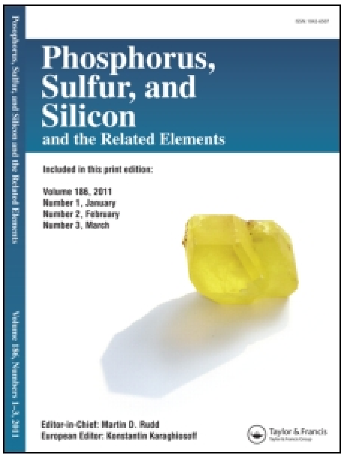

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A Structural and Theoretical Study of the Thiophosphinite and Dithiophosphinate Anions

Natalie E. Mansfield[a]; Martyn P. Coles[a]; Peter B. Hitchcock[a]
[a] Department of Chemistry, University of Sussex, Falmer, Brighton, UK

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A Structural and Theoretical Study of the Thiophosphinite and Dithiophosphinate Anions

Natalie E. Mansfield, Martyn P. Coles, and Peter B. Hitchcock
Department of Chemistry, University of Sussex, Falmer, Brighton, UK

Two novel lithium compounds containing either the phosphorus-chalcogenide anions $[Ph_2PS]^-$ *or* $[Cy_2PS_2]^-$ *were isolated as decomposition products in the attempted formation of phospha(V)guanidinate anions. Lithium diphenylthiophosphinite was structurally characterized as the dimeric TMEDA adduct* $[Li(Ph_2PS)(TMEDA)]_2$ *(1), in which a rare example of the* κ^1*-S bonding mode was observed for the anion. The dicyclohexyldithiophosphinate anion was incorporated into an aggregated structure with molecular formula* $[Li_5(Cy_2PS_2)_4(OH)]_2$ *(2). DFT calculations were performed on the isolated* $[R_2PS]^-$ *and* $[R_2PS_2]^-$ *anions (R = Ph, Cy), indicating delocalization of electron density into the P-S bonds for each model, in agreement with bond-lengths taken from crystallographic data.*

Keywords Coordination compound; crystal structure; dithiophosphinate; DFT; lithium; thiophosphinite

INTRODUCTION

We have been utilizing phospha(III) guanidines of general formula $R_2PCNR'NHR'$ (R = Ph, Cy; R′ = ^iPr, Cy)[1,2] as a source of neutral and anionic ligands in coordination chemistry for a number of years. Incorporation of both nitrogen and phosphorus functionalities affords many possible bonding modes at a metal center, and this diversity has been noted in the solid state using X-ray diffraction experiments for a range of transition metal- and main-group compounds.[3–5] The original purpose of this work was to explore the behavior of the corresponding phospha(V)guanidinate anions in coordination chemistry, where additional bonding modes are potentially available through chalcogen·metal

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Address correspondence to Dr. Martyn P. Coles, Department of Chemistry, University of Sussex, Falmer, Brighton, BN1 9QJ, United Kingdom. E-mail: m.p.coles@sussex.ac.uk

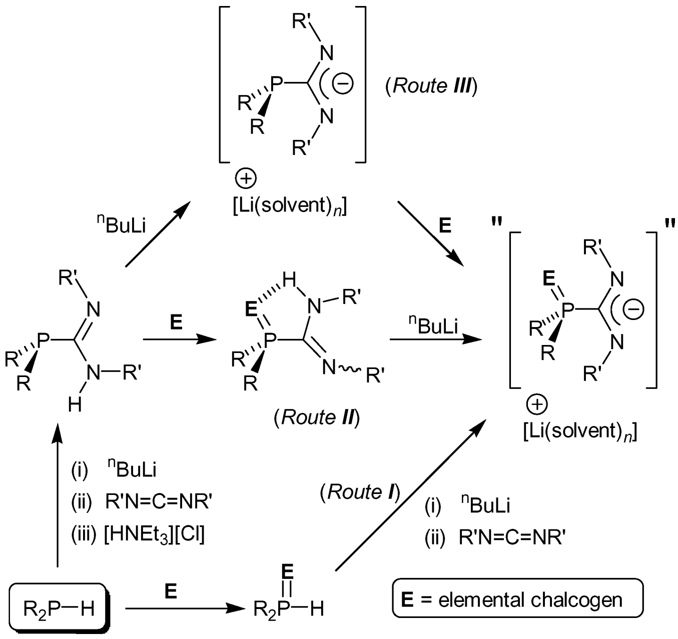
interactions. However, the synthetic routes and conditions employed did not lead to the desired compounds, and only decomposition products containing the thiophosphinite or dithiophosphinate anions ($[R_2PS]^-$ and $[R_2PS_2]^-$, respectively) were isolated. The molecular structures of the resultant lithium species are, however, of interest in themselves as they reveal a number of previously unobserved bonding patterns for these widely studied anions. Density functional studies on the isolated anions have been conducted to further our understanding of the bonding within the products.

RESULTS AND DISCUSSION

Our first attempt at synthesizing the phospha(V)guanidinate anion involved formation of the chalcogenidophosphinite anion, $[R_2PE]^-$, via deprotonation of the secondary phosphine chalcogenide. Given that the conjugate acids of the thiophosphinites exist as the secondary phosphine sulfides unless highly electron withdrawing phosphorus substituents are present,[6] we anticipated the presence of a *P*-centered anion as a component of the reaction mixture that would react with a carbodiimide via P–C bond formation, analogous to the $P^{(III)}$ phosphaguanidines (*Route I*).[1,2] However, important work in the area by Davies *et al.* has shown that the negative charge in the analogous selenophosphinite anion is essentially localized at selenium, illustrated by an upfield shift in the ^{77}Se NMR spectrum and the observation of Se-Li bonds in the molecular structure of $[Li(Ph_2PSe)(TMEDA)]_2$.[7] See Scheme 1.

