

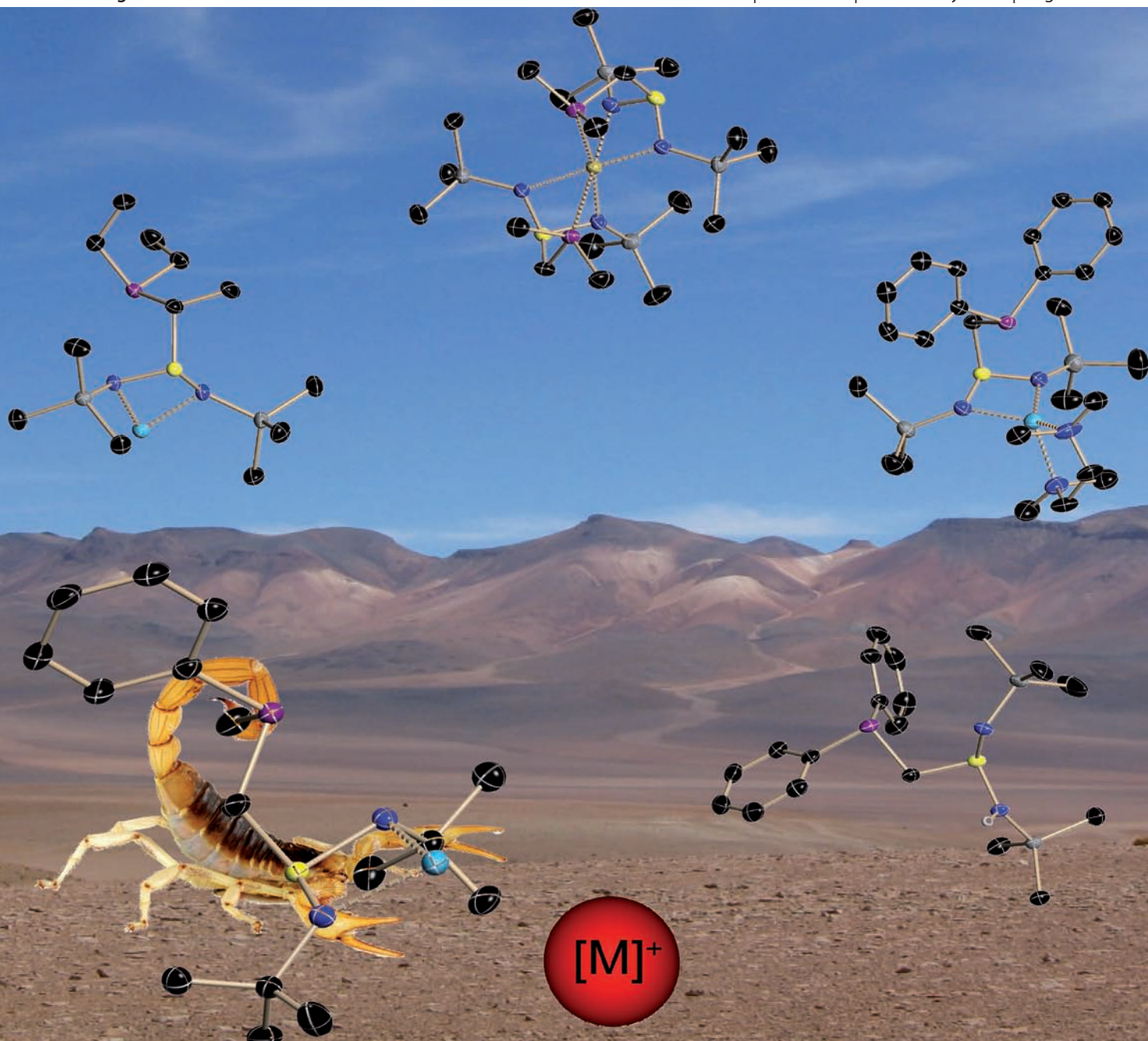
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PAPER

Access to new Janus head ligands: linking sulfur diimides and phosphanes for hemilabile tripodal scorpionates†

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Reactions of lithium dialkyl/phenyl phosphanylmethylides, RR'PCH(X)Li (R, R' = Me, Et, Ph and R = Me, R' = Ph; X = H or Me), with sulfur diimides S(NR'')₂ (R'' = 'Bu or SiMe₃) in an equimolar ratio yielded Janus head complexes with the structural motif [Li{RR'PCH(X)S(NR'')₂}]₂ (R'' = 'Bu, SiMe₃). The basic core of these dimeric complexes is composed of a (LiN)₂ four-membered ring containing two four-coordinated lithium atoms. A lithium complex of the new Janus head ligand with another structural motif [TMEDA·Li{Ph₂PCH₂S(NSiMe₃)₂}] (**6**) could be isolated from the reaction of [Ph₂PCH₂Li·TMEDA] with S(NSiMe₃)₂. Two monomeric complexes [Mg{Me₂PCH₂S(NR'')₂}] (**7**, **8**) were synthesised by a straightforward reaction of [Li{Me₂PCH₂S(NR'')₂}] with MgCl₂ in pentane. The magnesium atom is chelated by one phosphorus atom and two nitrogen atoms of each unit of the hemilabile ligand in a tripodal manner, leading to octahedral geometry around the magnesium cation. A complete analysis of [Ph₂PCH₂(SNSiMe₃)(HNSiMe₃)] (**9**) is also described in which one nitrogen atom of the imido moiety is protonated.

Introduction

Over the past few years our group has concentrated on heteroatomic-substituted multidentate ligand systems featuring two pendent arms and a second coordination site, which can also be referred to as “claw” ligands¹ or scorpionates.² Our principal strategy is to develop these ligands which bear coordination sites for both hard and soft metal centres in terms of the HSAB concept.^{3,4} If both coordination sites of the ligand point in opposite directions we call that a Janus head ligand. The functionalization of organodiimidosulfonates may be expanded by the introduction of an additional donor site in the backbone of the carbon substituent at the central sulfur atom. Ideally, this donor should be soft. By these means, simultaneous coordination of hard and soft metals in heterobimetallic complexes would be feasible, promoting their catalytic versatility.

If the length of the connecting clamp is large enough, both the apical and ancillary donors of the ambidentate ligands will be able to coordinate the same metal. In addition, such ambidentate systems will provide rigid and well defined coordination geometries leading to interesting chemical properties and reactivity patterns.

