LITHIUM AND MAGNESIUM PHOSPHINO- AND ARSINOARYLTHIOLATES

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The molecular structure of 2-PPh$_2$C$_6$H$_4$SH (**PSH**) and the preparation and structural characterization of the lithium and magnesium salts of 2-EPh$_2$C$_6$H$_4$SH (E = P, As), [Li{(μ-SC$_6$H$_4$-2-PPh$_2$)-κ*S*}(TMEDA)]$_2$ (**1**) (TMEDA = *N,N,N',N'*-tetramethylethylenediamine), Mg{(SC$_6$H$_4$-2-AsPh$_2$)-κ*S*}$_2$(THF)$_4$ (**2**) and Mg{(SC$_6$H$_4$-2-PPh$_2$)-κ^2*S,P*}$_2$(THF)$_2$ (**3**) are presented.

INTRODUCTION

The coordination chemistry of phosphino- and arsinoarylthiol ligands of the type 2-EPh$_2$C$_6$H$_4$SH (**ESH**), 2-EPh-(C$_6$H$_4$SH)$_2$ (**ES$_2$H$_2$**) and 2-E-(C$_6$H$_4$SH)$_3$ (**ES$_3$H$_3$**) (E = P, As)[1,2] has been the topic of our investigations for many years, due to their wide range of coordination modes in main group[3] and transition metal complexes[4] and potential applications of their metal complexes in catalysis,[4b,5] materials science[6] and medicinal chemistry.[7] Following our interest in the synthesis of main group metal complexes, we synthesized and fully characterized the dimeric tetracoordinate lithium salt [Li{(μ-SC$_6$H$_4$-2-PPh$_2$)-κ*S*}(TMEDA)]$_2$ (**1**) and the monomeric six-coordinate magnesium complexes Mg{(SC$_6$H$_4$-2-AsPh$_2$)-κ*S*}$_2$(THF)$_4$ (**2**) and Mg{(SC$_6$H$_4$-2-PPh$_2$)-κ^2*S,P*}$_2$(THF)$_2$ (**3**). Although the phosphinoarylthiols **PS$_x$H$_x$** (*x* = 1, 2, 3) are known, the molecular structures of **PS$_2$H$_2$** and **PS$_3$H$_3$** were only recently determined.[4a] Here, we complete this series with the structure of 2-PPh$_2$C$_6$H$_4$SH (**PSH**).

Group 1 and group 2 metal complexes of this type of ligands are largely unexplored; only the tetranuclear lithium complex [Li$_4${PPh(C$_6$H$_3$-2-S-3-SiMe$_3$)$_2$-κ^3*S,S',P*}$_2$(DME)$_2$}] (DME = MeOCH$_2$CH$_2$OMe) is known.[8] However, the number of known lithium thiolates is impressive and is related to their central role as reagents for the synthesis of a large variety of metal chalcogenolato complexes. Selected examples are [Li{μ-SCH(SiMe$_3$)$_2$}(THF)$_2$]$_2$,[9] Li(SMes*)(THF)$_3$ (Mes* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$),[10] Li$_2$(μ-SC$_6$H$_3$-2,6-Mes$_2$)$_2$(Et$_2$O)$_2$, (Mes = 2,4,6-Me$_3$C$_6$H$_2$),[11] [Li(μ-S(CH$_2$)$_x$Ph)(py)$_2$]$_\infty$ (*x* = 0 and 1, py = pyridine), Li(SC$_6$H$_4$-2-Me)(py)$_3$[12] and [Li$_4${PPh(C$_6$H$_3$-2-S-3-SiMe$_3$)$_2$-κ^3*S,S',P*}$_2$(DME)$_2$}].[8]

Since 1990, when the first magnesium chalcogenolate was obtained and structurally characterised,[13] a wide variety of ligands were used for coordination to magnesium, providing critical information about association and aggregation trends within this group of compounds.[14,15] The coordination number at magnesium is strongly related to the steric properties of the ligands: two-

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coordinate in Mg(SC$_6$H$_3$-2,6-Trip$_2$)$_2$ (Trip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$),[16] three-coordinate in [Mg(μ-STriph)(STriph)]$_2$ (Triph = 2,4,6-Ph$_3$C$_6$H$_2$) and four-coordinate in Mg(SMes*)$_2$(Et$_2$O)$_2$.[17] With less bulky ligands the coordination numbers 5–7 were also observed.[18,19]

The potential application of lithium and magnesium thiolates as transmetallation reagents was investigated. By treating the lithium salt Li(**PS**) with GaCl$_3$, Ga{(SC$_6$H$_4$-2-PPh$_2$)-κ^2*S,P*}{(SC$_6$H$_4$-2-PPh$_2$)-κ*S*}$_2$ was obtained.[3a] In the reaction of Mg{(SC$_6$H$_4$-2-PPh$_2$)-κ^2*S,P*}$_2$ with Fe(CO)$_5$, the unexpected formation of [Fe{(SC$_6$H$_4$-2-PPh$_2$)-κ^2*S,P*}$_2$(CO)$_2$] (in very low yield) was observed.[20]

RESULTS AND DISCUSSION

Molecular structure of 2-PPh$_2$-C$_6$H$_4$SH (PSH)