In our approach, we formed the diphenylthiophosphinite anion, $[Ph_2PS]^-$, by the addition of ^{n}BuLi to a solution of $Ph_2P(S)H$ in THF. The reaction mixture was added to a solution of $^iPrN{=}C{=}N^iPr$, resulting in formation of a colorless solution. Despite trying numerous conditions and solvent combinations, no pure solid product could be isolated from this solution. Excess TMEDA was therefore added to the reaction mixture to aid crystallization, affording colorless crystals (**1**) that were analyzed by X-ray diffraction. No other clean product could be isolated from this reaction.[8]

The molecular structure of **1** is shown in Figure 1; crystal structure and refinement data is collected in Table I and selected bond lengths and angles in Table II. Compound **1** consists of the TMEDA adduct of the lithium thiophosphinite anion, $[Li(Ph_2PS)(TMEDA)]_2$. In the solid-state, **1** crystallizes as a dimer in which the sulfur atoms of the $[Ph_2PS]^-$ anion bridge between two 'Li(TMEDA)' cations, giving a highly puckered metallacycle, with a fold-angle of 141.8° between the two Li_2S planes (Figure 1b). Within the metallacycle, the



SCHEME 1 Potential routes to Li-salts of the phospha(V)guanidinate anion.

internal angles are considerably more acute at sulfur [S(1) 76.86(16)°; S(2) 77.53(16)°] than lithium [Li(1) 95.35(17); Li(2) 95.10(17)°], with an overall S· · ·S distance of 3.622 Å. The sum of the angles at phosphorus [Σ_{angles}: P(1) 306.51°; P(2) 304.54°] and sulfur [Σ_{angles}: S(1) 294.79°; S(2) 301.42°] indicate that that each atom is pyramidal. The lithium atoms are in a distorted tetrahedral geometry [Li(1) 88.5(2)°–123.7(2)°; Li(2) 87.9(2)°–126.9(2)°], with the most acute angle resulting from the chelating TMEDA ligand.

The phosphorus-sulfur bond lengths in **1** [2.0661(11) Å and 2.0710(11) Å] are an intermediate value between P—S single bonds [2.12 Å][9] and the P=S double bond within $Ph_2P{=}S$ [average value of several crystal structures = 1.95 Å], consistent with delocalization of π-electron density into this bond. The sulfur-lithium distances [2.427(5) Å - 2.482(5) Å] are unremarkable, being within the range noted in similar dimeric lithium thiolates.

Despite being the subject of numerous studies,[6] metallated thiophosphinites in which a sulfur-metal bond constitutes the only interactions with the anion (**i**, Figure 2) are rare and structurally characterized examples are limited to a single example involving the

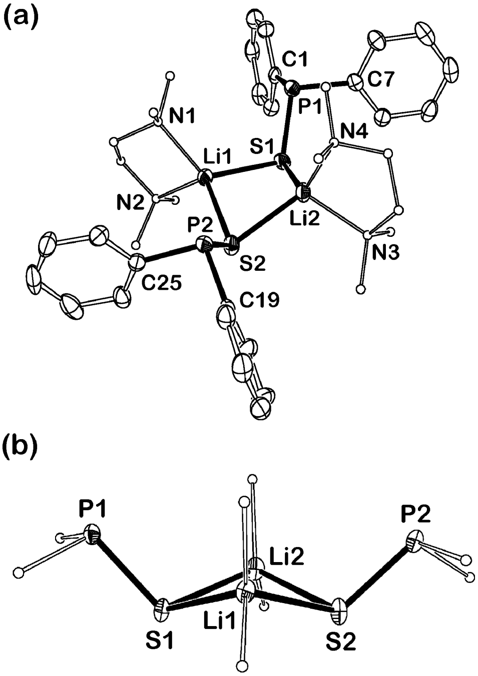
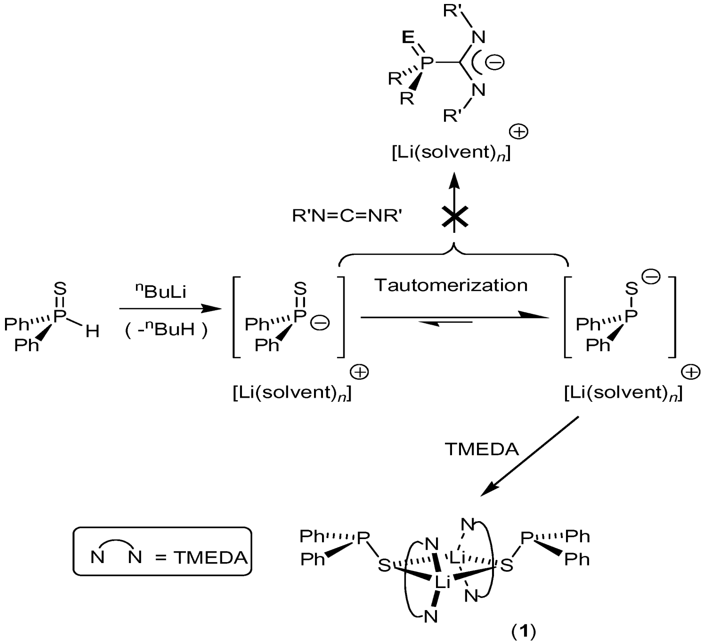


FIGURE 1 (a) ORTEP of $[Li(Ph_2PS)(TMEDA)]_2$ (**1**) (ellipsoids at 30%, TMEDA molecules reduced to 'ball and stick' representation and hydrogens omitted for clarity); (b) The core of **1**, highlighting the folded Li_2S_2 metallacycle.