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† Electronic supplementary information (ESI) available: Experimental and crystallographic data, including the coordinates of all the species. CCDC reference numbers 779986–779988 and 779990–779995. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00665c

A literature survey shows that several tripodal ligand systems with group 15 elements as bridgehead atoms are known.^{4–15}

However, in most of these cases the metal is coordinated by the ancillary donors. Anionic ligands consisting of carbanions and heavier group 14 elements are another possibility for creating Janus head systems (Fig. 1).¹⁶

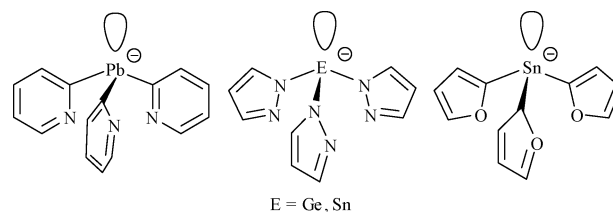


Fig. 1 Some tripodal ligand systems.

It is apparent from recent breakthroughs in this area that such ligands are about to be further developed and promising results are likely to occur.¹⁷ Multifunctional ligands with podand topology provide intrinsically well defined coordination geometries with interesting bonding aspects and reactivity patterns. There is growing interest in multidentate hemilabile ligand systems featuring dual functionality. The modification of classical chelating ligands to produce novel and fluxional multidentate systems has opened up an exciting area of research in the last few years.¹⁸ Janus head complexes are finding ever increasing applications in areas like heterolytic H₂-splitting,¹⁹ NLO (non linear optic) materials,²⁰ organic transformation,²¹ asymmetric catalysis,²² cross coupling,¹¹ microbial agents²³ or light emitting diodes (LEDs).²⁴

The complexes of magnesium metal with a ligand containing sulfur, nitrogen and phosphorus atoms may be promising precursors for semiconducting materials in the sol–gel or CVD process.²⁵ Recently, the construction of (hetero)bimetallic or even multimetallic complexes using Janus head ligands became an interesting field of research since such complexes may serve as model compounds for one-dimensionally conducting polymers.^{16,25,26} We have already targeted group 15 element centred ligands,^{1a,b} which are able to employ their substituent periphery in metal coordination, and reported on lithium sulfur ylides.^{27,28}

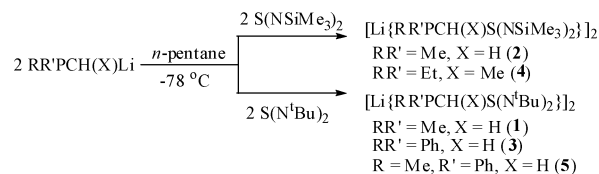
The complex $[(\text{H}_5\text{C}_3)\text{Ni}\{\text{t-Bu}_2\text{PCH}_2\text{S}(\text{NSiMe}_3)_2\}]_2$, has been reported in a patent as an active catalyst for the co-polymerization of ethylene with polar co-monomers without further study.²⁹ Therefore we have inserted bis(*tert*-butyl)sulfur diimide into the Li–C bond of organolithium species to link a sulfur diimide with a phosphanyl moiety to study the coordination geometry of the resulting ligand.

We report herein the synthesis, characterization and single crystal X-ray structure elucidation of $[\text{Li}\{\text{RR}'\text{PCH}(\text{X})\text{S}(\text{NR}'')_2\}]_2$ ($\text{R}'' = \text{t-Bu}$, $\text{X} = \text{H}$, $\text{RR}' = \text{Me}$ (1)/Ph (3), $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$ (5); $\text{R}'' = \text{SiMe}_3$, $\text{X} = \text{H}$, $\text{RR}' = \text{Me}$ (2); $\text{R}'' = \text{SiMe}_3$, $\text{X} = \text{Me}$, $\text{RR}' = \text{Et}$ (4), $[\text{TMEDA}\cdot\text{Li}\{\text{Ph}_2\text{PCH}_2\text{S}(\text{NSiMe}_3)_2\}]_2$ (6), $[\text{Mg}\{\text{Me}_2\text{PCH}_2\text{S}(\text{N}^t\text{Bu})_2\}]_2$ (7), $[\text{Mg}\{\text{Me}_2\text{PCH}_2\text{S}(\text{NSiMe}_3)_2\}]_2$ (8) and $[\text{Ph}_2\text{PCH}_2(\text{SNSiMe}_3)(\text{HNSiMe}_3)]$ (9).[†]

