto focused on bidentate compounds such as  $\text{R}_2\text{PCH}_2\text{CH}_2\text{S}^-$  and  $2-\text{R}_2\text{PC}_6\text{H}_4\text{S}^-$ ,<sup>3–10</sup> while the potentially tridentate ligands  $\text{RP}(\text{CH}_2\text{CH}_2\text{S}^-)_2$  and  $\text{RP}(\text{C}_6\text{H}_4\text{S}^-)_2$  have received less attention.<sup>11–14</sup>

A recent synthesis of phosphinoarenethiols by initial lithiation at the 2 position of benzenethiol (and subsequent treatment with corresponding chlorophosphines) has in principle made the co-ordination compounds of  $\text{RP}(\text{C}_6\text{H}_3\text{S}^-)_2$  ( $\text{R} = \text{Ph}$ ,  $\text{R}' = \text{H}$ ,  $\text{H}_2\text{L}^1$ , or  $\text{SiMe}_3$ ,  $\text{H}_2\text{L}^2$ , Scheme 1), conveniently accessible.<sup>15</sup> A feature of these compounds is that their steric and electronic properties and the hydrocarbon solubility of the derived complexes can readily be varied by changing the nature of  $\text{R}$  and  $\text{R}'$ . The ligands  $\text{L}^1$  or  $\text{L}^2$  can provide phosphine-donor binding to a metal, and then each thiolato sulfur may function as a monodentate, doubly or triply bridging donor to the metals. This generates a wide range of possible bonding modes, Scheme 2 (the  $\text{P} \rightarrow \text{M}$  designation optionally may be non-bonding). The dianion  $\text{L}^1$  generally binds in a *fac* manner in octahedral co-ordination, but *mer* ligation is possible with higher co-ordination numbers.

Our aim was to investigate the co-ordination chemistry in the context of main-group and *f* elements; no metal complex of  $\text{L}^2$  had previously been reported. In this paper, we present data on some complexes of  $\text{L}^1$  or  $\text{L}^2$  with  $\text{Li}$ ,  $\text{Sn}$ ,  $\text{Sm}$  and  $\text{Yb}$ .

## Results and Discussion

Routes to the compounds  $[\{\text{Li}_2\text{L}^2(\text{dme})\}_2]$  **1**,  $[\{\text{SnL}^2\}_2]$  **2**,  $[\text{NHEt}_3][\text{SmL}^1_2(\text{py})_2]\cdot 2\text{py}$  **3** and  $[\text{NHEt}_3][\text{SmL}^2_2(\text{py})_2]\cdot 2\text{py}$  **4** are summarised in Scheme 1 ( $\text{dme} = \text{MeOCH}_2\text{CH}_2\text{OMe}$ ,  $\text{py} = \text{C}_5\text{H}_5\text{N}$ ). Yields, colours, melting points, elemental analyses and mass spectral data are shown in



**Scheme 1** Syntheses of compounds **1–4**. (i)  $2 \text{LiBu}^n$ , hexane, 18 h, ca. 298 K, recrystallisation from toluene and dme; (ii)  $[\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2]$ , hexane, 18 h, ca. 298 K; (iii)  $0.5 [\text{SmI}_3(\text{thf})_2]$ , excess of  $\text{NEt}_3$ , thf, 24 h, ca. 298 K, recrystallisation from py

**Table 1** Yields, colours, melting points, analytical and mass spectral data for complexes 1–4

| Compound | Yield <sup>a</sup> (%) | Colour     | M.p. <sup>b</sup> (°C) | Analysis <sup>c</sup> (%)                   | Electron impact mass spectrum, <i>m/z</i> |
|----------|------------------------|------------|------------------------|---|---|
| 1        | 92                     | Colourless | <i>d</i>               | C 58.5 (58.7)<br>H 6.4 (6.9)                | 964<br>( <i>M</i> <sup>+</sup> – 2dme)    |
| 2        | 65                     | Yellow     | 264–265                | C 50.5 (50.1)<br>H 5.1 (5.1)                | 588 ( <i>M</i> <sup>+</sup> )             |
| 3        | 80                     | Yellow     | <i>d</i>               | C 61.0 (61.2)<br>H 5.1 (5.1)<br>N 5.6 (5.8) | <i>d</i>                                  |
| 4        | 82                     | Yellow     | Colour change<br>> 70  | C 58.5 (59.0)<br>H 6.1 (6.3)<br>N 4.7 (4.7) | <i>d</i>                                  |

<sup>a</sup> Not optimised. <sup>b</sup> Measured in a sealed capillary under an atmosphere of argon. <sup>c</sup> Calculated values in parentheses. <sup>d</sup> Not applicable.

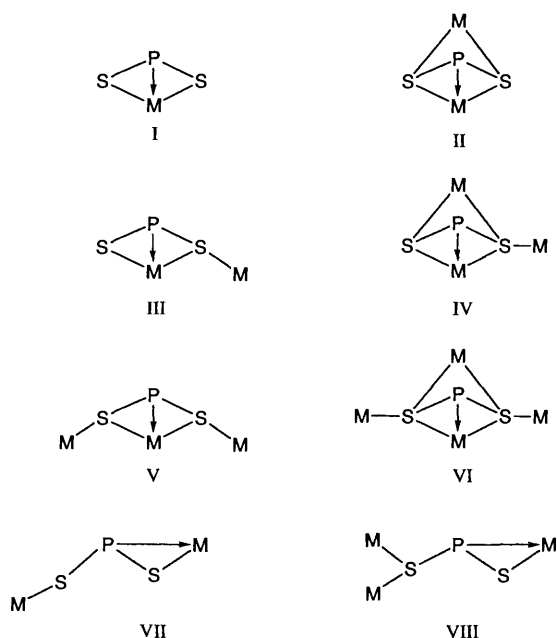
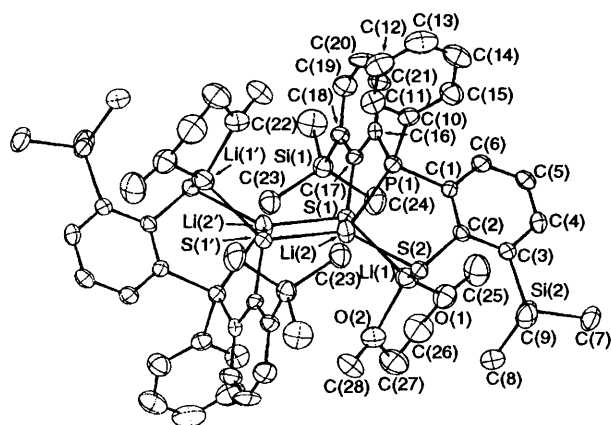
**Scheme 2** Alternative bonding modes of the ligand  $L^2$ **Fig. 1** Molecular structure and atom numbering scheme for complex 1

Table 1. The  $^1\text{H}$ ,  $^{31}\text{P}\{-^1\text{H}\}$ ,  $^{119}\text{Sn}\{-^1\text{H}\}$  and  $^7\text{Li}\{-^1\text{H}\}$  NMR spectral data are summarised in Table 2.