2-PPh$_2$-C$_6$H$_4$SH (**PSH**) was synthesised according to the literature procedure.[1,21] The ^{1}H, ^{31}P and ^{13}C NMR data are in agreement with those

reported in the literature.[21] Colourless crystals (plates) of 2-PPh$_2$C$_6$H$_4$SH were obtained from a diethyl ether/*n*-hexane solution at room temperature. **PSH** crystallises in the triclinic space group *P* $\bar{1}$ with two molecules in the unit cell (Fig. 1). The phosphorus atom is coordinated in a slightly distorted pyramidal fashion by the three carbon atoms of the aromatic rings with angles of 100.6(1)° [C(13)–P(1)–C(1)], 102.9(1)° [C(1)–P(1)–C(7)] and 103.5(1)° [C(13)–P(1)–C(7)] (Table 1), close to the tetrahedral angle of 109.5°. These values are comparable with those found in **PS$_2$H$_2$** and **PS$_3$H$_3$**[4] and are slightly smaller than the corresponding C–P–C angles found in 2-(Ph$_2$PO)-6-(Me$_3$Si)C$_6$H$_3$SH [106.4(2)–107.7(2)°].[21] The C–P bond lengths [1.831(2)–1.833(2) Å] are in the expected range and comparable with those in 2-(Ph$_2$PO)-6-(Me$_3$Si)C$_6$H$_3$SH [1.823(4)–1.829(4) Å],[21] **PS$_2$H$_2$** [1.833(3)–1.834(3) Å] and **PS$_3$H$_3$** [1.833(2)–1.835(2) Å][4] and other phosphines [1.780–1.846 Å].[22] The S(1)–C(2) distance [1.773(2) Å] is within the range for S–C single bonds.[23]

Table 1

Selected bond lengths (Å) and bond angles (°) in **PSH**

S(1)–H(1s)	1.26(3)	C(2)–S(1)–H(1s)	96.0(2)
S(1)–C(2)	1.773(2)	C(1)–C(2)–S(1)	118.6(2)
P(1)–C(1)	1.833(2)	C(13)–P(1)–C(1)	100.6(1)
P(1)–C(7)	1.833(2)	C(13)–P(1)–C(7)	103.5(1)
P(1)–C(13)	1.831(2)	C(1)–P(1)–C(7)	102.9(1)
C(1)–C(2)	1.403(3)	C(1)–C(2)–P(1)	117.6(2)
C(7)–C(8)	1.389(3)	C(8)–C(7)–P(1)	116.9(2)
C(14)–C(13)	1.392(3)	C(14)–C(13)–P(1)	117.9(2)
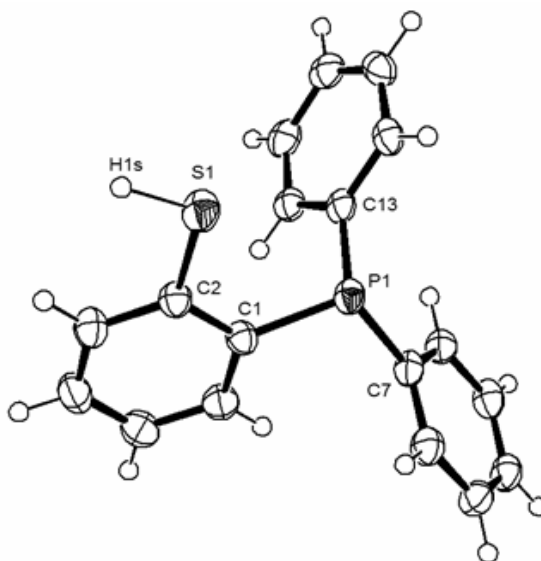
Fig. 1 – Molecular structure of 2-PPh$_2$-C$_6$H$_4$SH (**PSH**).

[Li{(μ-SC$_6$H$_4$-2-PPh$_2$)-κS}(TMEDA)]$_2$ (1)

The TMEDA-free lithium salt Li(**PS**) was obtained in high yield under mild conditions as a white solid from the reaction of **PSH** with ^{n}BuLi in toluene. Pale yellow prisms suitable for X-ray diffraction were obtained at room temperature from a saturated toluene solution containing TMEDA. The ^{31}P{^{1}H} and ^{7}Li{^{1}H} NMR spectra of [Li{(μ-SC$_6$H$_4$-2-PPh$_2$)-κS}(TMEDA)]$_2$ (**1**) show only one signal at –14.2 ppm and 0.7 ppm, respectively. The integral ratio for the aliphatic and aromatic resonances in the ^{1}H NMR spectrum of **1** in [D$_8$]THF was consistent with the presence of one TMEDA per molecule of **PS**$^-$. The proton resonance of **1** was assigned by ^{1}H and ^{1}H-COSY. The absence of $\nu_{S–H}$ at 2400–2500 cm^{-1} in the IR spectrum indicates the presence of anionic thiolato ligands. The spectrum also shows bands at 1040 and 747 cm^{-1} attributed to $\nu_{P–C}$ and $\nu_{C–S}$, respectively. X-ray diffraction studies showed that compound **1** (Fig. 2) crystallises in the triclinic space group $P\bar{1}$ with one molecule in the unit cell.

Compound **1** is a centrosymmetric dimer with a planar four-membered Li$_2$S$_2$ ring. Each lithium atom is surrounded in a distorted tetrahedral fashion by two thiolato sulfur atoms and two TMEDA nitrogen atoms, with a Li(1#)–S(1)–Li(1) angle of 78.1(1)° and S(1#)–Li(1)–S(1) angle of 101.9(2)° (Table 2). The large N(1)–Li(1)–S(1) angle of 125.4(2)° is compensated by a small N(1)–Li(1)–N(2) angle of 87.5(2)°, whereas the N(2)–Li(1)–S(1) angle of 113.4(2)° is closer to the tetrahedral angle. The lithium–sulfur bond lengths of 2.429(3) and 2.462(3) Å for **1** are in the range of sulfur–lithium distances previously reported for lithium thiolates having four-coordinate lithium [2.366–2.661 Å].[8,10-12,24,25] The S–C bond length of 1.754(2) Å is in the same range of previously reported S–C bonds in lithium arylthiolates [av. 1.76 Å].[11-24,25,26] The Li–N bonds [2.108(4) and 2.089(4) Å] are slightly shorter than those found in [Li$_3${(2-SC$_6$H$_4$)(CH$_2$MeNCH$_2$CH$_2$NMe$_2$)(TMEDA)}]$_2$ [2.143 (9) and 2.156(9) Å][25] or in [Li{(μ-CH$_2$SMe)-κC}(TMEDA)]$_2$ [av. 2.154 Å].[27]
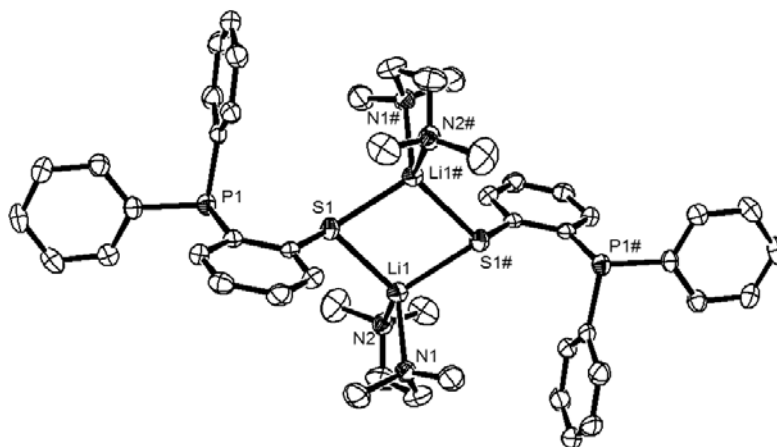