bis(cyclopentadienyl)titanium fragment,[10] although the diphenylthiophosphinite anion has also been observed in a κ^1-*S*-mode to the boron of a carborane cage.[11] The ligand is much more commonly involved in bonding to a metal through either the phosphorus atom (**ii**), as a chelating κ^1-*S*, *P*-ligand using a combination of the phosphorus and sulfur heteroatoms (**iii**), or as a bridge between two metal centers in a κ^1-*S*:κ^2-*P*-mode (**iv**). It is also worth noting that, whilst the Li_2S_2 motif involving three-coordinate sulfur has been previously noted in a range of alkyl,[12] aryl[13] and silyl[14] thiolate compounds, the only structurally characterized example in which a phosphorus-chalcogen moiety is present involves the thiophosphonamide anion.[15]

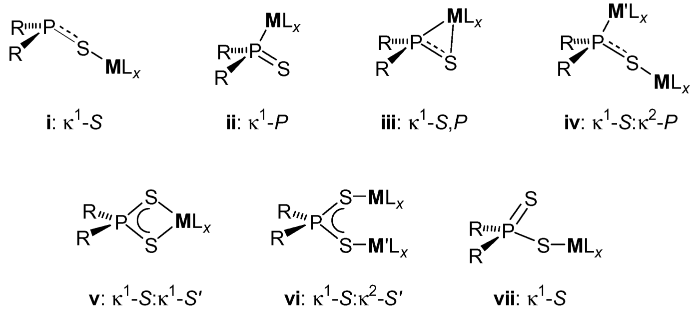
Isolation of the thiophosphinite anion from this reaction mixture indicates that tautomerization between the $P^{(V)}$ center in the starting reagent and the isolated $P^{(III)}$ salt has occurred (Scheme 2). Formation of the four-membered metallacycle with bridging sulfur atoms and no phosphorus·lithium contacts suggests that the negative charge in the resultant anion is strongly associated with the chalcogen atom, as noted



(1)

SCHEME 2 Proposed mechanistic pathway to compound **1**.

above. Given that only a low yield of **1** was obtained, it is not possible to definitively say that the anticipated reaction with the carbodiimide did not occur; however, the accumulation of electron density at the chalcogen inferred from the crystal structure of **1** would disfavor formation of the P–C bond, with the TMEDA therefore trapping the $P^{(III)}$ anion


i: κ¹-*S* **ii**: κ¹-*P* **iii**: κ¹-*S*,*P* **iv**: κ¹-*S*:κ²-*P*

v: κ¹-*S*:κ¹-*S*′ **vi**: κ¹-*S*:κ²-*S*′ **vii**: κ¹-*S*

FIGURE 2 Previously observed bonding modes for the thiophosphinite anion (**i** - **iv**) and the dithiophosphinate anion (**v**–**vii**).

TABLE I Crystal Structure and Refinement Data for 1 and 2

	1	2
Formula	$C_{36}H_{52}Li_2N_4P_2S_2$	$C_{96}H_{178}Li_{10}O_2P_8S_{16}$
Formula weight	680.72	2194.50
Temperature (K)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal size (mm)	0.40 × 0.40 × 0.40	0.40 × 0.40 × 0.30
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No.14)	$P2_1/n$ (No.14)
a (Å)	13.7492(1)	16.0724(3)
b (Å)	17.3027(2)	17.0719(3)
c (Å)	17.1022(2)	22.0287(4)
β (°)	100.87(1)	99.309(1)
V (Å^3)	3995.57(7)	5964.77(19)
Z	4	2
D_c (Mg m^{-3})	1.13	1.22
Absorption coefficient (mm^{-1})	0.24	0.44
θ range for data collection (°)	3.74 to 24.76	3.41 to 26.08
Reflections collected	31864	46751
Independent reflections	6704 [$R_{\text{int}} = 0.174$]	11581 [$R_{\text{int}} = 0.049$]
Reflections with $I > 2\sigma(I)$	5834	9680
Data/restraints/parameters	6704 / 0 / 415	11581 / 0 / 599
Goodness-of-fit on F^2	1.061	1.049
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.069$, $wR_1 = 0.188$	$R_1 = 0.043$, $wR_1 = 0.101$
R indices (all data)	$R_1 = 0.078$, $wR_1 = 0.196$	$R_1 = 0.055$, $wR_1 = 0.109$
Largest diff. peak / hole (e Å^{-3})	1.08 and −0.49	1.86 and −1.04

(Scheme 2). An alternative route to phospha(V)guanidinate was therefore examined.

Reaction of isolated phospha(III)guanidines with ^{n}BuLi in THF is a known route to the corresponding phosphaguanidinate anions, $[R_2PCNR'_2]^-$ and has been used successfully in the generation of a number of metal derivatives.[4] Recent work from the Chivers' group has shown that reaction of a lithiated (imido)diphosphineimide with elemental sulfur affords the corresponding NP(S)PN species, in which simple oxidation of the $P^{(III)}$ center to $P^{(V)}$ has occurred with no detrimental effect on the remainder of the ligand.[16] We therefore considered the possibility of reacting a solution of the phospha(III)guanidinate with sulfur as a viable route to the target compounds (Scheme 1, *Route III*).