### The lithium complex $\{[\text{Li}_2\text{L}^2(\text{dme})]_2\}$ 1

The dilithio complex of  $\text{H}_2\text{L}^2$  was obtained under mild conditions and in high yield from the reaction of  $\text{LiBu}^n$  in hexane [*i*] in Scheme 1] and was recrystallised from toluene and dme. Elemental analysis was consistent with its form-

ulation, but its structure was not apparent from the spectroscopy; hence an X-ray structural investigation was undertaken. No dilithium dithiolate had previously been characterised crystallographically, although such data on lithium thiolates are well documented. Examples include  $\{[\text{Li}[\mu\text{-SC}(\text{SiMe}_3)_3]_2(\text{thf})_3]_2\}$ ,<sup>16</sup>  $\{[\text{Li}[\mu\text{-SCH}(\text{SiMe}_3)_2](\text{thf})_2]_2\}$ ,<sup>16</sup>  $[\text{Li}(\text{SC}_6\text{H}_4\text{Bu}^1\text{-2,4,6})(\text{thf})_3]$ ,<sup>17</sup>  $[\text{Li}(\text{SC}_6\text{H}_2\text{Ph}_3\text{-2,4,6})(\text{thf})_3]$ ,<sup>18</sup>  $[\text{Li}(\text{SC}_6\text{H}_4\text{Me}_2)(\text{py})]$ ,<sup>19</sup>  $[\text{Li}(\mu\text{-SPh})(\text{py})_2]_\infty$ ,<sup>19</sup>  $[\text{Li}(\mu\text{-SCH}_2\text{Ph})(\text{py})]_\infty$ <sup>19</sup> and  $\{[\text{Li}[\mu\text{-SC}_6\text{H}_3(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})_2\text{-2,6}](\text{OEt}_2)_2]_2\}$ <sup>20</sup> (thf = tetrahydrofuran).

An X-ray single-crystal diffraction study showed (Fig. 1, Table 3) that complex 1 crystallised in the space group  $P\bar{1}$  with two independent molecules, each of which lies on a crystallographic inversion centre. Since they are not significantly different with respect to their structural features and bond lengths and angles, only one of them is described in detail. The molecular structure of 1 shows it to be tetranuclear with a  $\text{Li}_4\text{S}_4$  core, which has the chair conformation comprising three  $\text{Li}_2\text{S}_2$  rings each sharing an edge. A similar geometry was found in  $\{[\text{Li}(\mu\text{-SCH}_2\text{Ph})(\text{py})]_\infty\}$  which has a repeat of chair-like  $\text{Li}_4\text{S}_4$  units; the overall skeletal structure was described as a 'wave-shaped ladder'.<sup>19</sup> The atom Li(1) in complex 1 is co-ordinated by two sulfurs and two oxygens (from dme), while Li(2) is ligated by three sulfurs and one phosphorus atom. The ligand  $L^2$  is co-ordinated in a pentadentate-bridging manner (mode IV in Scheme 2). Thus, in addition to the bonding between Li(2) and the phosphorus atom of  $L^2$ , one of the sulfurs serves as a triply bridging ligand to three lithiums, the other S being doubly bridging. This is the first example of this mode of ligation for a phosphinodithiolate ligand.

In comparison with related lithium thiolates, the  $\text{Li}\cdots\text{Li}$  distances of 3.09(2) and 3.11(2) Å in complex 1 are similar to those found in  $\{[\text{Li}(\mu\text{-SCH}_2\text{Ph})(\text{py})]_\infty\}$ ,<sup>19</sup> 3.092(8) and 3.243(8) Å, and significantly longer than in gaseous lithium, 2.67 Å.<sup>21</sup> The Li–S bond lengths [except for Li(2)–S(1)] are within the range 2.38–2.55 Å similar to those found in previously reported lithium thiolates having four-co-ordinated lithium.<sup>20</sup> The Li(2)–S(1) bond length of 2.661(12) Å is significantly longer than that of the other Li–S bonds, presumably due to the ring strain arising from the relatively small bite angles of the  $L^2$  ligand. The Li–P bond length of 2.400(12) Å in 1 is shorter than in  $\{[\text{Li}(\mu\text{-OCBu}^1_2\text{CH}_2\text{PR}_2)]_2\}$  [2.50(1) Å for R = Me or 2.651(6) Å for R = Ph].<sup>22</sup>

The integral ratios for the methyl and phenyl resonances in the  $^1\text{H}$  NMR spectrum of complex 1 in  $\text{C}_6\text{D}_5\text{CD}_3$  were consistent with the proposed formulation. The  $^7\text{Li}\{-^1\text{H}\}$  NMR spectrum showed two broad signals at  $\delta$  2.97 and 0.17 with half-widths of 145.82 and 142.90 Hz, respectively at 305 K; these merged into a singlet at  $\delta$  1.88 at 318 K. Upon cooling to 200 K the latter changed into a doublet at  $\delta$  3.75 [ $^1J(^{31}\text{P}\text{-}^7\text{Li})$  53.93 Hz] and a singlet at  $\delta$  0.23. The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum showed only a weak broad singlet at  $\delta$  –12.97 at 305 K, which upon cooling to 200 K split into an ill resolved peak at  $\delta$