† Single-crystal structural analysis: The X-ray data sets were collected at 100(2) K on a Bruker TXS Mo rotating anode (1, 3, 4, 7 ($T = 250$ K), 8, 9) or an INCOATEC Mo micro source³⁹ (2, 5, 6) with mirror-monochromated Mo- K_α radiation ($\lambda = 0.71073$ Å). The single crystals were mounted in inert oil under argon atmosphere by applying special cryo application techniques.⁴⁰ Structures were solved by direct methods with SHELXS and refined by full-matrix least squares on F^2 for all data with SHELXL.^{41,42} Non-hydrogen atoms were refined with anisotropic displacement parameters. All H atoms were placed in calculated positions and refined using a “riding-model”. **[Li{Me₂PCH₂S(N^tBu)₂}]₂ (1):** $\text{C}_{22}\text{H}_{52}\text{N}_4\text{P}_2\text{S}_2\text{Li}_2$, $M = 512.62$, triclinic, $P\bar{1}$, $a = 9.4916(4)$ Å, $b = 9.6726(4)$ Å, $c = 18.7808(8)$ Å, $\alpha = 98.772(1)^\circ$, $\beta = 92.004(1)^\circ$, $\gamma = 114.778(1)^\circ$, $V = 1537.76(11)$ Å³, $Z = 2$, 27 095 reflections measured, 7923 independent reflections ($R_{\text{int}} = 0.0191$), 305 parameters, R_1 (all data) = 0.0341, $R_1 [I > 2\sigma(I)] = 0.0266$, wR_2 (all data) = 0.0693, $wR_2 [I > 2\sigma(I)] = 0.0657$, $\text{GoF} = 1.054$, largest diff. peak and hole 0.433 and -0.304 eÅ⁻³. **[Li{Me₂PCH₂S(NSiMe₃)₂}]₂ (2):** $\text{C}_{18}\text{H}_{52}\text{N}_4\text{Si}_4\text{P}_2\text{S}_2\text{Li}_2$, $M = 576.94$, triclinic, $P\bar{1}$, $a = 10.2715(11)$ Å, $b = 10.356(11)$ Å, $c = 10.4832(11)$ Å, $\alpha = 68.636(1)^\circ$, $\beta = 65.728(1)^\circ$, $\gamma = 60.990(1)^\circ$, $V = 869.77(16)$ Å³, $Z = 1$, 21 105 reflections measured, 3546 independent reflections ($R_{\text{int}} = 0.0145$), 153 parameters, R_1 (all data) = 0.0236, $R_1 [I > 2\sigma(I)] = 0.0216$, wR_2 (all data) = 0.0619, $wR_2 [I > 2\sigma(I)] = 0.0607$, $\text{GoF} = 0.861$, largest diff. peak and hole 0.314 and -0.223 eÅ⁻³. **[Li{Ph₂PCH₂S(N^tBu)₂}]₂ (3):** $\text{C}_{42}\text{H}_{60}\text{N}_4\text{P}_2\text{S}_2\text{Li}_2$, $M = 760.91$, triclinic, $P\bar{1}$, $a = 9.6236(11)$ Å, $b = 10.1512(12)$ Å, $c = 11.3253(13)$ Å, $\alpha = 73.936(2)^\circ$, $\beta = 84.728(2)^\circ$, $\gamma = 88.960(2)^\circ$, $V = 1058.7(2)$ Å³, $Z = 1$, 25 994 reflections measured, 5259 independent reflections ($R_{\text{int}} = 0.0399$), 241 parameters, R_1 (all data) = 0.0564, $R_1 [I > 2\sigma(I)] = 0.0391$, wR_2 (all data) = 0.1026, $wR_2 [I > 2\sigma(I)] = 0.0976$, $\text{GoF} = 1.054$, largest diff. peak and hole 0.391 and -0.381 eÅ⁻³. **[Li{Et₂PCH(Me)S(NSiMe₃)₂}]₂ (4):** $\text{C}_{24}\text{H}_{64}\text{N}_4\text{Si}_4\text{P}_2\text{S}_2\text{Li}_2$, $M = 661.09$, triclinic, $P\bar{1}$, $a = 10.6002(6)$ Å, $b = 10.635(1)$ Å, $c = 10.7744(6)$ Å, $\alpha = 100.785(1)^\circ$, $\beta = 117.366(1)^\circ$, $\gamma = 103.446(1)^\circ$, $V = 986.48(12)$ Å³, $Z = 1$, 39 887 reflections measured, 4676 independent reflections ($R_{\text{int}} = 0.0146$), 181 parameters, R_1 (all data) = 0.0299, $R_1 [I > 2\sigma(I)] = 0.0277$, wR_2 (all data) = 0.0768, $wR_2 [I > 2\sigma(I)] = 0.0747$, $\text{GoF} = 1.068$, largest diff. peak and hole 0.686 and -0.453 eÅ⁻³. **[Li{Ph(Me)PCH₂S(N^tBu)₂}]₂ (5):** $\text{C}_{32}\text{H}_{56}\text{N}_4\text{P}_2\text{S}_2\text{Li}_2$, $M = 636.75$, monoclinic, $P2_1/c$, $a = 10.5006(14)$ Å, $b = 20.753(3)$ Å, $c = 8.5699(11)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 97.279(2)^\circ$, $V = 1852.5(4)$ Å³, $Z = 2$, 39 157 reflections measured, 3784 independent reflections ($R_{\text{int}} = 0.0274$), 197 parameters, R_1 (all data) = 0.0325, $R_1 [I > 2\sigma(I)] = 0.0305$, wR_2 (all data) = 0.0788, $wR_2 [I > 2\sigma(I)] = 0.0778$, $\text{GoF} = 1.050$, largest diff. peak and hole 0.409 and -0.247 eÅ⁻³. **[TMEDA·Li{Ph₂PCH₂S(NSiMe₃)₂}]**

Results and discussion

The linkage of sulfur diimide and phosphane in order to gain access to a new type of Janus head ligand is achieved by an equimolar reaction of lithium dialkyl/phenyl phosphanyl-methanide, $\text{RR}'\text{PCH}(\text{X})\text{Li}$ ($\text{RR}' = \text{Me}$, $\text{X} = \text{H}$ (1, 2); $\text{RR}' = \text{Ph}$, $\text{X} = \text{H}$ (3); $\text{R} = \text{Et}$, $\text{X} = \text{Me}$ (4); $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$, $\text{X} = \text{H}$ (5)) with bis(trimethylsilyl)sulfur diimide, $\text{S}(\text{NSiMe}_3)_2$, or bis(*tert*-butyl)sulfur diimide, $\text{S}(\text{N}^t\text{Bu})_2$, in *n*-pentane under anhydrous and inert gas conditions (Scheme 1).



Scheme 1

Compounds 1–5 were obtained as white solids. The elemental analyses were found to be consistent with the molecular formulae.

Compound 1 crystallizes from *n*-pentane as colourless plates in the triclinic space group $P\bar{1}$. A dimer is formed owing to the inadequate bite of the ligand to the small lithium cation (Fig. 2). The Me_2P -sidearm is not coordinating to the already SN_2 -complexed lithium atom but to that of the second molecule. The main core of the system is a $(\text{LiN})_2$ four-membered ring with both the lithium atoms forming three N- and one P-contact each.

One nitrogen atom of each ligand unit is coordinated to both lithium atoms while the second coordinates just the lithium atom of one half of the dimer (Li1-N1/Li2-N4). The phosphorus coordination to that lithium atom (Li1-P2/Li2-P1) provides additional stability to the complex (Fig. 3). Both halves of the dimer show almost no differences in bond lengths and angles. All S–N distances (1.6144(9)–1.6351(9) Å) are slightly shorter than an