Reaction between $Li(Cy_2PC\{NCy\}_2)$,[5] and elemental sulfur in toluene afforded a small number of colorless crystals upon work-up. Analysis using NMR spectroscopic techniques was prevented by the extremely low solubility of the product, precluding the acquisition of

TABLE II Selected Bond Lengths (Å) and Angles (°) for $[Li(Ph_2PS)(TMEDA)]_2$ (1)

P(1)-S(1)	2.0661 (11)	P(2)-S(2)	2.0710 (11)
S(1)-Li(1)	2.440 (5)	S(1)-Li(2)	2.482 (5)
S(2)-Li(1)	2.459 (5)	S(2)-Li(2)	2.427 (5)
Li(1)-N(1)	2.083 (6)	Li(1)-N(2)	2.116 (6)
Li(2)-N(3)	2.101 (6)	Li(2)-N(4)	2.103 (6)
C(1)-P(1)-C(7)	99.19 (12)	C(19)-P(2)-C(25)	98.69 (13)
C(1)-P(1)-S(1)	103.88 (10)	C(19)-P(2)-S(2)	103.54 (11)
C(7)-P(1)-S(1)	103.44 (10)	C(25)-P(2)-S(2)	102.31 (11)
P(1)-S(1)-Li(1)	108.16 (13)	P(2)-S(2)-Li(1)	115.85 (13)
P(1)-S(1)-Li(2)	109.32 (13)	P(2)-S(2)-Li(2)	108.04 (13)
Li(1)-S(1)-Li(2)	76.86 (16)	Li(1)-S(2)-Li(2)	77.53 (16)

any reliable data. The crystals were however suitable for analysis by X-ray diffraction techniques, revealing a complex aggregated species of formula $[Li_5(Cy_2PS_2)_4(OH)]_2$ (**2**). The molecular structure of the asymmetric unit of **2** is shown in Figure 3; crystal structure and refinement data is collected in Table I and selected bond lengths and angles in Table III.

Rather than generating the desired $P^{(V)}$guanidinate anion, the molecular structure of **2** indicates that degradation has occurred *via*

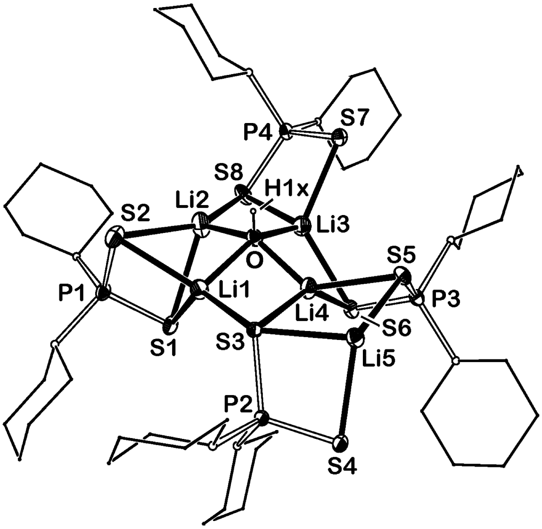


FIGURE 3 ORTEP of the asymmetric unit of **2** (ellipsoids at 30%, cyclohexyl reduced reduced to *stick* representation and hydrogens except H1x omitted for clarity).

TABLE III Selected Bond Lengths (Å) and Angles (°) for $[Li_5(Cy_2PS_2)_4(OH)]_2$ (2)

P(1)-S(1)	2.0121(9)	P(1)-S(2)	2.0069(10)
P(2)-S(3)	2.0377(8)	P(2)-S(4)	1.9986(8)
P(3)-S(5)	2.0295(8)	P(3)-S(6)	2.0202(9)
P(4)-S(7)	2.0155(8)	P(4)-S(8)	2.0069(9)
S(1)-Li(1)	2.532(5)	S(1)···Li(2)	2.648(6)
S(2)-Li(1)	2.476(5)	S(2)···Li(2)	2.791(5)
S(3)-Li(1)	2.438(4)	S(3)-Li(4)	2.488(4)
S(3)-Li(5)	2.501(4)	S(4)-Li(5)	2.425(4)
S(5)-Li(4)	2.479(4)	S(5)-Li(5)	2.506(4)
S(6)-Li(3)	2.454(5)	S(6)-Li(4)	2.512(4)
S(7)-Li(3)	2.427(5)	S(7)-Li(5')	2.444(4)
S(8)-Li(2)	2.468(5)	S(8)-Li(3)	2.511(5)
Li(1)-O	1.984(5)	Li(2)-O	1.898(5)
Li(3)-O	1.956(5)	Li(4)-O	1.921(5)
S(1)-P(1)-S(2)	109.57(4)	S(3)-P(2)-S(4)	111.95(4)
S(5)-P(3)-S(6)	112.32(4)	S(7)-P(4)-S(8)	113.66(4)
P(1)-S(1)-Li(1)	81.26(11)	P(1)-S(1)-Li(2)	79.98(12)
Li(1)-S(1)-Li(2)	57.48(15)	P(1)-S(2)-Li(1)	82.80(11)
P(1)-S(2)-Li(2)	76.52(13)	Li(1)-S(2)-Li(2)	56.12(15)
P(2)-S(3)-Li(1)	120.21(12)	P(2)-S(3)-Li(4)	114.56(12)
P(2)-S(3)-Li(5)	79.83(10)	Li(1)-S(3)-Li(4)	67.52(14)
Li(1)-S(3)-Li(5)	140.73(14)	Li(4)-S(3)-Li(5)	73.45(14)
P(2)-S(4)-Li(5)	82.47(10)	P(3)-S(5)-Li(4)	81.77(10)
P(3)-S(5)-Li(5)	126.33(11)	Li(4)-S(5)-Li(5)	73.51(13)
P(3)-S(6)-Li(3)	106.34(12)	P(3)-S(6)-Li(4)	81.13(10)
Li(3)-S(6)-Li(4)	63.12(15)	P(4)-S(7)-Li(3)	81.15(12)
P(4)-S(7)-Li(5')	114.65(10)	Li(3)-S(7)-Li(5')	123.21(15)
P(4)-S(8)-Li(2)	113.45(14)	P(4)-S(8)-Li(3)	79.21(12)
Li(2)-S(8)-Li(3)	64.04(16)		

rupture of the P–$C_{amidine}$ bond, to afford the dicyclohexyldithiophosphinate anion, $[Cy_2PS_2]^-$. The asymmetric unit is formed of four of these anions aggregated with five lithium cations, with the charge balance maintained by a hydroxyl group, assumed to originate from reaction with adventitious water[17]; repeating the reaction with the rigorous exclusion of moisture unfortunately did not afford tractable products. Two of these neutral $Li_5(Cy_2PS_2)_4(OH)$ units are joined by additional Li-S bonds [Li(5)-S(7′) = 2.444(4) Å], giving the overall formula for **2** as $[Li_5(Cy_2PS_2)_4(OH)]_2$ (Figure 4), in which the two asymmetric units are related by a crystallographic inversion center.