**Table 2** The NMR spectral chemical shifts ( $\delta$ ) with assignments for complexes **1–4** at 305 K\*

| Compound | $^1\text{H}$  | $^{31}\text{P}\{-^1\text{H}\}$   | $^7\text{Li}\{-^1\text{H}\}$ or $^{119}\text{Sn}\{-^1\text{H}\}$ | Solvent                           |
|----------|---|--|--|-----------------------------------|
| <b>1</b> | 0.55 (36 H, s, $\text{SiMe}_3$ ), 2.42 (12 H, s, Me of dme), 2.81 (8 H, s, $\text{CH}_2$ of dme), 6.94–6.77 (22 H, m, Ph), 7.37, 7.34                   | –12.9 (br s)   | 2.97 (2 Li, br), 0.17 (2 Li, br)                                 | $\text{CD}_3\text{C}_6\text{D}_5$ |
| <b>2</b> | 0.46 (24 H, s, $\text{SiMe}_3$ ), 6.60–7.08, 7.30–7.34 (22 H, m, Ph)  | 47.21 [s, with two satellite doublets, $^1J(^{31}\text{P}\text{--}^{119}\text{Sn}) = 1370.37$ , $^1J(^{31}\text{P}\text{--}^{117}\text{Sn}) = 1309.52$ Hz] | –49.91 [ $^1J(^{31}\text{P}\text{--}^{119}\text{Sn}) = 1370$ Hz] | $\text{CD}_3\text{C}_6\text{D}_5$ |
| <b>3</b> | 1.09 (9 H, t, $\text{HNCH}_2\text{CH}_3$ ), 3.14 (6 H, br, $\text{HNCH}_2\text{CH}_3$ ), 6.58–8.71 (46 H, m, aromatic)                                  | –102.67 (br s)   |  | $\text{C}_5\text{D}_5\text{N}$    |
| <b>4</b> | 0.55 (36 H, s, $\text{SiMe}_3$ ), 1.16 (9 H, t, $\text{HNCH}_2\text{CH}_3$ ), 3.16 (6 H, q, $\text{HNCH}_2\text{CH}_3$ ), 6.67–7.60 (42 H, m, aromatic) | –108.40 (br s)   |  | $\text{C}_5\text{D}_5\text{N}$    |

\* At 360.1 MHz for  $^1\text{H}$ , 101.2 MHz for  $^{31}\text{P}\{-^1\text{H}\}$  and 97.2 MHz for  $^7\text{Li}\{-^1\text{H}\}$ .

**Table 3** Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) with estimated standard deviations (e.s.d.s) in parentheses for  $[(\text{Li}_2\text{L}^2(\text{dme}))_2] \mathbf{1}$ 

|                      | A         | B         |                       | A         | B         |
|----------------------|-----------|-----------|-----------------------|-----------|-----------|
| Li(1)–O(2)           | 1.961(14) | 1.988(13) | Li(1)–O(1)            | 1.978(14) | 2.013(13) |
| Li(1)–S(2)           | 2.499(14) | 2.521(13) | Li(1)–S(1)            | 2.519(13) | 2.548(13) |
| Li(1) $\cdots$ Li(2) | 3.09(2)   | 3.12(2)   | Li(2)–S(2)            | 2.397(12) | 2.383(11) |
| Li(2)–P(1)           | 2.400(12) | 2.471(10) | Li(2)–S(1')           | 2.425(11) | 2.420(10) |
| Li(2)–S(1)           | 2.661(12) | 2.677(11) | Li(2) $\cdots$ Li(2') | 3.11(2)   | 3.10(2)   |
| O(2)–Li(1)–O(1)      | 83.9(6)   | 81.9(5)   | O(2)–Li(1)–S(2)       | 109.2(6)  | 109.0(6)  |
| O(1)–Li(1)–S(2)      | 136.7(7)  | 141.6(6)  | O(2)–Li(1)–S(1)       | 103.8(6)  | 101.2(5)  |
| O(1)–Li(1)–S(1)      | 114.4(6)  | 113.2(6)  | S(2)–Li(1)–S(1)       | 102.5(5)  | 101.5(4)  |
| S(2)–Li(2)–P(1)      | 85.9(4)   | 84.3(3)   | S(2)–Li(2)–S(1')      | 139.1(5)  | 139.3(5)  |
| P(1)–Li(2)–S(1')     | 130.8(6)  | 132.1(5)  | S(2)–Li(2)–S(1)       | 101.3(4)  | 101.6(4)  |
| P(1)–Li(2)–S(1)      | 75.8(3)   | 74.4(3)   | S(1')–Li(2)–S(1)      | 104.7(4)  | 105.3(4)  |
| Li(2')–S(1)–Li(1)    | 122.3(4)  | 122.9(4)  | Li(1)–S(1)–Li(2)      | 73.1(4)   | 73.2(4)   |
| Li(2')–S(1)–Li(2)    | 75.3(4)   | 74.7(4)   | Li(2)–S(2)–Li(1)      | 78.1(4)   | 78.8(4)   |

Primed atoms are related to unprimed ones by  $-x, -y, -z$ ; A and B refer to the two molecules.

**Table 4** Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) with e.s.d.s in parentheses for  $[(\text{SnL}^2)_2] \cdot 0.5\text{C}_6\text{H}_5\text{Me} \mathbf{2}$ 

|                   |          |               |          |
|-------------------|----------|---------------|----------|
| Sn–S(1)           | 2.629(3) | Sn–S(2)       | 2.526(4) |
| Sn $\cdots$ S(2') | 3.282(3) | Sn–P          | 2.609(4) |
| S(1)–Sn–S(2)      | 94.6(1)  | S(1)–Sn–S(2') | 151.5(1) |
| S(1)–Sn–P         | 71.3(1)  | S(2)–Sn–S(2') | 96.8(1)  |
| S(2)–Sn–P         | 78.8(1)  | S(2')–Sn–P    | 81.08(9) |
| Sn–S(2)–Sn'       | 93.2(1)  |               |          |

Primed atoms are related to unprimed ones by  $-x, 1-y, 1-z$ .

–12.21. These data indicate that complex **1** is fluxional. At 318 K the Li atoms are equivalent, while at 200 K the solution structure is consistent with that in the solid state, with only one of the Li atoms coupled to P.