Fig. 2 – Molecular structure of [Li{(μ-SC$_6$H$_4$-2-PPh$_2$)-κS}(TMEDA)]$_2$ (**1**). Hydrogen atoms are omitted for clarity.

Table 2

Selected bond lengths (Å) and bond angles (°) in **1**

|			
C(1)–S(1)	1.754(2)	C(1)–S(1)–Li(1)	113.2(2)
Li(1)–S(1)	2.429(3)	C(1)–S(1)–Li(1#)	122.1(1)
Li(1)–S(1#)	2.462(3)	Li(1)–S(1)–Li(1#)	78.1(1)
Li(1)–N(1)	2.108(4)	S(1)–Li(1)–S(1#)	101.9(2)
Li(1)–N(2)	2.089(4)	N(2)–Li(1)–N(1)	87.5(2)
Li(1)···Li(1#)	3.083(7)	N(1)–Li(1)–S(1)	125.4(2)
Li(1)···P(1)	3.139	N(1)–Li(1)–S(1#)	112.7(2)
		N(2)–Li(1)–S(1)	113.4(2)
		N(2)–Li(1)–S(1#)	116.8(2)
		C(2)–P(1)–C(7)	101.84(9)
		C(2)–P(1)–C(13)	101.4(1)
		C(7)–P(1)–C(13)	99.68(9)

In **1**, the Li···Li [3.083(7) Å] and Li···P [3.139 Å] distances are below the sum of the van der Waals radii of the atoms involved (Σ v.d.W. radii Li···Li = 3.64 Å, Li···P = 3.62 Å),[28] which could be indicative of some degree of Li···Li and Li···P interactions. The Li···Li distance is similar to those found in [Li(μ-SCH$_2$Ph)(py)$_2$]$_\infty$[12] [3.092(8) and 3.243(8) Å] and [Li$_4${PPh(C$_6$H$_3$-2-S-3-SiMe$_3$)$_2$-κ^{3}S,S',P}$_2$(DME)$_2$}][8] [3.09(2) and 3.11(2) Å].

Mg{(SC$_6$H$_4$-2-AsPh$_2$)-κ*S*}$_2$(THF)$_4$ (2) and Mg{(SC$_6$H$_4$-2-PPh$_2$)-κ^2*S,P*}$_2$(THF)$_2$ (3)

The magnesium compounds Mg{(SC$_6$H$_4$-2-AsPh$_2$)-κ*S*}$_2$(THF)$_4$ (**2**) and Mg{(SC$_6$H$_4$-2-PPh$_2$)-κ^2*S,P*}$_2$(THF)$_2$ (**3**) were synthesised in a straightforward manner by alkane elimination in the reaction between MgRR' (where R = butyl, R' = octyl) and two equivalents of **AsSH** or **PSH** in toluene at –78 °C (Scheme 1). The products were obtained in good yields as white solids. The reduced solubility of the products prevented to obtain crystals of the solvent-free compounds from

non-coordinating solvents. The solvated compounds were obtained by slow crystallisation from THF at 8 °C as colourless crystals (**2**), or by crystallisation from [D$_8$]THF in an NMR tube over a few weeks at room temperature (**3**).

The ^{31}P{^{1}H} NMR spectrum of **3** shows a singlet at –18.9 ppm, which is shifted upfield relative to the signal corresponding to the free ligand (–12.6 ppm) and indicates coordination of the phosphorus atoms. According to the IR spectrum (absence of ν$_{S-H}$ at 2400–2500 cm^{-1}), anionic thiolato ligands are present in complexes **2** and **3**. Mg{(SC$_6$H$_4$-2-AsPh$_2$)-κ*S*}$_2$(THF)$_4$ (**2**) and Mg{(SC$_6$H$_4$-2-PPh$_2$)-κ^2*S,P*}$_2$(THF)$_2$ (**3**) (Figs. 3 and 4) crystallise as monomeric species in the triclinic space group $P\bar{1}$ with two molecules in the unit cell and in the monoclinic space group $I2/a$ with four molecules in the unit cell, respectively. The asymmetric unit of **2** also contains two non-coordinating THF half-molecules. Selected bond lengths and angles are given in Table 3.
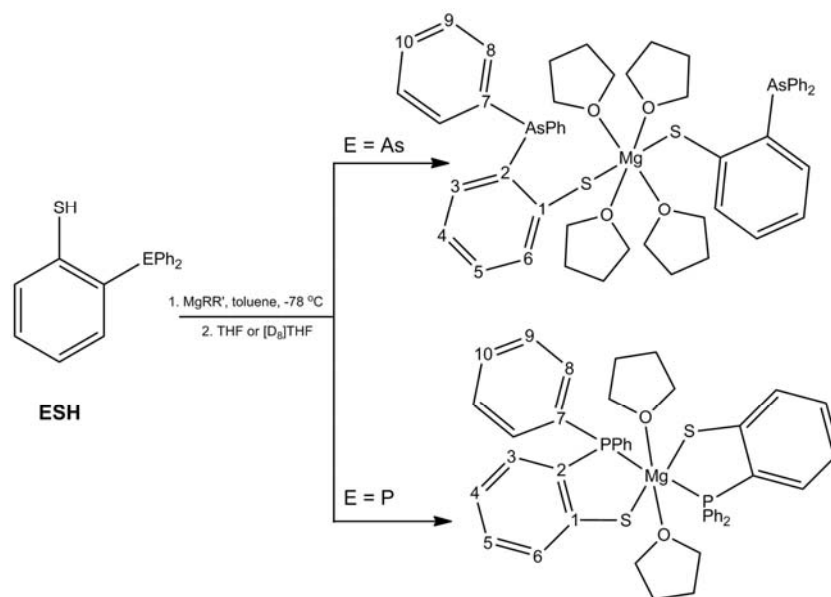