All five lithium atoms are four-coordinate and, unusually for polylithio-structures, are located in an approximate plane [max deviation from the mean Li(1)-Li(5) plane = 0.22 Å]. The Li···Li contacts

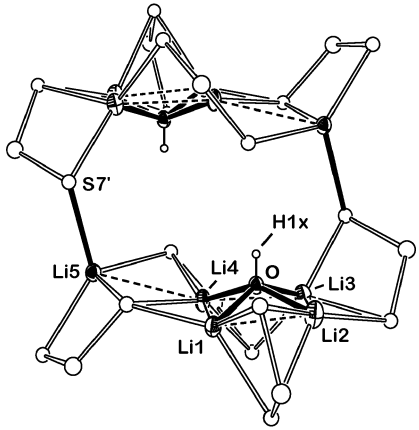


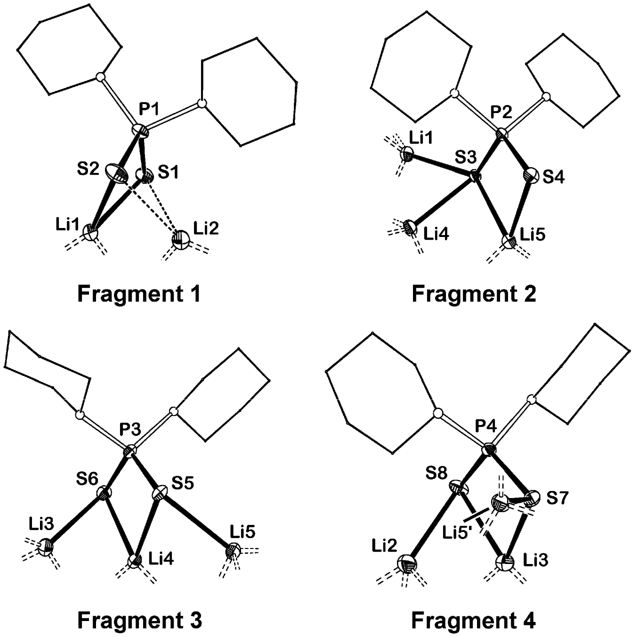
FIGURE 4 The inorganic core of **2** (excluding carbon and hydrogen atoms except H1x), highlighting the dimeric arrangement of $Li_5(Cy_2PS_2)_4(OH)$ units linked by Li(5)-S(7′) bonds, and the projection of the hydroxyl proton into the cavity of the dimer.

are unexceptional [range 2.492(7) Å – 2.983(6) Å] being comparable to those in related molecular $(Li)_n$-clusters.[18] The oxygen atom of the $[OH]^-$ group is located 0.579 Å above the plane formed by Li(1)-Li(4) [Li-O distances: 1.898(5) Å – 1.984(5) Å], with the hydrogen atom pointing into the cavity between the two components of the dimer (Figure 4). Such a μ_4-capping arrangement for the hydroxyl anion has previously been noted, for example in the tetralithium derivative of *tert*-butylcalix[4]arene,[19] and has been considered as being related to a component of the layered structure of LiOMe.[20] It should be noted that the deliberate encapsulation of LiOH into polylithio-[21] and group 13 metal[22] clusters can be readily achieved, with a diverse range of structures possible depending largely on the nature of the supporting ligands.

The dicyclohexyldithiophosphinate anion has been crystallographically characterized as a chelating (κ^1-*S*:κ^1-*S*′) group to a range of metals from throughout the periodic table (i.e., **v**, Figure 2), including main group (Tl)[23] transition metal (Ti, Cr, Cd, Hg)[10,24] lanthanide (Pr, Sm, Dy, Lu)[25] and actinide (U, Th)[26] elements. In the case of cadmium, this ligand was also found to bridge between metal centers (κ^1-*S*:κ^2-*S*′) (**vi**) and with thallium$^{(III)}$ a monodentate ($\kappa^1 - S$) mode was observed (**vii**), with retention of a non-coordinating P=S double bond. Many other examples of disubstituted dithiophosphinate anions are known[27] and a range of bonding modes have been observed. However, the molecular structure of compound **2** displays several previously unobserved ligand-metal interactions that are worthy of discussion.

Within the core structure of **2**, each of the four dithiophosphinate anions interacts to a different extent with the lithium cations (Figure 5). The first fragment centered on P(1) interacts with two formally four coordinate lithium atoms in what we describe as a κ^1-*S*:κ^1-*S*′:{*pseudo*-κ^2-*S*:κ^2-*S*′}-mode, containing characteristic Li(1)-S bonds [2.533(5) Å and 2.476(5) Å] with notably longer Li(2)-S interactions [2.647(6) Å and 2.792(5) Å]. All of these values are generally long compared with the remaining lithium-sulfur bonds within **2**, which fall in the range 2.425(4) Å–2.512(4) Å, and in comparison with experimentally determined values for Li$_2$S of 2.476 Å[28] and 2.494 Å.[29] This asymmetry in the bonding of the dithiophosphinate to the two lithium atoms also manifests itself in a pronounced difference in the angle between the approximate ‘PS$_2$’ and ‘LiS$_2$’ planes; the P(1)-S(1)-S(2) : Li(1)-S(1)-S(2) dihedral angle is 155.7°, while the corresponding angle involving the Li(2)-S(1)-S(2) plane is 129.0°.