### The tin complex $[(\text{SnL}^2)_2] \cdot 0.5\text{C}_6\text{H}_5\text{Me} \mathbf{2}$

Although phosphinothiolato complexes of tin have not previously been reported, a few pyridine-thiolatotin(IV) complexes have been structurally characterised, including  $[\text{SnCl}_2(\text{SC}_5\text{H}_4\text{N}-2)_2]$ ,<sup>23</sup>  $[\text{Sn}(\text{SC}_5\text{H}_4\text{N}-2)_2(\text{SC}_5\text{H}_4\text{N}-2)] \cdot \text{C}_5\text{H}_5\text{NS}$ ,<sup>24</sup> and  $[\text{Sn}\{2\text{-SC}_5\text{H}_3\text{N}(\text{SiMe}_3)-3\}_4]$ .<sup>25</sup> The tin(II) complex  $[\text{Sn}\{2\text{-SC}_5\text{H}_3\text{N}(\text{SiMe}_3)-3\}_2]$  was not stable, slowly disproportionating in acetonitrile to give tin metal and  $[\text{Sn}\{2\text{-SC}_5\text{H}_3\text{N}(\text{SiMe}_3)-3\}_4]$ .<sup>25</sup>

We have prepared the tin(II) complex  $[(\text{SnL}^2)_2] \cdot 0.5\text{C}_6\text{H}_5\text{Me} \mathbf{2}$  from  $\text{H}_2\text{L}^2$  and  $[\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2]$  in hexane, (ii) in Scheme 1. Both  $^{119}\text{Sn}$  and  $^{31}\text{P}$  NMR spectra provided useful probes to study its structure in solution. The crystal structure (Fig 2, Table 4) shows the complex to be a weakly bonded dimer in which one thiolato sulfur of each ligand serves as a bridging atom; the overall co-ordination of the  $\text{L}^2$  ligand corresponds to

mode III in Scheme 2, being tridentate with respect to one tin atom and having one of the sulfur atoms bridging to the second Sn atom. As far as the tin centres are concerned, these are best described as having distorted trigonal-bipyramidal geometry, with phosphorus, a bridging sulfur and the lone pair occupying the equatorial sites, and the two remaining sulfurs in the apical positions. The bonding of the bridging ligands is highly asymmetric with a Sn–S bond length of 2.526(4)  $\text{\AA}$  and a Sn  $\cdots$  S contact of 3.282(3)  $\text{\AA}$ , the terminal Sn–S bond length being 2.629(3)  $\text{\AA}$ . These observations are in contrast to those for  $[\text{Mo}_2\text{Cl}_3(\text{SC}_6\text{H}_4\text{PPh}_2-2)_3]$ ,<sup>10</sup> in which the related phosphinothiolato ligand forms a symmetrical bridge. Asymmetrical bridging is rare among oligomeric thiolate-bridged metal complexes. The long Sn  $\cdots$  S contact in **2** has some similarity to that found in  $[\text{Sn}(\text{NCS})\{\text{N}(\text{SiMe}_3)_2\}]$ , in which the V-shaped monomer shows weak intermolecular binding to neighbouring units, Sn  $\cdots$  S 3.047(2) and 3.316(2)  $\text{\AA}$ .<sup>26</sup> The Sn–S bond lengths in **2** may be compared with the 2.435(1)  $\text{\AA}$  in the two-co-ordinate tin compound  $[\text{Sn}(\text{SC}_6\text{H}_2\text{Bu}'_3-2,4,6)_2]$ , and the 2.471(5)  $\text{\AA}$  for the three-co-ordinate tin in the terminal Sn–S bond of  $(\text{RS})\text{Sn}(\mu\text{-SR})_2\text{Sn}(\mu\text{-SR})_2(\text{SR})$  (R =  $\text{C}_6\text{H}_3\text{Pr}^i-2,6$ ), or 2.589(4) and 2.838(4)  $\text{\AA}$  for the four-co-ordinate tin in the bridging Sn–S bond.<sup>27</sup> The Sn–P bond length of 2.609(4)  $\text{\AA}$  in complex **2** is similar to the 2.659(5) and 2.676(5)  $\text{\AA}$  for the three-co-ordinate tin in  $[\text{Sn}\{\text{PPh}_2\}_2\text{CH}\{\text{CH}(\text{PPh}_2)_2\}]$ ,<sup>28</sup> or 2.598(2), 2.602(2), 2.790(2) and 2.839(2)  $\text{\AA}$  in  $[\text{Sn}\{\text{PMe}_2\}_2\text{CPMe}_2]_2$ .<sup>29</sup>

The  $^1\text{H}$  NMR spectra of complex **2** and of  $\text{H}_2\text{L}^2$  were very similar, apart from additional signals from the SH proton at  $\delta$  4.56 [ $J(^1\text{H}\text{--}^{31}\text{P})$  5 Hz] and 4.57 in the latter. The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum of **2** showed a singlet at  $\delta$  47.21, with satellite doublets due to  $^1J(^{31}\text{P}\text{--}^{119}\text{Sn}) = 1370.37$  and  $^1J(^{31}\text{P}\text{--}^{117}\text{Sn}) = 1309.52$  Hz. The  $^{119}\text{Sn}\{-^1\text{H}\}$  NMR spectrum in  $\text{C}_6\text{D}_5\text{CD}_3$