Scheme 1

Table 3

Selected bond lengths (Å) and bond angles (°) in **2** and **3**

	2		**3**
bond lengths (Å)			
S(1)–C(2)	1.745(6)	S(1)–C(1)	1.759(2)
S(2)–C(20)	1.764(5)	S(1)–Mg(1)	2.5323(4)
S(1)–Mg(1)	2.550(2)	Mg(1)–P(1)	2.7050(4)
S(2)–Mg(1)	2.574(2)	Mg(1)–O(1)	2.109(2)
Mg(1)–O(1)	2.232(4)	Mg(1)–O(1)	2.133(2)
Mg(1)–O(2)	2.137(4)		
Mg(1)–O(3)	2.185(4)		
Mg(1)–O(4)	2.138(4)		

Table 3 (continued)

bond angles (°)

C(2)–S(1)–Mg(1)	114.6(2)	C(1)–S(1)–Mg(1)	99.21(6)
C(20)–S(2)–Mg(1)	115.2(2)	O(1#)–Mg(1)–O(1)	180.0
O(2)–Mg(1)–O(1)	95.1(2)	O(1)–Mg(1)–S(1)	92.01(2)
O(3)–Mg(1)–O(1)	178.8(1)	O(1#)–Mg(1)–S(1)	87.99(2)
O(2)–Mg(1)–O(3)	85.1(1)	S(1)–Mg(1)–S(1#)	175.98(4)
O(2)–Mg(1)–O(4)	170.0(2)	O(1)–Mg(1)–P(1)	91.06(2)
O(4)–Mg(1)–O(1)	94.8(2)	O(1#)–Mg(1)–P(1)	88.94(2)
O(4)–Mg(1)–O(3)	85.0(2)	S(1)–Mg(1)–P(1)	74.63(1)
O(1)–Mg(1)–S(1)	88.1(1)	S(1)–Mg(1)–P(1#)	105.30(2)
O(2)–Mg(1)–S(1)	86.5(1)	P(1#)–Mg(1)–P(1)	177.88(4)
O(3)–Mg(1)–S(1)	90.7(1)		
O(4)–Mg(1)–S(1)	95.2(1)		
O(1)–Mg(1)–S(2)	90.1(1)		
O(2)–Mg(1)–S(2)	92.6(1)		
O(3)–Mg(1)–S(2)	91.1(1)		
O(4)–Mg(1)–S(2)	86.1(1)		
S(1)–Mg(1)–S(2)	177.89(9)		
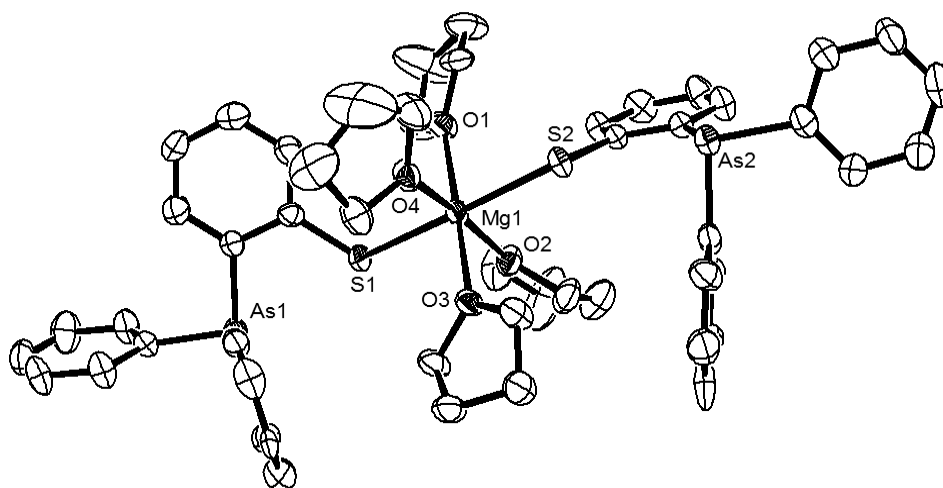
Fig. 3 – Molecular structure of Mg{(SC$_6$H$_4$-2-AsPh$_2$)-κS}$_2$(THF)$_4$ (**2**). Hydrogen atoms are omitted for clarity.

In the asymmetric unit of **3**, only one half of the molecule is found, with the other half being generated by symmetry operations. Magnesium is located on a twofold rotation axis, resulting in one independent thiolato and two independent THF molecules.