(6): $\text{C}_{27.5}\text{H}_{52}\text{N}_4\text{Si}_2\text{PSLi}$, $M = 564.89$, monoclinic, $C2/c$, $a = 33.944(5)$ Å, $b = 9.5352(13)$ Å, $c = 21.921(3)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 101.895(3)^\circ$, $V = 6942.4(17)$ Å³, $Z = 8$, 48 696 reflections measured, 6847 independent reflections ($R_{\text{int}} = 0.0632$), 441 parameters, 16 restraints, R_1 (all data) = 0.0505, $R_1 [I > 2\sigma(I)] = 0.0368$, wR_2 (all data) = 0.0942, $wR_2 [I > 2\sigma(I)] = 0.0871$, $\text{GoF} = 1.041$, largest diff. peak and hole 0.348 and -0.245 eÅ⁻³. **[Mg{Me₂PCH₂S(N^tBu)₂}]₂ (7):** $\text{C}_{22}\text{H}_{52}\text{N}_4\text{P}_2\text{S}_2\text{Mg}$, $M = 523.07$, orthorhombic, $Fdd2$, $a = 37.169(8)$ Å, $b = 10.175(2)$ Å, $c = 16.851(4)$ Å, $V = 6373(2)$ Å³, $Z = 8$, 21 122 reflections measured, 3270 independent reflections, $R_{\text{int}} = 0.0407$, 180 parameters, R_1 (all data) = 0.0467, $R_1 [I > 2\sigma(I)] = 0.0444$, wR_2 (all data) = 0.1147, $wR_2 [I > 2\sigma(I)] = 0.1137$, $\text{GoF} = 1.183$, largest diff. peak and hole 0.228 and -0.212 eÅ⁻³. **[Mg{Me₂PCH₂S(NSiMe₃)₂}]₂ (8):** $\text{C}_{18}\text{H}_{52}\text{N}_4\text{Si}_4\text{P}_2\text{S}_2\text{Mg}$, $M = 587.37$, monoclinic, $P2_1/n$, $a = 10.2563(5)$ Å, $b = 17.8142(8)$ Å, $c = 19.2917(9)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 99.273(1)^\circ$, $V = 3478.7(3)$ Å³, $Z = 4$, 156 125 reflections measured, 9326 independent reflections ($R_{\text{int}} = 0.0192$), 296 parameters, R_1 (all data) = 0.0238, $R_1 [I > 2\sigma(I)] = 0.0213$, wR_2 (all data) = 0.0630, $wR_2 [I > 2\sigma(I)] = 0.0612$, $\text{GoF} = 1.019$, largest diff. peak and hole 0.286 and -0.263 eÅ⁻³. **Ph₂PCH₂(SNSiMe₃)(HNSiMe₃) (9):** $\text{C}_{19}\text{H}_{31}\text{N}_2\text{Si}_2\text{PS}$, $M = 406.67$, monoclinic, $P2_1/n$, $a = 12.9937(7)$ Å, $b = 9.9367(6)$ Å, $c = 18.1145(1)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 99.843(1)^\circ$, $V = 2304.4(2)$ Å³, $Z = 4$, 43 786 reflections measured, 5491 independent reflections ($R_{\text{int}} = 0.016$), 235 parameters, R_1 (all data) = 0.0289, $R_1 [I > 2\sigma(I)] = 0.0278$, wR_2 (all data) = 0.0767, $wR_2 [I > 2\sigma(I)] = 0.0757$, $\text{GoF} = 1.052$, largest diff. peak and hole 0.596 and -0.340 eÅ⁻³. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 779986 (1), 779990 (2), 779987 (3), 779991 (4), 779992 (5), 779993 (6), 779988 (7), 779994 (8) and 779995 (9).

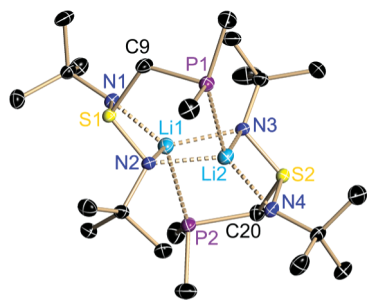


Fig. 2 Molecular structure of $[\text{Li}\{\text{Me}_2\text{PCH}_2\text{S}(\text{N}'\text{Bu})_2\}]_2$ (**1**) in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: S1–N1 1.6144(9), S1–N2 1.6351(9), S1–C9 1.8406(11), P1–C9 1.8403(11), Li1–N1 1.939(2), Li1–N2 2.398(2), Li2–P1 2.6425(19); N1–S1–N2 104.74(5), N1–S1–C9 106.38(5), N2–S1–C9 100.60(5), Li1–N2–Li2 69.23(7), N1–Li1–N2 71.93(7), N2–Li2–P1 76.79(6).

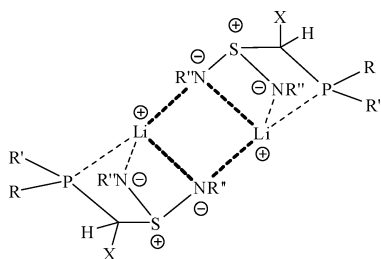


Fig. 3 Generic line drawing of complexes **1–5** (for R, R', R'' and X see Scheme 1).

average sulfur–nitrogen single bond (1.69 Å) and are in the range of other alkyl diimidodisulfates (1.598–1.657 Å).³⁰

The S–C bond lengths match with standard S–C_{sp3} single bonds (1.83 Å).³⁰ Hence, S1 is surrounded by single bonds only and adopts the tetrahedral environment akin to an sp³-hybridized atom. The N1–S1–N2 (104.74(5)°), N1–S1–C9 (106.38(5)°) and N2–S1–C9 (100.60(5)°) angles are reduced with respect to the ideal tetrahedral angle. This is according to the VSEPR theory, because the stereochemically active lone pair at S1 takes up most space. Li1–N1 and Li2–N2 are in the typical range of Li–N bonds (1.905–2.202 Å).³⁰ The Li2–P1 distance of 2.6425(19) Å is slightly longer than the average Li–P distances in Li(P–C–C=N) systems (2.520 Å).¹⁸ The acute N2–Li2–P1 angle of 76.79(6)° is typical for such systems (73.10–87.35°).²⁸

It is easily possible to modify the ligand structure by introducing different substituents at the sulfur atom. $[\text{Li}\{\text{Me}_2\text{PCH}_2\text{S}(\text{NSiMe}_3)_2\}]_2$ (**2**) crystallizes from *n*-pentane as colourless blocks in the triclinic space group *P* $\bar{1}$ (Fig. 4). The main core of the system consists of a (LiN)₂ heteroatomic ring just like in complex **1**. All S–N bond distances (1.6031(10)–1.621(10) Å) are slightly shorter than an average sulfur–nitrogen single bond (1.69 Å).³⁰ Probably there is the presence of S⁺–N[–] electrostatic bond shortening as described for many S–N systems from experimental and theoretical charge density investigations.³¹ The N1–S1–N2 (105.89(5)°), N1–S1–C1 (102.66(6)°) and N2–S1–C1 (101.53(5)°) bond angles are similar to **1**. The shared lithium coordination of N2 leads to longer Li–N distances (Li1–N2 2.315(2) and Li1'–N2 2.029 Å) compared to Li1–N1 (1.989(2) Å). Li1–N1 and Li1'–N2 are in the typical range of Li–N bonds (1.905–2.202 Å),³⁰ but Li1 seems to be weakly coordinated to N2.