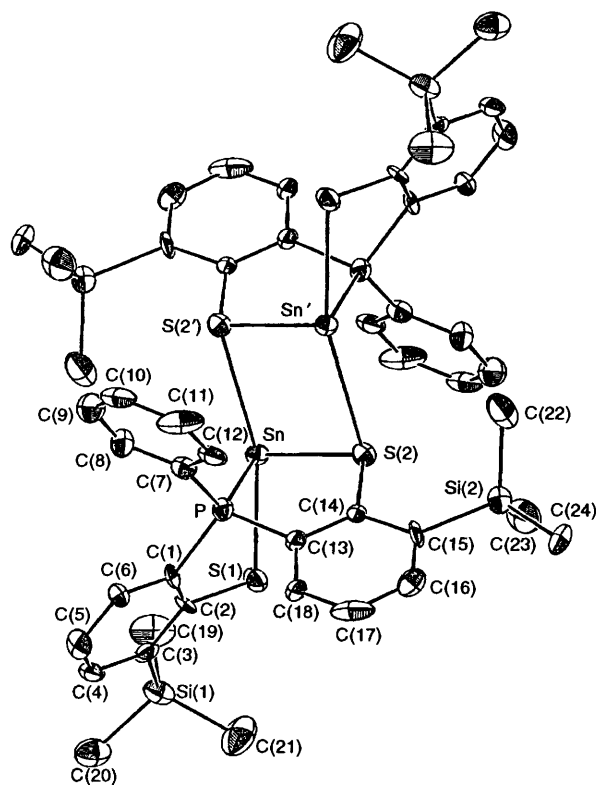


Fig. 2 Molecular structure and atom numbering scheme for complex 2

showed a doublet at  $\delta -49.91$ ,  $^1J(^{31}\text{P}-^{119}\text{Sn}) = 1370$  Hz. Thus, the spectral data for solutions of **2** are in accord with its crystal structure.

#### The samarium complexes $[\text{NHEt}_3][\text{SmL}_2(\text{py})_2] \cdot 2\text{py}$ **3** and $[\text{NHEt}_3][\text{SmL}_2(\text{py})_2] \cdot 2\text{py}$ **4**

Thiolatolanthanide(III) complexes are rare, probably because  $\text{Ln}^{3+}$  binds preferentially to hard ligands. Well characterised compounds include  $[\text{Sm}(\text{SC}_6\text{H}_2\text{Bu}^t\text{-2,4,6})_3]$ ,<sup>30</sup>  $[\{\text{Ce}(\eta\text{-C}_5\text{-H}_4\text{Bu}^t)_2(\mu\text{-SPR}^i)\}_2]$ ,<sup>31a</sup>  $[\{\text{Gd}[\text{N}(\text{SiMe}_3)_2]_2(\mu\text{-SBu}^t)\}_2]$ <sup>31b</sup> and  $[\text{La}(\eta\text{-C}_5\text{Me}_3)_2(\mu\text{-SBu}^t)_2\text{Li}(\text{thf})_2]$ .<sup>31c</sup> Treatment of  $\text{SmI}_3$  with  $\text{H}_2\text{L}^1$  or  $\text{H}_2\text{L}^2$  and an excess of triethylamine in thf under ambient conditions afforded in good yield complex **3** or **4**, respectively, (iii) in Scheme 1.

The crystal structure of complex **3** (Fig. 3, Table 5) shows that  $[\text{NHEt}_3][\text{SmL}_2(\text{py})_2] \cdot 2\text{py}$  consists of well separated cations and anions. The eight-fold co-ordination sphere of the anion may be described as approximating to a distinctly distorted dodecahedron, which comprises two interpenetrating tetrahedra, with sulfur atoms forming a flattened tetrahedron (B sites), and phosphorus together with nitrogen atoms constituting an elongated tetrahedron (A sites), IX. The distortion arises from the small bite angle of the  $\text{L}^1$  ligand and the inequivalence between the phosphorus and nitrogen atoms in the A sites. The Sm–S bond lengths of 2.835(2)–2.883(2) Å are somewhat longer than the 2.646(7)–2.652(9) Å found in  $[\text{Sm}(\text{SC}_6\text{H}_2\text{Bu}^t\text{-2,4,6})_3]$ ,<sup>30</sup> but somewhat closer to the 2.760(5) and 2.823(5) Å in  $[\{\text{Gd}[\text{N}(\text{SiMe}_3)_2]_2(\mu\text{-SBu}^t)\}_2]$ .<sup>31b</sup> The Sm–P distances of 2.974(2) and 2.980(2) Å in **3** undoubtedly show bonding character. Comparison is available with  $[\{\text{Sm}[\text{CH}(\text{PMe}_2)_2]_2(\mu\text{-PMe}_2\text{CHPMe}_2)\}_2]$ , having terminal Sm–P bond lengths ranging from 2.879(1) to 2.913(3) Å.<sup>32</sup> The compounds  $[\text{LnCl}\{\text{N}(\text{SiMe}_2\text{CH}_2\text{PR}_2)_2\}_2]$  (R = Me or Ph. Ln = Y, La, Ce, Er, Yb or Lu) have been reported and the yttrium compound has been crystallographically characterised.<sup>33</sup> A crystal structure determination was carried out on **4**. However, due to decomposition during the data collection, the structure is not of significant quality for meaningful discussion

Table 5 Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for  $[\text{NHEt}_3][\text{SmL}_2(\text{py})_2] \cdot 2\text{py}$  **3**

|              |           |              |           |
|--------------|-----------|--------------|-----------|
| Sm–S(1)      | 2.883(2)  | Sm–S(2)      | 2.835(2)  |
| Sm–S(3)      | 2.845(2)  | Sm–S(4)      | 2.862(2)  |
| Sm–P(1)      | 2.980(2)  | Sm–P(2)      | 2.974(2)  |
| Sm–N(1)      | 2.663(5)  | Sm–N(2)      | 2.649(5)  |
| S(1)–Sm–S(2) | 105.00(5) | S(1)–Sm–S(3) | 84.91(5)  |
| S(1)–Sm–S(4) | 146.92(5) | S(1)–Sm–P(1) | 65.37(4)  |
| S(1)–Sm–P(2) | 142.40(4) | S(1)–Sm–N(1) | 72.1(1)   |
| S(1)–Sm–N(2) | 80.6(1)   | S(2)–Sm–S(3) | 135.14(5) |
| S(2)–Sm–S(4) | 91.28(5)  | S(2)–Sm–P(1) | 64.14(4)  |
| S(2)–Sm–P(2) | 85.02(5)  | S(2)–Sm–N(1) | 148.3(1)  |
| S(2)–Sm–N(2) | 73.3(1)   | S(3)–Sm–S(4) | 103.78(5) |
| S(3)–Sm–P(1) | 82.22(4)  | S(3)–Sm–P(2) | 64.27(4)  |
| S(3)–Sm–N(1) | 76.5(1)   | S(3)–Sm–N(2) | 151.0(1)  |
| S(4)–Sm–P(1) | 146.70(5) | S(4)–Sm–P(2) | 66.20(5)  |
| S(4)–Sm–N(1) | 79.0(1)   | S(4)–Sm–N(2) | 76.7(1)   |
| P(1)–Sm–P(2) | 88.45(4)  | P(1)–Sm–N(1) | 133.7(1)  |
| P(1)–Sm–N(2) | 113.6(1)  | P(2)–Sm–N(1) | 117.1(1)  |
| P(2)–Sm–N(2) | 136.4(1)  | N(1)–Sm–N(2) | 75.2(2)   |