The geometry at phosphorus is distorted tetrahedral [angles in the range 105.25(11)° to 112.50(9)°] with a S-P-S angle of 109.57(4)°. The phosphorus–sulfur bond lengths [2.0121(9) Å and 2.0069(10) Å] are



Fragment 1

Fragment 2

Fragment 3

Fragment 4

FIGURE 5 ORTEP representations of the four individual bonding modes of the dicyclohexyldithiophosphinate anion in compound **2**.

towards the short end of the range found within **2** [1.9986(8) Å - 2.0377(8) Å], close to the values found in the non-contacted ion pair, $[TePh_3][Ph_2PS_2]$.[30] The values are consistent with delocalisation across the S-P-S fragment, as noted above for **1**.

The second fragment at P(2) displays a κ^1-*S*:$\kappa^{1,2,3}$-*S*′-bonding pattern in which S(4) is unique within **2** as the only two-coordinate sulfur atom, subtended by an acute P(2)-S(4)-Li(5) angle of 82.47(10)°. In contrast, S(3) caps three lithium atoms with bonds lengths in the range 2.438(4) Å to 2.501(4) Å, generating a four coordinate sulfur with angles in the range 67.52(14)°–140.73(14)°. The phosphorus is distorted tetrahedral with an S-P-S angle of 111.95(4)°, larger than the corresponding angle at P(1) due to lateral interactions with Li(1) and Li(4). As expected, asymmetric P-S bond distances are noted [P(2)-S(3) 2.0377(8) Å; P(2)-S(4) 1.9986(8)] with the longer distance to the triply bridging chalcogen, as expected.

The bonding pattern about Fragments 3 and 4 is similar in so much as it may be described as $\kappa^{1,2}$-*S*:$\kappa^{1,3}$-*S*′, with the anion interacting with a total of three lithium atoms in each case. One of the lithium atoms is chelated by the ligand, and the remaining two bond separately to each of the sulfur atoms from the $[Cy_2PS_2]^-$ anion. The geometry does, however, differ significantly with respect to the projection of the non-chelating S-Li bonds, relative to the plane of the ‘PS_2Li’ metallacycle. In Fragment 3, lithium atoms 3 and 5 are *transoid* about the chelate ring, whilst in Fragment 4 a *cisoid* arrangement is noted, with the S(7)-Li(5′) bond providing the link between the two $Li_5(Cy_2PS_2)_4(OH)$ units in **2**. There does not appear to be a correlation between the Li-S bonds lengths and the type of bonding to lithium, with both chelated and non-chelated bonds spanning the range 2.427(5) Å - 2.512(4) Å. The P-S distances [2.0069(9) Å - 2.0295(8) Å] are typical for this ligand and the S-P-S angles [P(3) 112.32(4)°; P(4) 113.66(4)°] are larger than at P(1) and P(2), reflecting the interaction of each sulfur with additional lithium atoms.

COMPUTATIONAL STUDY

Density functional theory (DFT) calculations were performed on isolated $[R_2PS]^-$ and $[R_2PS_2]^-$ anions, where R = Ph and Cy for both classes of ion. Clearly, in lithium complexes of the type described in this paper, ionic contributions will dominate over any covalent lithium-sulfur interactions and the overall directionality of the S-Li bonds and ultimate connectivity that form in the solid-state will be largely due to packing forces within the crystal. However, understanding the

TABLE IV Calculated and Observed Bond Lengths and Angles for $[R_2PS]^-$ (A, R = Ph; B, R = Cy)

	Observed	Calculated
	R = Ph (**A**)[a]	
P-S	2.066 Å and 2.0710 Å	2.066 Å
P-C	1.848 Å–1.858 Å	1.893 Å
Σ_{angles} P	304.54° and 306.51°	309.23°
	R = Cy (**B**)[b]	
P-S	2.107 Å and 2.110 Å	2.086 Å
P-C	1.844 Å–1.85 Å	1.939 Å and 1.928 Å
Σ_{angles} P	304.2° and 307.1°	306.03°

[a]Values taken from compound **1**; and [b]values taken from $Cp_2Ti(Cy_2PS)_2$, see Reference 9.

distribution of π-electron density throughout the P—S bond(s), and the role that the phosphorus substituents have on the energies associated with these orbitals is an important study and will hopefully lead to a further understanding of the bonding within thiophosphinites and dithiophosphinates.

Full optimization of the structures led to bond lengths and angles that are generally in good agreement with the experimentally determined values (Tables IV and V). A significant difference is noted in the S-P-S angles for the model dithiophosphinate complex **D** [121.26°] compared with the values taken from compound **2** [109.57° to 113.66°]. This is attributed to the presence of chelated a lithium atom to each of

TABLE V Calculated and Observed Bond Lengths and Angles for $[R_2PS_2]^-$ (C, R = Ph; D, R = Cy)

	Observed	Calculated
	R = Ph (C)[a]	
P—S	1.975 Å and 2.004 Å	2.016 Å
P—C	1.833 Å and 1.836 Å	1.878 Å
S—P—S	115.7°	121.23°
	R = Cy (D)[b]	
P—S	1.9986 Å–2.0377 Å	2.027 Å
P—C	1.831 Å–1.843 Å	1.895 Å
S—P—S	109.57°–113.66°	121.26°

[a]Values taken from $[Ph_3Te][Ph_2PS_2]$, in which only weak secondary cation·anions interactions are present, see Reference 29; and [b]range of values taken from compound **2**.