In both complexes **2** and **3**, magnesium is six-coordinate, surrounded in a distorted octahedral fashion by two monodentate **AsS**⁻ or bidentate **PS**⁻ ligands (with a *trans* orientation of the S atoms [S–Mg–S 177.89(9)° (**2**) and 175.98(4)° (**3**)]) and four (**2**) or two (**3**) mutually *trans* oriented THF ligands, respectively. Neutral magnesium thiolates with a coordination number of six are not very common; the first six-coordinate magnesium thiolate was reported in 1998 by S. Chadwick *et al.*[19] The O–Mg–S angles are in the range of 86.5(1)–95.2(1)° (**2**) and 87.99(2)–92.01(2)° (**3**). The P(2)–

Mg(1)–P(1) group is almost linear in **3** [177.88(4)°]. Due to the different coordination modes (monodentate in **2**, bidentate in **3**), the C–S–Mg bond angles are very different [114.6(2)° and 115.2(2)° in **2**, 99.21(6)° in **3**].

The Mg–S bond length of **3** is slightly shorter [2.5323(4) Å] than those in **2** [2.550(2) Å and 2.574(2) Å]. The Mg–S bond lengths are slightly smaller than that found in the six-coordinate magnesium complex Mg(SC$_6$H$_5$)$_2$(py)$_4$ [2.6247(5) Å][19] but are comparable with the sum of the ionic radii for six-coordinate Mg^{2+} and S^{2-} [2.56 Å],[29] supporting the view of a mainly ionic interaction between the cation and the ligand. This is also supported by ab initio calculations of Pappas, who described Mg–S interactions as predominantly ionic.[30]
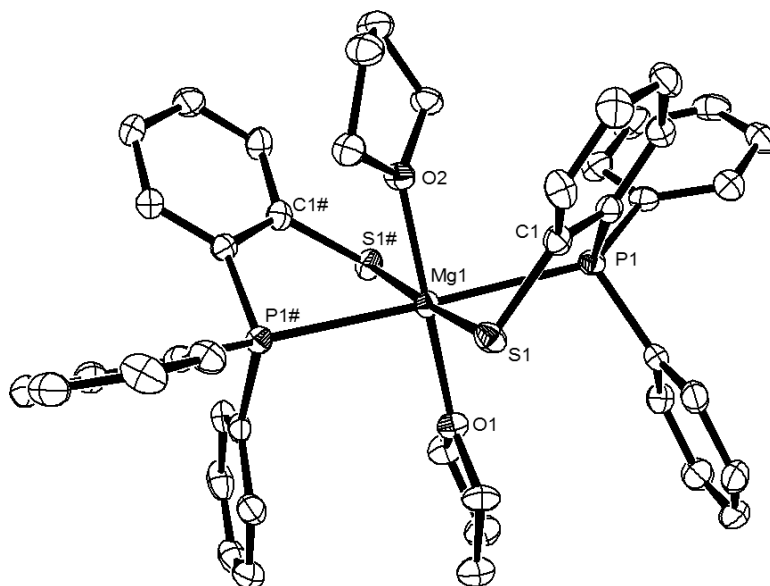
Fig. 4 – Molecular structure of Mg{(SC$_6$H$_4$-2-PPh$_2$)-κ^{2}S,P}$_2$(THF)$_2$ (**3**). Hydrogen atoms are omitted for clarity.

The S–C bond lengths in **2** [1.745(6) and 1.764(5) Å] and **3** [1.759(2) Å] are within the normal range for S–C single bonds.[23] The Mg–O bonds of the coordinated THF ligands range from 2.137(4) to 2.232(4) Å in **2**. They are slightly shorter in **3** [2.109(2) and 2.133(2) Å] probably due to the bidentate coordination of the **PS**-ligand. However, the Mg–O bond lengths are comparable to those in Mg{(Me$_3$SiC(PMe$_2$)$_2$)-κ^{2}P,P'}$_2$(THF)$_2$ [2.137(2) and 2.122(2) Å][31] or Mg{(Me$_3$SiNC(Ph)PSiMe$_3$)-κ^{2}N,P}$_2$(THF)$_2$ [2.135(2) and 2.120(2) Å][32] and are significantly longer than in Mg$_6$(PSi^{i}Pr$_3$)$_6$(THF)$_4$ [2.046(2)–2.059(2) Å][33] or in tetrahedral complexes such as MgPh$_2$(THF)$_2$ [av. 2.03 Å][34] or Mg{E(SiMe$_3$)$_2$}$_2$(THF)$_2$ [E = P, As; av. 2.05 Å].[35]

In **3**, the **PS**$^-$ ligand is also coordinated to the magnesium cation via the phosphorus atom [Mg(1)–P(1) 2.7050(4) Å] and is thus a rare example of a magnesium–phosphine complex.[31,36] The Mg–P bond length in **3** is close to that in the six-coordinate magnesium phosphine complex Mg{(2,6-(Me$_2$PCH$_2$)$_2$-C$_6$H$_3$)-κ^{3}C,P,P'}$_2$ [2.761(1) and 2.770(1) Å].[36b]

Monodentate versus bidentate coordination of arsino- and phosphinoarylthiolates in 2 and 3. Geometries for the monodentate arsenic-containing derivative **2** and for the bidentate phosphorus-containing derivative **3** were optimised with DFT calculations (B3LYP/6-31G*). Two additional hypothetical structures were also computed: a complex in which arsenic in **2** was replaced by phosphorus, and a complex in which phosphorus in **3** was replaced by arsenic. This allowed for calculation of energy preferences between the monodentate and the bidentate isomers in arsenic derivative **2** and phosphorus derivative **3**. Surprisingly, the experimentally observed monodentate isomer of **2** was less stable than its hypothetical bidentate/chelate counterpart by 3.3 kcal/mol, while the reverse situation was found for **3**, with the experimentally observed chelate being less stable than its hypothetical monodentate counterpart by 4.5 kcal/mol. While energy differences of this magnitude are not entirely reliable with DFT on systems of this size, the trend nevertheless remains valid: the phosphorus-containing ligand appears thermodynamically more prone to form a monodentate complex with magnesium than the arsenic-containing ligand. This tendency is mirrored in the partial atomic charges on the non-magnesium-bound arsenic and phosphorus atoms in the two monodentate complexes: 0.20 on arsenic versus 0.34 for phosphorus; since bonding to Mg^{2+} is electrostatic in nature, clearly the phosphorus atom would be less likely than the arsenic atom to bind to the already positively charged magnesium centre. Nevertheless, the experimental data show a reversed trend, with arsenic but not phosphorus yielding a monodentate complex. The DFT and crystallographic data may be reconciled by Fig. 5, where the space available above As and P is illustrated: due to its longer As–C bonds, the arsenic remains much more solvent-accessible than phosphorus, which implies that this isomer may