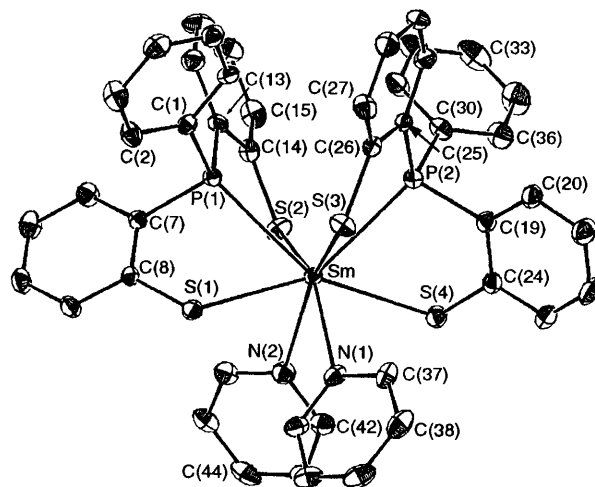


Fig. 3 Molecular structure and atom numbering scheme for the anion of complex **3**

of the bond lengths and angles, although the main features are clear. Not surprisingly, it is directly analogous to that of **3**.

The elemental analysis and  $^1\text{H}$  NMR spectra are entirely consistent with the solid-state structures of complexes **3** and **4**. The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectra showed broad singlets at  $\delta -102.67$  (**3**) and  $-108.40$  (**4**). The broadening is probably due to the bonding of the phosphorus to the paramagnetic  $\text{Sm}^{\text{III}}$  ( $f^5$ ).

#### Attempted preparation of ytterbium(II) complexes

Attempts were made to obtain a phosphinothiolatoytterbium(II) complex by reaction of  $\text{YbI}_2$  with  $[\{\text{Li}_2\text{L}^2(\text{dme})\}_2]$  **1**. Both black (**5**) and red (**6**) crystals precipitated. Product **5** was extremely air-sensitive, and the relative ratio of **5** to **6** critically depended on the amount of oxygen (adventitiously or deliberately) present. If an excess of moisture or  $\text{O}_2$  was present **6** was oxidised further to a yellow product. Product **5** showed a sharp  $^1\text{H}$  NMR spectrum, consistent with its being an ytterbium(II) complex. Product **6**, however, gave a very broad and widely shifted  $^1\text{H}$  NMR spectrum; a mass susceptibility of  $\chi = 4.775 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$  indicated that it contained paramagnetic  $\text{Yb}^{\text{III}}$ .

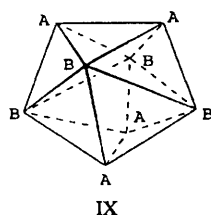
#### Experimental

All manipulations were carried out under argon using a high-vacuum manifold and conventional Schlenk techniques.

**Table 6** Structure determination data for complexes 1–4\*

|   | 1  | 2  | 3   | 4   |
|---|--|--|---|---|
| Formula   | C <sub>56</sub> H <sub>78</sub> Li <sub>4</sub> O <sub>4</sub> P <sub>2</sub> S <sub>4</sub> Si <sub>4</sub> | C <sub>31</sub> H <sub>37</sub> PS <sub>2</sub> Si <sub>2</sub> Sn | C <sub>62</sub> H <sub>62</sub> N <sub>5</sub> P <sub>2</sub> S <sub>4</sub> Sm | C <sub>74</sub> H <sub>94</sub> N <sub>5</sub> P <sub>2</sub> S <sub>4</sub> Si <sub>4</sub> Sm |
| <i>M</i>  | 1145.5   | 679.6  | 1217.8  | 1506.5  |
| Crystal system  | Triclinic  | Triclinic  | Monoclinic  | Triclinic   |
| Space group   | <i>P</i> $\bar{1}$   | <i>P</i> $\bar{1}$   | <i>P</i> 2 <sub>1</sub>   | <i>P</i> $\bar{1}$  |
| <i>a</i> /Å   | 12.809(3)  | 9.785(3)   | 11.297(2)   | 14.121(6)   |
| <i>b</i> /Å   | 14.641(2)  | 12.040(3)  | 19.673(8)   | 14.377(7)   |
| <i>c</i> /Å   | 17.867(4)  | 14.961(4)  | 13.308(3)   | 21.412(11)  |
| $\alpha$ /°   | 89.48(2)   | 82.96(2)   |   | 99.26(4)  |
| $\beta$ /°  | 84.11(2)   | 80.06(2)   | 90.64(2)  | 92.66(4)  |
| $\gamma$ /°   | 78.09(2)   | 71.30(2)   |   | 113.74(4)   |
| <i>U</i> /Å <sup>3</sup>                                      | 3261   | 1640   | 2957  | 3898(4)   |
| <i>D<sub>c</sub></i> /g cm <sup>-3</sup>                      | 1.62   | 1.38   | 1.37  | 1.28  |
| $\mu$ (Mo-K $\alpha$ )/cm <sup>-1</sup>                       | 0.31   | 10.4   | 12.3  | 10.0  |
| $\theta_{\max}$ for data/°                                    | 25   | 25   | 25  | 22  |
| Unique reflections  | 11 450   | 5574   | 5367  | 9511  |
| Significant reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] | 5238   | 3327   | 4531  | 4680  |
| <i>R</i>  | 0.070  | 0.081  | 0.029   | 0.146   |
| <i>R'</i> (for 2–4), <i>wR2</i> (for 1)                       | 0.156  | 0.081  | 0.035   | 0.207   |

\* Details in common:  $Z = 2$ ;  $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ ;  $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{\frac{1}{2}}$ ;  $wR2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|^2)^2]^{\frac{1}{2}}$ .