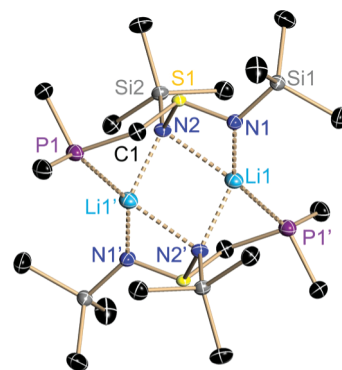


Fig. 4 Molecular structure of $[\text{Li}\{\text{Me}_2\text{PCH}_2\text{S}(\text{NSiMe}_3)_2\}]_2$ (**2**) in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level, hydrogen atoms are omitted for clarity. Atoms labeled with prime (') are symmetry equivalents generated by $1 - x$, $2 - y$, $1 - z$. Selected bond lengths [Å] and angles [°]: S1–N1 1.6031(10), S1–N2 1.6221(10), S1–C1 1.8286(12), P1–C1 1.8406(13), Li1–N1 1.989(2), Li1–N2 2.315(2), Li1–P1' 2.655(2); N1–S1–N2 105.89(5), N1–S1–C1 102.66(6), N2–S1–C1 101.53(5), Li1–N2–Li1' 80.96(9), N1–Li1–N2 73.00(8), N2–Li1'–P1 79.63(7).

Inspection of the molecular structures of **1** and **2** reveals that the N₂SCP ligand is indeed tridentate. Although the bite of the ligand system is not optimized for lithium cations, the complexes formed are surprisingly stable.

The complex $[\text{Li}\{\text{Ph}_2\text{PCH}_2\text{S}(\text{N}'\text{Bu})_2\}]_2$ (**3**) was synthesized by equimolar reaction of lithio(diphenylphosphino)methane-tetramethylethylenediamine, $[\text{Ph}_2\text{PCH}_2\text{Li}\cdot\text{TMEDA}]$, with S(N'Bu)₂ in *n*-pentane to modify the substituents at the phosphorus atom. It was crystallized from toluene, yielding colourless crystals in the space group *P* $\bar{1}$ with half a molecule in the asymmetric unit.

The main core of the system also consists of a (LiN)₂ four-membered heteroatomic ring (Fig. 5). The structural characteristics of **3** are thus akin to complexes **1** and **2**. Nevertheless the molecule has a centre of inversion. The bond lengths and angles of **3** fall within the expected ranges.

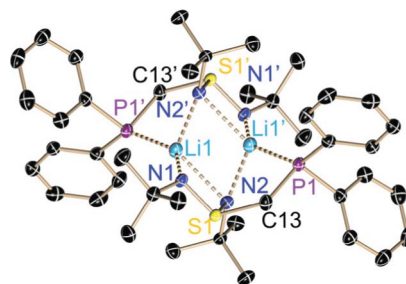


Fig. 5 Molecular structure of $[\text{Li}\{\text{Ph}_2\text{PCH}_2\text{S}(\text{N}'\text{Bu})_2\}]_2$ (**3**) in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level, hydrogen atoms are omitted for clarity. Atoms labeled with prime (') are symmetry equivalents generated by $1 - x$, $1 - y$, $-z$. Selected bond lengths [Å] and angles [°]: S1–N1 1.6120(14), S1–N2 1.6925(14), S1–C13 1.8412(17), P1–C13 1.8404(17), Li1–N1 1.959(3), Li1–N2 2.318(3), Li1–P1 2.657(3); N1–S1–N2 104.15(7), N1–S1–C13 106.45(8), N2–S1–C13 101.29(7), Li1–N2–S1 84.68(9), N1–Li1–N2 72.88(10), N1–Li1–P1 147.48(14), N2–Li1–P1 117.31(12).

In order to obtain more insight into the coordinative behavior of the new N_2SCP system, further modifications at the P,S bridging carbon atom were introduced. The compound $[Li\{Et_2PCH(Me)S(NSiMe_3)_2\}]_2$ (**4**) is isostructural to **2** (Fig. 6). It is also obtained as a dimer and the main core of the system is a $(LiN)_2$ four-membered ring with both the lithium atoms displaying four contacts to the donor atoms of each ligand (Fig. 5). Different to **2**, in **4** chirality is introduced at the P,S bridging methylene carbon atom C7. Due to the center of inversion in the middle of the $(LiN)_2$ four-membered ring **4** crystallizes as a racemate. The S–N bond distances are almost equal to **2** and are 1.5906(10) Å for S1–N1 and 1.6235(10) Å for S1–N2, respectively. The two (SN_2) units are inclined by 116.9° with respect to the $(LiN)_2$ ring and the ethyl phosphane moieties reside on opposite sides of the (SN_2) planes. Thus, the steric strain between the trimethylsilyl groups is minimized. The S–C bond length of 1.8300(12) Å exactly matches the value reported for the presence of a standard S– C_{sp^3} single bond.³⁰ So, a tetrahedral environment around the sulfur atom is assumed. The N1–S1–N2 (104.22(5)°), N1–S1–C7 (102.57(6)°) and N2–S1–C7 (102.80(6)°) angles are similar to **2**. It is noteworthy that the Li–N bond distances in **4** differ less from each other than in **2**. The bond distance for Li1–N2 (2.219(2) Å) is larger compared to Li1–N1 (2.028(2) Å) since N2 is coordinated to both the lithium atoms. However, the Li1–N1 and Li1–N2 bond distances are in the typical range of Li–N bonds as described for compound **2**. The N2–Li1'–P1 angle of 83.25(7)° is less acute in **4** compared to **2**, due to the bulkier groups on the phosphorus atom.

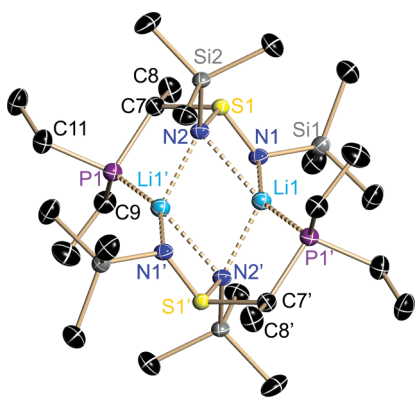


Fig. 6 Molecular structure of $[Li\{Et_2PCH(Me)S(NSiMe_3)_2\}]_2$ (**4**) in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level, hydrogen atoms are omitted for clarity. Atoms labeled with prime (') are symmetry equivalents generated by $1 - x, 2 - y, 1 - z$. Selected bond lengths [Å] and angles [°]: S1–N1 1.5906(10), S1–N2 1.6235(10), S1–C7 1.8300(12), P1–C7 1.8682(13), Li1–N1 2.028(2), Li1–N2 2.219(2), Li1'–P1 2.622(2); N1–S1–N2 104.22(5), N1–S1–C7 106.57(6), N2–S1–C7 102.80(6), Li1'–N2–Li1 69.46(10), N1–Li1–N2 73.19(8), N2–Li1'–P1 83.25(7).