accumulate in solution, as favoured by solvation events at arsenic compared to phosphorus. The increased compactness in the monodentate phosphorus isomer implies closer contact of

phosphorus with magnesium, which favours re-closing of the chelate ring and ultimately crystallization of the chelate form, as observed experimentally.
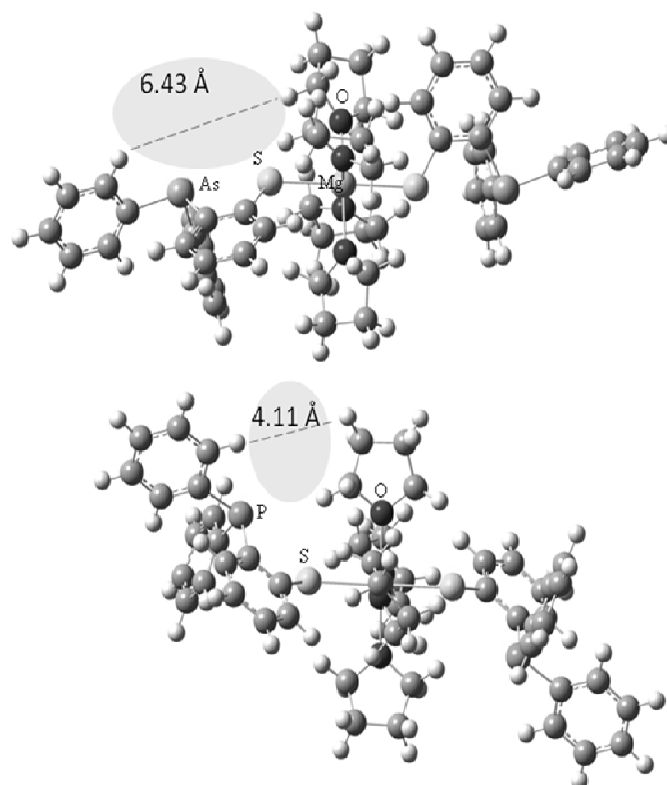

Fig. 5 – DFT-optimised geometries of the monodentate isomers with arsenic (top) and phosphorus (bottom).
The space available above As and P is highlighted, and the shortest distance between two atoms sitting above P/As is labelled.

The thermodynamic data obtained for the compounds discussed above was unexpected, insofar as phosphorus would have been expected to exhibit a higher affinity than arsenic towards magnesium, simply based on chemical hardness considerations. To investigate this apparent contradiction, we also examined two much simpler models, $[Mg(PMe_3)_2]^{2+}$ and $[Mg(AsMe_3)_2]^{2+}$, with the same computational methodology. In each of these models, we computed the energy cost of elongating one of the Mg–P/As bonds. Elongation to 3 Å from the equilibrium distance of about 2.6 Å in both models resulted in an increase in energy by 6.7 kcal/mol in the case of phosphorus and 3.9 kcal/mol in the case of arsenic. Thus, the calculations do yield the expected information, that the Mg–As bond is distinctly more labile (by ca. 40%, according to the data given here) than the Mg–P bond in arsine/phosphine complexes. This would then provide a kinetic-based argument for the fact that a chelate complex with a Mg–P bond

was observed experimentally, unlike the corresponding arsenic compound.

The reason why in our complexes the arsenic chelate appears thermodynamically more likely than the phosphorus one may also be related to the small size of the central metal atom, which implies inherent crowding of the ligand and implicitly a key role of intra/inter-ligand noncovalent interactions in the solid state. We propose that indeed these non-covalent interactions, further affected by the different sizes of As and P, hold the key to dictating the hapticity preference in our complexes; this would then need to be considered when comparing these results with those obtained on metal centres of larger radii with the same types of ligands.

EXPERIMENTAL

General Procedures. All manipulations were carried out under an inert atmosphere of dry nitrogen. Cyclohexane,

n-hexane, toluene, diethyl ether and THF were dried over sodium/benzophenone, distilled under an atmosphere of dry argon and stored over a potassium mirror. TMEDA was refluxed over CaH_2, distilled and kept under nitrogen. The deuterated solvents for NMR spectroscopy were used as purchased and kept under inert atmosphere; [D_8]THF was kept over molecular sieves. $CDCl_3$ was dried over $LiAlH_4$, distilled and kept over molecular sieves. *[n]*BuLi (2.2 м in *n*-hexane solution) and MgRR' (20% in *n*-heptane solution) were provided by Chemetall, Germany. 2-EPh_2-C_6H_4SH (E = P (**PSH**), As (**AsSH**)) were prepared from thiophenol by *ortho*-lithiation/electrophilic substitution,[1,2,21] using Schlenk techniques and dry solvents.