Solvents were distilled over appropriate drying agents and thoroughly degassed prior to use. The NMR spectra were recorded on a Bruker WM 360 or AC-250SY instrument, mass spectra with a Fisons VG Autospec instrument. Elemental analyses were determined by Medac Ltd., Brunel University.

The ligand precursors H<sub>2</sub>L<sup>1,15</sup>, H<sub>2</sub>L<sup>2,15</sup> and the other starting materials [Sn{N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>,<sup>34</sup> [Sm{N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>-(thf)<sub>2</sub>,<sup>35</sup> [SmI<sub>3</sub>(thf)<sub>2</sub>]<sub>2</sub><sup>36</sup> and YbI<sub>2</sub><sup>37</sup> were synthesised according to literature methods. The phosphinodithiol H<sub>2</sub>L<sup>2</sup> was recrystallised from ethanol, dried *in vacuo* at 50–70 °C over 5 d, and stored in the dark.

### Preparations

{[Li<sub>2</sub>L<sup>2</sup>(dme)]<sub>2</sub>} **1**. *n*-Butyllithium (2 cm<sup>3</sup> of a 2.5 mol dm<sup>-3</sup> solution, 5 mmol) in hexane (*ca.* 10 cm<sup>3</sup>) was added at ambient temperature to a stirred solution of compound H<sub>2</sub>L<sup>2</sup> (1.08 g, 2.29 mmol) in hexane (*ca.* 10 cm<sup>3</sup>). After addition of *ca.* 1 cm<sup>3</sup> of the LiBu<sup>n</sup> solution a white precipitate was observed. The mixture was stirred at room temperature for 18 h. The white precipitate (1.05 g, 95% based on the formation Li<sub>2</sub>L<sup>2</sup>) was filtered off and dried *in vacuo*. Crystals suitable for X-ray diffraction and NMR spectroscopy were grown from a saturated toluene solution at –30 °C containing a few drops of dme.

{[SnL<sup>2</sup>]<sub>2</sub>}·0.5C<sub>6</sub>H<sub>5</sub>Me **2**. The phosphinodithiol H<sub>2</sub>L<sup>2</sup> (0.27 g, 0.57 mmol) in hexane (20 cm<sup>3</sup>) was slowly added to [Sn{N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (0.24 g, 0.55 mmol) in hexane (30 cm<sup>3</sup>). The mixture was stirred at room temperature for 18 h; a yellow solid was filtered off, freed from volatiles *in vacuo* and recrystallised from toluene (2–4 cm<sup>3</sup>) at –30 °C yielding compound **2** (0.22 g, 65%).

[NHEt<sub>3</sub>][SmL<sup>2</sup>(py)<sub>2</sub>]·2py **3** and [NHEt<sub>3</sub>][SmL<sup>2</sup>(py)<sub>2</sub>]·2py **4**. The phosphinodithiol H<sub>2</sub>L<sup>2</sup> (0.26 g, 0.55 mmol) in thf (10 cm<sup>3</sup>) was added to a stirred suspension of [SmI<sub>3</sub>(thf)<sub>2</sub>]<sub>2</sub> (0.16 g, 0.24 mmol) in thf (30 cm<sup>3</sup>) followed by NEt<sub>3</sub> (0.4 cm<sup>3</sup>, 2.87 mmol). The mixture was stirred at room temperature for 24 h.

The solvent was removed *in vacuo*. Addition of pyridine (20 cm<sup>3</sup>), filtration from solid residues and recrystallisation of the filtrate at –30 °C yielded yellow crystals of complex **4** (0.26 g, 94%). Complex **3** (80%) was prepared in an analogous manner.

### Attempts to prepare ytterbium(II) complexes

Compound **1** (0.12 g, 0.25 mmol) dissolved in thf (10 cm<sup>3</sup>) was slowly added to a stirred suspension of YbI<sub>2</sub> (0.16 g, 0.38 mmol) in thf (20 cm<sup>3</sup>) at 0 °C during 30 min. The solution was stirred at room temperature for 48 h, followed by removal of solvent *in vacuo* and extraction of the product into hexane (20 cm<sup>3</sup>). Black crystals of product **5** were obtained by fractional crystallisation from the hexane solution. Some red crystals of a product **6** were also isolated due to oxidation of **5**.

### Crystallography

In each case unique data sets were collected on an Enraf-Nonius CAD4 diffractometer with monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.710 73$  Å). For complex **1** data were measured at room temperature using a crystal sealed in a capillary under argon, for **2–4** at 173 K using a crystal coated in oil. Data were corrected for Lorentz-polarisation effects and also for absorption (except for **1**) using DIFABS<sup>38</sup> for **2** and **3** after isotropic refinement, or  $\psi$ -scan data for **4**. A decay correction was applied for **4**. Each structure was solved using the heavy-atom routines of SHELXS 86,<sup>39</sup> and refined by full-matrix least squares. For **1** refinement was based on *F*<sup>2</sup> using SHELXL 93<sup>40</sup> with all unique data and with non-H atoms anisotropic and H atoms in riding mode with *U*<sub>iso</sub>(H) equal to 1.2*U*<sub>eq</sub>(C) or 1.5*U*<sub>eq</sub>(C) for methyl groups. The weighting scheme was that defined by the program. For **2–4**, refinement was based on *F* using programs from the Enraf-Nonius MOLEN<sup>41</sup> package with reflections having *I* > 2 $\sigma$ (*I*) and H atoms at fixed calculated positions and *U*<sub>iso</sub>(H) = 1.3*U*<sub>eq</sub>(C), except for those on the toluene in **2** and those in **4**, which were omitted. The weighting scheme was *w* =  $\sigma^{-2}$ (*F*). Further details are given in Table 6.

Complete atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

### Acknowledgements

We thank EPSRC for the award of a fellowship (for J. H.) and the Leverhulme Trustees for an Emeritus Fellowship (for M. F. L.).