From the NMR spectra of **1–4** in solution it is obvious that the complexes show a dynamic behaviour different to the solid state. Both the $^7Li\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra reveal a coupling between two lithium atoms and one phosphorus atom and *vice versa* (septet in ^{31}P and a triplet in the 7Li NMR). This can only be rationalized with a flipping Li–P-bond and on average the contact of a single phosphorus atom to two lithium atoms in solution

(Fig. 7). Similar dynamic behaviour has already been observed in other systems.³²

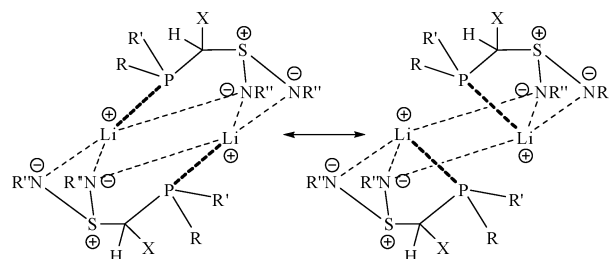


Fig. 7 Dynamic behaviour of complexes **1–5** in solution.

This hypothesis can be proven by the Li–P coupling constants of approximately 19 Hz and the $^{13}C\{^1H\}$ NMR spectra of **3**. The phenyl carbon atoms show various multiplets, whose structure can only be explained if both phosphorus atoms are coupled to each other and thus influence the carbon atoms in the rings. With phosphorus decoupling, however, those multiplets change into singlets.

The NMR spectra of **4** show a signal doubling which is due to the two diastereomers that are present in solution since C7 and C7' are stereocentres. The $^{31}P\{^1H\}$ spectrum for example shows two septets at –30.74 and –27.34 ppm. Consequently, the 1H and $^{13}C\{^1H\}$ spectra are even more complicated, as the alkyl signals lie very close to each other and are therefore overlaid.

Another possibility to generate a stereocentre in the ligand is to introduce a phosphorus side-arm with two different P-bound substituents. $[Li\{Ph(Me)PCH_2S(N^tBu)_2\}]_2$ (**5**) crystallizes from *n*-pentane in the monoclinic space group $P2_1/c$. Compound **5** is also obtained as a dimer and the main core of the system is the known $(LiN)_2$ four-membered ring. Most of the overall structural features are similar to those in **1–4**. Due to the centre of inversion in the middle of the $(LiN)_2$ heteroatomic ring, **5** as well as **4** crystallizes as a racemate. The solid state structure is shown in Fig. 8.

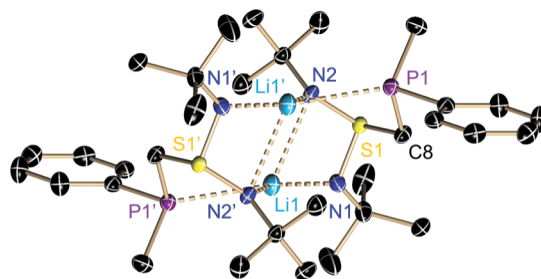


Fig. 8 Molecular structure of $[Li\{Ph(Me)PCH_2S(N^tBu)_2\}]_2$ (**5**) in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level, hydrogen atoms are omitted for clarity. Atoms labeled with prime (') are symmetry equivalents generated by $2 - x, 2 - y, 2 - z$. Selected bond lengths [Å] and angles [°]: S1–N1 1.6107(11), S1–N2 1.6278(11), S1–C8 1.8398(13), P1–C8 1.8463(14), Li1–N1 1.957(3), Li1–N2 2.506(3), Li1'–P1 2.644(2); N1–S1–N2 105.68(6), N1–S1–C8 104.97(6), N2–S1–C8 98.81(6), Li1'–N2–Li1 69.23(7), N1–Li1–N2 76.86(11), N2–Li1'–P1 76.66(7).

The S–N bond distances are almost equal and lie in the range of 1.6107(11)–1.6278(11) Å. The two (SN_2) units are tilted by 134.4° with respect to the $(LiN)_2$ ring with the phosphane moiety residing on opposite sides of the (SN_2) planes, which is due to the different

steric situation in **5** compared to **4**. The N1–S1–N2 (105.68(6)°) and N1–S1–C8 (104.97(6)°) angles are almost in the same range as for compounds **2** and **4**. However, the N2–S1–C8 angle of 98.81(6)° is slightly more acute than in **2** and **4**. The acute N2–Li1–P1 angle of 76.66(7)° is known for such systems (73.10–87.35°),²⁸ however, this angle is the most acute among compounds **1–4**.

The NMR spectra show a signal doubling that is due to two diastereomers which are present in solution, according to compound **4**. In solution the phenyl rings can be arranged like in the solid state (*trans*) or the phosphorus side-arm can rotate about the S–C bond. As a result both phenyl rings are on the same side of the molecule (*cis*). Both diastereomers have very similar chemical shifts and their NMR signals are therefore overlaid. Thus it is impossible to assign specific shifts to one specific diastereomer, although it can be assumed that the *trans* isomer prevails as it reduces steric strain in the ligand. Integration of the PCH₃ signals shows a ratio of 1 to 0.75 for *trans* to *cis*. As in all compounds of this type, the P–Li–P system is also obvious from the ¹³C{¹H} spectra. The ¹³C nuclei are coupled to both phosphorus atoms over the Li-bridge. Thus the resulting multiplets can be explained. In ³¹P decoupled spectra the couplings disappear.

Discussions of the crystal structures of [Li{Me₂PCH₂S(N^tBu)₂}]₂ (**1**), [Li{Me₂PCH₂S(NSiMe₃)₂}]₂ (**2**), [Li{Ph₂PCH₂S(N^tBu)₂}]₂ (**3**), [Li{Et₂PCH(Me)S(NSiMe₃)₂}]₂ (**4**) and [Li{Ph(Me)PCH₂S(N^tBu)₂}]₂ (**5**) reveal that the N₂SCP ligands are indeed tridentate, containing hard nitrogen and soft phosphorus donor sites. Although the bite of the ligand system is not optimized for lithium cations, the complexes formed are quite stable. Even the softer phosphorus site coordinates the hard lithium cation, yet in solution. It seems that the R₂PCH₂S(NR')₂⁻ anions are indeed the ligands which are complexing in the desired way. Furthermore, the formation of dimers seems to be favored as it helps to balance the electron deficiency of the metal cations.