Elemental analysis was performed with a Vario EL–Heraeus microanalyser. IR spectra were recorded using a Perkin-Elmer System 2000 spectrometer in the range 4000–400 and 400–200 cm^{-1} using KBr and CsI pellets, respectively. ^1H and ^{31}P NMR spectra were recorded on a Bruker Avance DRX-400 instrument. ^1H: TMS as internal standard, ^{31}P NMR: external 85% H_3PO_4. The crystallographic data were collected on a Stoe IPDS-1 imaging plate diffractometer, Φ-scan rotation (compound **2**) and on a CCD

Oxford Xcalibur S diffractometer (Agilent Technologies), ω and φ scan mode, data reduction with XRED[37] and numerical absorption correction (Stoe IPDS-1) or CrysAlisPro including empirical absorption correction with SCALE3 ABSPACK[38] (compounds **PSH**, **1**, **3**). Radiation: MoK_α (λ = 0.71073 Å). Structure refinement was carried out with SHELXL-97.[39] Non-hydrogen atoms, except for poorly defined disordered regions, were refined anisotropically, and H atoms were calculated on idealised positions. Structure figures were generated with ORTEP.[40] Thermal ellipsoids are drawn at 50% probability if not otherwise mentioned. The relevant crystallographic data and refinement details are shown in Table 4. CCDC 865542 (**PSH**), 865543 (**1**), 865544 (**2**) and 865545 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Geometries have been optimized with the B3LYP functional[41] and the 6-31G* basis set as implemented in the Gaussian 09 software package.[42]

Table 4

Summary of data collection, structure solution and refinement for **PSH**, **1**, **2** and **3**

	PSH	1	2	3
empirical formula	$C_{18}H_{15}PS$	$C_{48}H_{60}Li_2N_4P_2S_2$	$C_{56}H_{68}As_2MgO_5S_2$	$C_{44}H_{44}MgO_2P_2S_2$
fw	294.33	832.94	1059.37	755.16
T, K	130(2)	130(2)	213(2)	130(2)
cryst syst	Triclinic	Triclinic	Triclinic	Monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$I2/a$
unit cell dimens				
a, Å	8.4532(4)	10.489(4)	12.205(1)	11.0201(6)
b, Å	10.4129(5)	11.056(2)	12.944(1)	14.6090(5)
c, Å	10.5759(4	11.283(4)	18.542(2)	23.3605(7)
α, deg	112.638(4)	98.50(2)	74.95(1)	90
β, deg.	99.503(4)	114.57(4)	71.03(1)	95.417(3)
γ, deg	111.733(4)	94.22(2)	81.81(1)	90
sym. transf. used to generate equiv. atoms	-	#1 -x+2,-y+2,-z+2	-	#1 -x-1/2,y,-z+2
vol, Å³	744.97(6)	1163.4(6)	2669.8(4)	3744.1(3)
Z	2	1	2	4
$D_{calc,}$ Mg/m³	1.312	1.189	1.318	1.340
μ (Mo Kα), mm⁻¹	0.311	0.220	1.387	0.283
F(000)	308	444	1108	1592
crystal size, mm³	0.4 x 0.2 x 0.05	0.2 x 0.15 x 0.08	0.25 x 0.25 x 0.15	0.3 x 0.15 x 0.10
$\theta_{Min}/\theta_{Max}$, deg.	2.67/26.37	2.64/26.37	2.39 to 28.08	2.79/28.28
no of reflns. collected	13124	17876	33008	48701
no of indep. reflns.	3048 [$R_{(int)}$ = 0.0460]	4742 [$R_{(int)}$ = 0.0603]	11954 [$R_{(int)}$ = 0.0763]	4662 [$R_{(int)}$ = 0.0634]
Completeness to θ_{Max}, %	99.8	99.8	91.9	99.9
final R indices [I>2σ(I)]	R_1 = 0.0424 wR₂ = 0.1046	R_1 = 0.0380 wR₂ = 0.0651	R_1 = 0.0583 wR₂ = 0.1419	R_1 = 0.0317 wR₂ = 0.0738
R indices (all data)	R_1 = 0.0671 wR₂ = 0.1126	R_1 = 0.0853 wR₂ = 0.0776	R_1 = 0.1180 wR₂ = 0.1532	R_1 = 0.0593 wR₂ = 0.0816
goodness-of-fit on F²	0.958	0.899	0.895	0.931
largest diff. peak, e·Å⁻³	0.625 and −0.266	0.234 and −0.237	1.681 and −0.414	0.400 and −0.305

Synthesis of [Li{(μ-SC₆H₄-2-PPh₂)-κS}(TMEDA)]₂ (1).

Synthesis of [Li{(μ-SC₆H₄-2-PPh₂)-κS}(TMEDA)]₂ (1).
n-Butyllithium (2.4 ml of a 2.2 M solution in n-hexane, 5.29 mmol) was added at 0 °C to a stirred solution of **PSH** (1.55 g, 5.29 mmol) in toluene (20 ml). After addition of half of the ^{n}BuLi solution a white precipitate formed and the solution turned yellow. The mixture was allowed to stir for 20 h at room temperature. Then the volume was reduced to 50%, and the white solid was isolated by filtration and dried in vacuo (yield: 1.28 g, 4.04 mmol, 76.3% based on **PSH**). Pale yellow crystals suitable for X-ray diffraction were obtained at room temperature from the filtrate after addition of TMEDA. The product does not melt up to 350 °C. ^{1}H NMR (δ, [D$_8$]THF, ppm): 7.33 (t, 1H, aryl-H), 7.17–7.20 (s, 10H, aryl-H), 6.72 (t, 1H, aryl-H), 6.44 (t, 1H, aryl-H), 6.35 (br, 1H, aryl-H), 2.30 (s, 4H, N(CH_2) in TMEDA), 2.15 (s, 12H, N(CH_3) in TMEDA). ^{31}P{^{1}H} NMR (δ, [D$_8$]THF, ppm): −14.2. ^{7}Li{^{1}H} NMR (δ, [D$_8$]THF, ppm): 0.7. Anal. Calcd: C 69.21, H 7.26, N 6.73, S 7.70. Found: C 69.20, H 7.28, N 7.13, S 8.00 for C$_{24}$H$_{30}$LiN$_2$PS: M = 416.479. $ν_{max}$ (KBr)/cm^{-1}: 3050m, 2956s, 2868m, 2835s, 2792s, 1952vw, 1906vw, 1829vw, 1584w, 1563m, 1462s, 1434s, 1414s, 1354w, 1290m, 1256m, 1180w, 1156w, 1126m, 1091s, 1040s, 1025s, 950w, 792w, 747vs, 697s, 582w, 532w, 500m, 464m, 435w.