## References

- 1 P. J. Blower and J. R. Dilworth, *Coord. Chem. Rev.*, 1987, **76**, 121.
- 2 J. R. Dilworth and J. Hu, *Adv. Inorg. Chem.*, 1993, **40**, 411.
- 3 K. Issleib and W. Gans, *Z. Anorg. Allg. Chem.*, 1981, **475**, 116; 1982, **491**, 163.
- 4 J. Chatt, J. R. Dilworth, J. A. Schmutz and J. Zubieta, *J. Chem. Soc., Dalton Trans.*, 1979, 1595.
- 5 D. W. Stephan, *Inorg. Chem.*, 1984, **23**, 2207.
- 6 G. S. White and D. W. Stephan, *Inorg. Chem.*, 1985, **24**, 1499.
- 7 M. Savignac, P. Cadiot and F. Mathey, *Inorg. Chim. Acta*, 1980, **45**, L43.
- 8 J. R. Dilworth, A. J. Hutson, S. Morton, M. Harman, M. B. Hursthouse, J. Zubieta, C. M. Archer and J. R. Kelly, *Polyhedron*, 1992, **11**, 2151.
- 9 E. Block, G. Ofori-Okai, H. Kang and J. Zubieta, *Inorg. Chim. Acta*, 1991, **188**, 7.
- 10 E. Block, H. Kang, G. Ofori-Okai and J. Zubieta, *Inorg. Chim. Acta*, 1989, **166**, 155.
- 11 P. J. Blower, J. R. Dilworth, G. J. Leigh, B. D. Neaves, F. B. Normanton, J. Hutchinson and J. Zubieta, *J. Chem. Soc., Dalton Trans.*, 1985, 2647.
- 12 J. R. Dilworth, Y. Zheng and J. R. Miller, *J. Chem. Soc., Dalton Trans.*, 1992, 1757.
- 13 R. J. Smith, A. K. Powell, N. Barnard, J. R. Dilworth and P. J. Blower, *J. Chem. Soc., Chem. Commun.*, 1993, 54.
- 14 E. Block, M. Gernon, H. Kang, G. Ofori-Okai and J. Zubieta, *Inorg. Chem.*, 1991, **30**, 1736.
- 15 E. Block, G. Ofori-Okai and J. Zubieta, *J. Am. Chem. Soc.*, 1989, **111**, 2327; E. Block, V. Eswarakrishnan, M. Gernon, G. Ofori-Okai, C. Saha, K. Tang and J. Zubieta, *J. Am. Chem. Soc.*, 1989, **111**, 658.
- 16 M. Aslam, R. A. Bartlett, E. Block, M. M. Olmstead, P. P. Power and G. E. Sigel, *J. Chem. Soc., Chem. Commun.*, 1985, 1674.
- 17 G. A. Sigel and P. P. Power, *Inorg. Chem.*, 1987, **26**, 2819.
- 18 K. Ruhlandt-Senge and P. P. Power, *Bull. Soc. Chim. Fr.*, 1992, **129**, 594.
- 19 A. J. Banister, W. Clegg and W. R. Gill, *J. Chem. Soc., Chem. Commun.*, 1987, 850.
- 20 J. J. Ellison and P. P. Power, *Inorg. Chem.*, 1994, **33**, 4231.
- 21 L. E. Sutton (Editor), *Tables of Interatomic Distances and Configuration in Molecules*, The Chemical Society, London, 1958.
- 22 L. M. Engelhardt, J. M. Harrowfield, M. F. Lappert, I. A. MacKinnon, B. H. Newton, C. L. Raston, B. W. Skelton and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1986, 846.
- 23 M. Masaki, S. Matsunami and H. Ueda, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 3298.
- 24 L. C. Damude, P. A. W. Dean, V. Manivannan, R. S. Srivastava and J. J. Vittal, *Can. J. Chem.*, 1990, **68**, 1323.
- 25 E. Block, G. Ofori-Okai, H. Kang, J. Wu and J. Zubieta, *Inorg. Chim. Acta*, 1991, **190**, 5.
- 26 R. W. Chorley, P. B. Hitchcock and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1992, 1451.
- 27 P. B. Hitchcock, M. F. Lappert, B. J. Samways and E. L. Weinberg, *J. Chem. Soc., Chem. Commun.*, 1983, 1492.
- 28 A. L. Balch and D. E. Oram, *Organometallics*, 1986, **5**, 2159.
- 29 H. H. Karsch, A. Appelt and G. Müller, *Organometallics*, 1986, **5**, 1664.
- 30 B. Çetinkaya, P. B. Hitchcock, M. F. Lappert and R. G. Smith, *J. Chem. Soc., Chem. Commun.*, 1992, 932.
- 31 (a) S. D. Stults, R. A. Andersen and A. Zalkin, *Organometallics*, 1990, **9**, 1623; (b) H. C. Aspinall, D. C. Bradley, M. B. Hursthouse, K. D. Sales and N. P. C. Walker, *J. Chem. Soc., Chem. Commun.*, 1985, 1585; (c) H. Schumann, I. Albrecht, M. Gallagher, E. Hahn, C. Muchmore and J. Pickardt, *J. Organomet. Chem.*, 1988, **349**, 103.
- 32 H. H. Karsch, G. Ferazin and P. Bissinger, *J. Chem. Soc., Chem. Commun.*, 1994, 505.
- 33 M. D. Fryzuk, T. S. Haddad, D. J. Berg and S. J. Rettig, *Pure Appl. Chem.*, 1991, **63**, 845.
- 34 M. J. S. Gynane, D. H. Harris, M. F. Lappert, P. P. Power, P. Rivière and M. Rivière-Baudet, *J. Chem. Soc., Dalton Trans.*, 1977, 2004.
- 35 W. J. Evans, D. K. Drummond, H. Zhang and J. L. Atwood, *Inorg. Chem.*, 1988, **27**, 575.
- 36 P. L. Watson, T. H. Tulip and I. Williams, *Organometallics*, 1990, **9**, 1999.
- 37 T. D. Tilley, J. M. Boncella, D. J. Berg, C. J. Burns and R. A. Andersen, *Inorg. Synth.*, 1990, **27**, 146.
- 38 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A* 1983, **39**, 158.
- 39 G. M. Sheldrick, SHELXS 86, Program for the Solution of Crystal Structures, University of Göttingen, 1985.
- 40 G. M. Sheldrick, SHELXL 93, Program for Crystal Structures Refinement, University of Göttingen, 1993.
- 41 C. K. Fair, MOLEN, Structure Determination System, Enraf-Nonius, Delft, 1990.

Received 1st November 1995; Paper 5/07209C