The reaction of [Ph₂PCH₂Li·TMEDA] with S(N^tBu)₂ yielded diphenylphosphinomethane-sulfurdiimide as lithium-dimer (**3**) but when the tertiary butyl groups of the imido moiety were replaced by trimethylsilyl groups the compound obtained was [TMEDA·Li{Ph₂PCH₂S(NSiMe₃)₂}] (**6**) (Fig. 9). These results were unexpected as per our strategy and are probably due to the different electronic situation in the S(NSiMe₃)₂ moiety. Compound **6** crystallizes from *n*-pentane as a monomer in the monoclinic space group *C2/c* with half a pentane molecule in the asymmetric unit.

The coordination mode in this compound is new compared to complexes **1–5**. The lithium cation is four-fold N-coordinated. The phosphorus atom is not taking part in the coordination as the Li...P distance of 3.23 Å is too long to be regarded a bond.³³

Nevertheless, an orientation towards the lithium ion can be observed which is due to electrostatic attractions. Furthermore, the S1–C13–P1 angle of 108.79(9)° indicates the inclination of the phosphorus atom towards the lithium cation. Both phenyl rings are twisted by 90° with respect to each other, facilitating close packing of the molecules in the crystal. The central (SN₂Li) ring is almost perfectly planar with the phosphorus atom residing above this plane. It is aligned with C13, S1, Li1 and both nitrogen atoms of the TMEDA molecule. The N1–S1–N2 angle of 103.72(8)° is slightly more acute than in the lithium complexes **1–5**. The Li–N distances range from 2.039(4) Å (Li1–N2) to 2.167(10) Å (Li1–N3) with the bonds from the TMEDA molecule being marginally

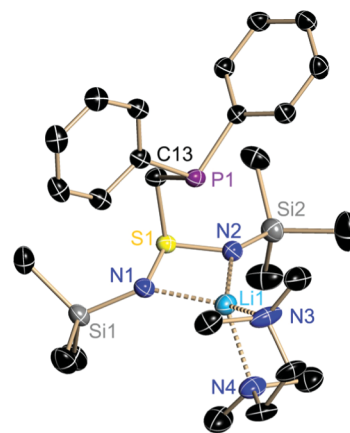
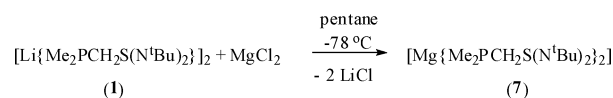


Fig. 9 Molecular structure of [TMEDA·Li{Ph₂PCH₂S(NSiMe₃)₂}] (**6**) in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C13–P1 1.8557(18), C13–S1 1.8338(18), N1–S1 1.6070(15), N2–S1 1.6032(16), N1–Si1 1.7150(16), N2–Si2 1.7114(16); N1–S1–N2 103.72(8), S1–C13–P1 108.79(9), S1–N1–Si1 117.55(9), N1–Li1–N2 75.80(12), N3–Li1–N4 83.7(3).

longer than the bonds from the diimido anion. As the phosphorus side-arm is not donating to the Li cation it is free for binding to any other soft metal thus providing the opportunity to generate heterobimetallic complexes.

The complexation potential of these Janus head scorpionates is also evident from the facile formation of a stable monomeric complex with magnesium (**7**) (Scheme 2).



Scheme 2

The reaction of **1** with MgCl₂ in a 1 : 1 molar ratio afforded the spirocyclic species [Mg{Me₂PCH₂S(N^tBu)₂}] (**7**). The formation of this magnesium complex demonstrates that the new Janus head ligands are valuable multidentate chelating ligands due to the intramolecular phosphane donor site held in close spatial proximity to the functional imido groups. Complex **7** crystallizes from *n*-pentane as colourless plates in the orthorhombic space group *Fdd2* (Fig. 10) with half a molecule in the asymmetric unit. As the compound undergoes a phase transition at about 220 K the X-ray diffraction data set had to be collected at –23 °C (see ESI†).

The monomeric structure shows a distorted octahedral geometry at the central magnesium dication. The molecule has crystallographically imposed two-fold symmetry with the magnesium atom situated on the two-fold axis. The magnesium is bound by two nitrogen atoms and one phosphorus atom of each phosphanyl side-arm as a five-membered chelating ring with bite angles of 74.24(8)° (N1–Mg1–P1) to 70.82(8)° (N2–Mg1–P1). This means that the N₂SCP ligand behaves in a tridentate manner thus demonstrating tripodal donation by means of two terminal nitrogen atoms and side-arm donation by the phosphorus atom. This side-arm donation brings these ligands into focus as multidentate systems for metal complexation.

Coordination of the magnesium atom shows Mg–N distances in the range of 2.102(2) to 2.138(2) Å. These values are

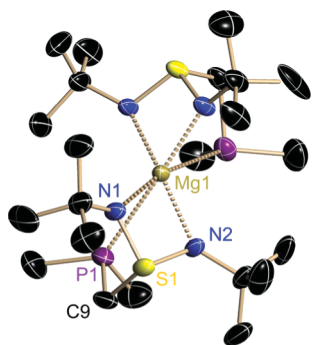


Fig. 10 Molecular structure of $[\text{Mg}\{\text{Me}_2\text{PCH}_2\text{S}(\text{N}^i\text{Bu})_2\}_2]$ (**7**) in the crystal. Anisotropic displacement parameters are depicted at the 30% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: S1–N1 1.617(2), S1–N2 1.622(2), S1–C9 1.838(4), Mg1–N1 2.102(2), Mg1–N2 2.138(2), Mg1–P1 2.9855(13); S1–N1–Mg1 95.69(12), S1–N2–Mg1 94.14(11), N1–Mg1–N2 70.07(9) N1–S1–N2 97.43(12).