Synthesis of Mg{(SC₆H₄-2-AsPh₂)-κS}₂(THF)₄ (2). An n-heptane solution of MgRR' (R = butyl, R' = octyl) (0.284 g, 1.42 g of a 20% solution, 1.46 mmol) was added dropwise at −78 °C to a stirred solution of **AsSH** (0.99 g, 2.92 mmol) in toluene (15 ml). Then the reaction mixture was warmed to room temperature and stirred for another 20 h. The white precipitate obtained was isolated by filtration and dried in vacuo (yield: 0.77 g, 1.10 mmol, 75.3% based on **AsSH**). Colourless crystalline needles were obtained by recrystallisation from THF at 8 °C. Mp: 110–122 °C. ^{1}H NMR (δ, CDCl$_3$, ppm): 7.60–6.73 (m, 28H, aryl-H), 3.77 (m, 20H, CH_2O (coordinated THF and THF in the asymmetric unit)), 1.71 (m, 20H, CH_2 (coordinated THF and THF in the asymmetric unit)). ^{13}C{^{1}H} NMR (δ, CDCl$_3$, ppm): 151.53 (C^1), 140.22 (C^2), 138.72 (C^7), 134.27 (C^6), 134.05 (C^8), 132.19 (C^3), 128.64 (C^5), 128.15 (C^{10}), 127.93 (C^9), 122.50 (C^4), 68.72 (CH$_2$O (THF)), 25.29 (CH$_2$ (THF)). Anal. Calcd: C 63.02, H 6.40, S 6.98, Found: C 62.97, H 6.38, S 6.96 for C$_{56}$H$_{68}$As$_2$MgO$_5$S$_2$: M = 1059.37. $ν_{max}$ (KBr)/cm^{-1}: 3045m, 2973m, 2881m, 1950vw, 1814vw, 1578w, 1564m, 1480m, 1457w, 1432s, 1421m, 1262m, 1243w, 1183w, 1121w, 1090m, 1067m, 1023s, 999m, 913w, 871m, 736s, 715w, 697s, 517w, 471m, 448m. $ν_{max}$(CsI)/cm^{-1}: 393m, 344s (Mg–O), 320s, 307m, 295s, 248w.

Synthesis of Mg{(SC₆H₄-2-PPh₂)-κ²S,P}₂(THF)₂ (3). In a similar procedure as was used for the synthesis of **2**, an n-heptane solution of MgRR' (R = butyl, R' = octyl) (0.205 g, 1.022 g of a 20% solution, 1.054 mmol) was added dropwise at −78 °C to a stirred solution of **PSH** (0.62 g, 2.109 mmol) in toluene (15 ml). The white precipitate obtained was isolated by filtration and dried in vacuo (yield: 0.57 g, 0.934 mmol, 88.6% based on **PSH**). The product is a white solid which melts at 266 °C, soluble in tetrahydrofuran, slightly soluble in diethyl ether, chloroform, TMEDA and dimethoxydiethyl ether (diglyme) and insoluble in methanol or n-hexane. A few crystals of **3** grew in an NMR tube (solvent [D$_8$]THF) over a few weeks. Except for NMR spectra, all other methods (IR, MS) and elemental analysis were performed on the crude product before crystallisation (**3** without coordinated THF). Attempts to recrystallise the product from THF, either at room

temperature or low temperature, were unsuccessful. ^{1}H NMR (δ, [D$_8$]THF, ppm): 7.51–6.64 (m, 28H, aryl-H). ^{13}C{^{1}H} NMR (δ, [D$_8$]THF, ppm): 137.42 (C^1), 135.75 (C^2), 134.68 (t, J$_{CP}$ = 7.44 Hz, C^7), 134.20 (C^6), 131.69 (C^3), 128.65 (C^8), 128.32 (C^{12}), 127.97 (C^9), 127.88 (C^{11}), 127.36 (C^{10}), 125.02 (C^4), 120.72 (C^5). ^{31}P{^{1}H} NMR (δ, [D$_8$]THF, ppm): −18.9. Anal. Calcd: C 70.77, H 4.62, S 10.50, Found: C 69.88, H 4.76, S 10.57 for C$_{36}$H$_{28}$MgP$_2$S$_2$: M = 610.99. $ν_{max}$ (KBr)/cm^{-1}: 3050m, 2962w, 1954vw, 1888vw, 1815vw, 1585w, 1571m, 1479m, 1435s, 1420s, 1326vw, 1306w, 1261m, 1182w, 1158w, 1096s, 1070m, 1044m, 1027m, 999w, 915w, 864w, 803w, 742vs, 694vs, 549w, 498m (Mg–P), 469m, 426vw.

CONCLUSIONS

A lithium phosphinoarylthiolate and two magnesium phosphino- or arsinoarylthiolates were synthesised and characterised: [Li{(μ-SC$_6$H$_4$-2-PPh$_2$)-κS}(TMEDA)]$_2$ (**1**), Mg{(SC$_6$H$_4$-2-AsPh$_2$)-κS}$_2$(THF)$_4$ (**2**) and Mg{(SC$_6$H$_4$-2-PPh$_2$)-κ^{2}S,P}$_2$(THF)$_2$ (**3**). The central structural unit of **1** is a planar four-membered Li$_2$S$_2$ ring in which each lithium atom is surrounded in a distorted tetrahedral fashion by two thiolato sulfur atoms and two TMEDA nitrogen atoms. In **2** and **3**, the Mg^{2+} cation is octahedrally coordinated by two **AsS**$^-$ (**2**) or **PS**$^-$ (**3**) ligands and four (**2**) or two THF ligands (**3**), indicating different coordination behaviour of the ligands: monodentate for **AsS**$^-$ and bidentate for **PS**$^-$.

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