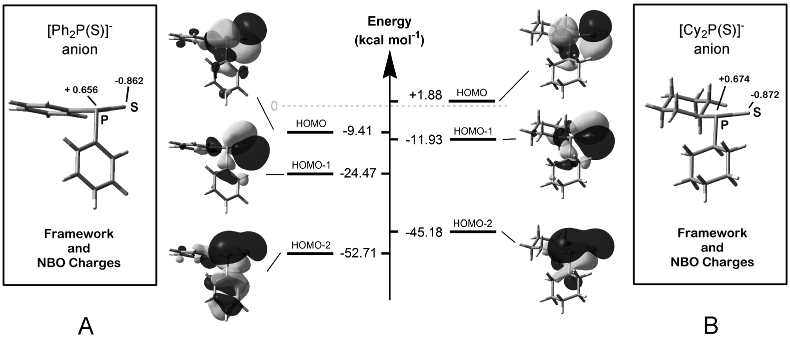


FIGURE 6 Molecular orbital and energy level diagram for thiophosphinite anions $[R_2PS]^-$ (**A**, R = Ph; **B**, R = Cy).

the anions within **2**, which prevent the two P-S bonds from relaxing to their most stable configuration.

Similar molecular orbital profiles are noted for both of the thiophosphinite anions $[R_2PS]^-$ (**A**, R = Ph; **B**, R = Cy), with a general increase ($\sim$10 kcal mol^{-1}) in the relative energies of the three highest occupied MOs in the Cy-substituted derivative, **B** (Fig. 6). The calculated (NBO) charges on both sulfur [**A**, −0.862; **B**, −0.872] and phosphorus [**A**, +0.656; **B**, +0.674] are similar in each model, with a slight decrease in the positive charge at phosphorus in **A** attributed to the more electron withdrawing phenyl substituents. The negative charge at sulfur is consistent with the formation of the S-Li bonds, as noted in the X-ray crystal structure of **1**.

In **A** and **B**, the HOMO places electron density at both the phosphorus and sulfur atoms within a π^*-symmetry orbital associated with the phosphorus-sulfur bond. The main component of the HOMO-1 may be considered as a *p*-type lone-pair orbital at sulfur orthogonal to the P-S bond, although a notable distortion towards phosphorus results in electron density from this orbital contributing to the overall P-S bonding. In contrast, the HOMO-2 clearly shows an element of π-bonding that spans the P-S bond, consistent with a resultant bond order between one and two, as inferred from the P-S bond length within the crystal structure.

The dithiophosphinate anions $[R_2PS_2]^-$ (**C**, R = Ph; **D**, R = Cy) indicate an overall molecular orbital picture that is also largely independent of the nature of the *P*-substituent with respect to the shapes of the molecular orbitals, with a higher energy of $\sim$7 kcal mol^{-1} for the HOMO to HOMO-3 orbitals of dicyclohexyl compound, **D** (Fig. 7). A considerably greater positive charge is calculated for the phosphorus atoms in **C** and **D** compared with the corresponding thiophosphinite anions due

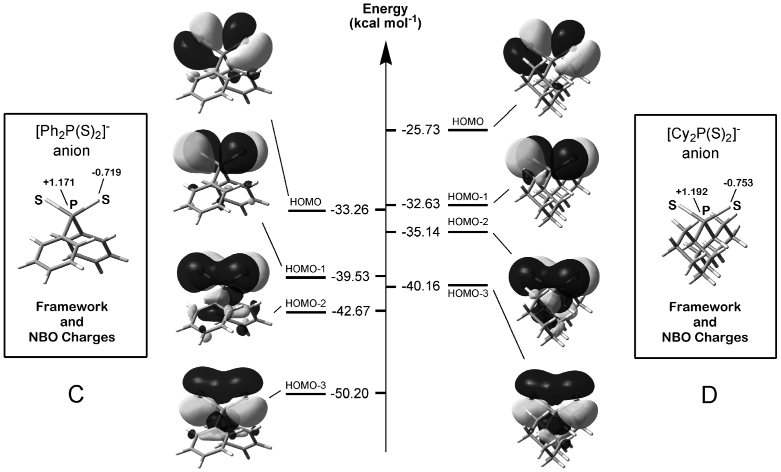


FIGURE 7 Molecular orbital and energy level diagram for thiophosphinate anions [R_2PS_2]$^-$ (**C**, R = Ph; **D**, R = Cy).

to the presence of two sulfur atoms; the charge is slightly enhanced in **C**, again attributed to the phenyl groups.

In both models **C** and **D** highest energy occupied MOs are associated with the S-P-S portion of the molecule. Both the HOMO and HOMO-1 are predominantly composed of *p*-type lone-pairs on each sulfur, with a distortion of the lobes towards the phosphorus, as noted above for the HOMO-1 in **A** and **B**. The major lobes of the HOMO-2 and HOMO-3 orbitals in **C** and **D** are of π-symmetry and extend across the S-P-S atoms, consistent with the observed delocalized bonding across this portion of the molecule.

It is clearly evident from these model studies that considerable electron density is located at the sulfur atoms within both classes of anion, and that several different filled orbitals are, in principle, available for interaction with empty orbitals of the appropriate symmetry and energy at a metal center. It is likely this concentration of charge that has led to these ions being such versatile ligands in coordination chemistry to metals from across the periodic table.

EXPERIMENTAL

General Experimental Details

All manipulations were carried out under an inert atmosphere using high vacuum Schlenk-line techniques or in a nitrogen-filled glove box operating at <1 ppm oxygen. Solvents were dried and distilled from an appropriate drying agent. The compounds Ph_2PH (Aldrich), Cy_2PH

(Strem), S (Aldrich), ^{n}BuLi (2.5 M in hexanes, Acros) and TMEDA (Aldrich, distilled and stored under a nitrogen atmosphere) were purchased from commercial sources and used as received, unless stated otherwise. The compounds $R_2PCNR'NHR'$[1,2], $R_2P(E)CNR'NHR'$[2,31] and $Li(Cy_2PCN^iPr_2)$[5] were made according to literature procedures. NMR spectra were recorded using a Varian 400 MHz spectrometer at 400.1 (${}^{1}H$), 100.6 (${}^{13}C{}^{1}H$), 155.4 (${}^{7}Li{}^{1}H$) and 161.9 (${}^{31}P{}^{1}H$) MHz, from samples at 30°C in [${}^{2}H_6$]-benzene, unless otherwise stated; coupling constants are quoted in Hz. Proton and carbon chemical shifts were referenced internally to residual solvent resonances. Elemental analysis was performed by Steve Boyer at the London Metropolitan University.

[Li(Ph$_2$PS)(TMEDA)]$_2$ (1)

A solution of ^{n}BuLi (2.25 mL of a 2.5 M solution in hexanes, 5.63 mmol) was added dropwise to a stirred solution of $Ph_2P(S)H$ (1.17 g, 5.37 mmol) in THF (~30 mL) at −78°C. The resultant orange solution was stirred at low temperature for 30 min and allowed to warm to room temperature and stirred for a further 1 h. The solution was re-cooled to −78°C and a solution of ${}^{i}PrN{=}C{=}N^iPr$ (0.84 mL, 5.37 mmol) in THF (~20 mL) was added resulting in decolorization of the solution. The volatiles were removed under reduced pressure to afford a sticky white solid. Attempted crystallization failed and so excess TMEDA (1.60 mL, 10.74 mmol) was added to a toluene solution and the mixture cooled to -30°C, affording colorless crystals that were shown by X-ray diffraction to correspond to $[Li(Ph_2PS)(TMEDA)]_2$ (**1**).

Compound **1** was independently synthesized according to the following procedure. A slurry of excess elemental sulfur (0.13 g, 4.02 mmol, 1.5 equivalents) in toluene (15 mL) was added to a solution of Ph_2PH (0.50 g, 2.68 mmol) in 25 mL toluene at room temperature. The initially cloudy solution was stirred for 1 h, after which time the solution was clear and the formation of the P(V) sulfide, $Ph_2P(S)H$ was assumed to have gone to completion. The solution was cooled to 0°C and ^{n}BuLi (1.10 mL of a 2.5 M solution in hexanes, 2.68 mmol) was added dropwise *via* syringe, generating a white precipitate of the lithium salt. Excess TMEDA (0.60 mL, 4.02 mmol) was added at 0°C causing the precipitate to dissolve. The resultant mixture was allowed to warm to room temperature and stirred overnight, affording a slightly cloudy solution. Filtration and removal of the volatiles afforded colorless crystals of the desired product. Yield 0.67 g, 73%. ^{1}H NMR: δ 8.54 (dd, $J_{PH} = 16$, $J_{HH} = 8$, 4H, $o\text{-}C_6H_5$), 7.12 (dt, $J_{HH} = 16$, $J_{PH} = 4$, 2H, $p\text{-}C_6H_5$), 7.01 (m, 4H, $m\text{-}C_6H_5$), 1.89 (s, 12H, NMe_2), 1.66 (s, 4H, CH_2). ${}^{13}C{}^{1}H$ NMR: δ 144.0 (d, $J_{CP} = 79$, $i - C_6H_5$), 134.3 (d, $J_{CP} = 17$, C_6H_5), 131.0 (d, $J_{CP} = 11$,

C_6H_5), 129.5 (d, $J_{CP} = 3$, C_6H_5), 56.2 (CH_2), 45.6 (N*Me*). $^{31}P{^1H}$ NMR: 61.4 (s). $^{7}Li{^1H}$ NMR: δ 1.32 (s).

$[Li_5(Cy_2PS_2)_4(OH)]_2$ (2)

Precooled toluene (−78°C) was added to a solid mixture of $Li(Cy_2PCNCy_2)$ (0.10 g, 0.32 mmol) and elemental S (0.01 g, 0.32 mmol) to afford a yellow /white suspension. The mixture was allowed to warm to ambient temperature, and stirred for 16 h. Removal of volatiles from the resultant cloudy, white solution afforded a crude white solid. Crystallization of **2** was achieved by slow cooling a hot (∼ 70°C) heptane to ambient temperature, affording colorless crystals. Yield 36 mg (42% based on sulfur). Anal. calcd. for $C_{96}H_{178}Li_{10}O_2P_8S_{16}$ (2194.50): C 52.54, H 8.18%. Found C 52.49, H 8.25%. IR (Nujol mull, KBr): 3680 $cm^{-1} \upsilon(OH)$.

Crystallographic Details

Details of the crystal data, intensity collection, and refinement for complexes **1** and **2** are listed in Table I. Crystals were covered in oil and suitable single crystals were selected under a microscope and mounted on a Kappa CCD diffractometer. The structures were refined with SHELXL-97.[32] Additional features are described below:

$[Li_5(Cy_2PS_2)_4(OH)]_2$ (2)

The H atom of the OH group was refined; other H atoms were in riding mode. There is a residual peak of ca. 1.8 electrons close to S(2), which is assumed to be spurious; the difference map is otherwise clean.

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 635424 for compound **1** and 635425 for compound **2**.

Theoretical Methods

The geometries and energies of the non-coordinated thiophosphinite and dithiophosphinate anions, $[R_2PS]^-$ and $[R_2PS_2]^-$, were obtained using density functional theory, specifically the Becke three parameter exchange functional (B3)[33] and the Lee correlation functional (LYP).[34] The 6-31G(d) basis set[35] was chosen and all B3LYP calculations, including NBO analysis[36] were carried out with the Gaussian03[37] suite of programs. The initial geometries of the phosphorus-sulfur cores were taken from X-ray data [anion based on P(1) of compound **2** for models **C** and **D**], with the appropriate substitution of phenyl and cyclohexyl substituents at phosphorus accomplished using GaussView. Each stationary point was confirmed to be a minimum having zero imaginary vibrational frequencies.

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