similar to those reported for compounds containing a sulfur-bonded imido nitrogen donor (2.035–2.295 Å).³⁰ However, there is a significant difference between the Mg1–N1 (2.102(2) Å) and Mg1–N2 (2.138(2) Å) bonds. The Mg–N bond distances are marginally longer than in $[\text{Mg}\{(\text{NSiMe}_3)_2\text{SN}(\text{SiMe}_3)_2\}_2]$ (2.0592(6) Å).²⁵ The Mg–P bond length is not consistent with the predicted covalent value (2.65 Å). The distance of 2.9855(13) Å is elongated in comparison to Mg–P distances in other mononuclear and dinuclear magnesium phosphanides *e.g.* $[\text{BuMg}\{\text{P}(\text{CH}(\text{SiMe}_3)_2)(\text{C}_6\text{H}_4\text{-2-OMe})\}_2]$ (2.5760(8) and 2.5978(8) Å), $\text{Mg}[\text{P}\{\text{CH}(\text{SiMe}_3)_2\}\{\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2\}_2]$ (2.556(1) Å) and $[\text{Mg}\{[O, O']\text{-}(\text{Me}_2\text{PCH}_2)_2\text{C}_6\text{H}_3\}_2]$ (2.761(1) and 2.770(1) Å).³⁴ This elongation of the Mg–P bond distance is attributed to the side-arm donation of a phosphanyl rather than coordination of a phosphanide. It suggests a possible application of this ligand in catalytic processes. With a different central metal, it would be feasible to reversibly cleave the metal–phosphorus bond to generate a pendent donor site for substrates or other softer metal cations. The N–S–N bond angle (97.43(12)°) is more acute than in **1** and those in alkali metal derivatives (104.2–110.7°), but spans almost the same range as in comparable compounds with Mg^{2+} or other dicationic metals (97.6–98.9°).²⁵ This can be attributed to the higher charge on the magnesium dication, leading to a stronger repulsion between the positively charged sulfur atom and the metal ion.

The magnesium complex $[\text{Mg}\{\text{Me}_2\text{PCH}_2\text{S}(\text{NSiMe}_3)_2\}_2]$ (**8**) was equally isolated by a transmetallation reaction of **2** with MgCl_2 in an equimolar ratio. Unlike compound **7**, which crystallizes in the orthorhombic space group $Fdd2$ and undergoes a phase transition at about 220 K, this phenomenon could not be observed in **8**. The complex crystallizes from *n*-pentane as colourless blocks in the monoclinic space group $P2_1/n$ and is monomeric. The phosphanyl diimido moiety is attached to the magnesium atom in the same tripodal fashion involving donation from two terminal nitrogen atoms and the side-arm donation from the phosphorus atom leading to an approximately octahedral coordination polyhedron (Fig. 11). The structural motif is the same as in the magnesium compound **7**.

When the reaction of $[\text{Ph}_2\text{PCH}_2\text{Li}\cdot\text{TMEDA}]$ and $\text{S}(\text{NSiMe}_3)_2$ was carried out in toluene instead of pentane, protona-

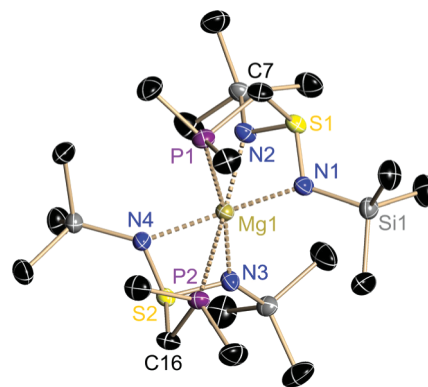
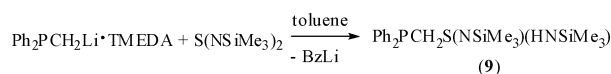


Fig. 11 Molecular structure of $[\text{Mg}\{\text{Me}_2\text{PCH}_2\text{S}(\text{NSiMe}_3)_2\}_2]$ (**8**) in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: S1–N1 1.6123(8), S1–N2 1.6111(8), Mg1–N1 2.1481(8), Mg1–N2 2.1276(8), Mg1–P1 2.8570(4); N1–S1–N2 100.44(4), N1–S1–C7 101.86(4), S1–C7–P1 107.75(5), S1–N1–Mg1 92.37(3), S1–N2–Mg1 93.15(4), N1–Mg1–N2 70.81(3), N1–Mg1–P1 72.54(2).

tion of the ligand occurred, resulting in the formation of $[\text{Ph}_2\text{PCH}_2\text{S}(\text{NSiMe}_3)(\text{HNSiMe}_3)]$ (**9**). At the moment it is supposed that this happened according to the C–H bond activation reaction described in Scheme 3. Thus, a toluene molecule is deprotonated, resulting in the formation of **9** and benzyl lithium.



Scheme 3

Compound **9** crystallizes from toluene layered with *n*-pentane in the monoclinic space group $P2_1/n$ as a monomer. The solid state structure is shown in Fig. 12.

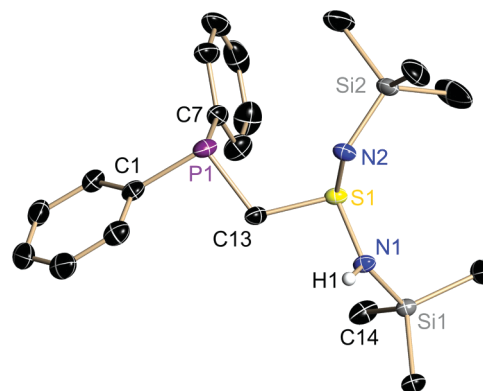


Fig. 12 Molecular structure of $[\text{Ph}_2\text{PCH}_2\text{S}(\text{NSiMe}_3)(\text{HNSiMe}_3)]$ (**9**) in the crystal. Anisotropic displacement parameters are depicted at the 50% probability level, hydrogen atoms except H1, which was freely refined, are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–P1 1.8404(13), C13–P1 1.8526(11), C13–S1 1.8092(12), N1–S1 1.6520(9), N2–S1 1.5698(10), N1–Si1 1.7421(10), N2–Si2 1.7184(10); N1–S1–N2 109.26(5), N2–S1–C13 102.99(5), N1–S1–C13 98.36(5), S1–N1–Si1 123.18(6), S1–N2–Si2 122.50(6), C7–P1–C13 102.17(7).

The bond distances for P1–C1 (1.8404(13) Å) and P1–C13 (1.8526(11) Å) are similar to those of **1–5**. The S1–C13 bond

distance is also slightly shorter than in complexes **1–5**. The N1–S1–N2 (109.26(5)°) as well as the S1–C13–P1 angle (113.54(6)°) are widened compared to the lithiated species. The S–N bond distances of 1.6520(9) (S1–N1) and 1.5698(10) Å (S1–N2) are very close to the predicted values for a single and double bond.³⁰ They also match the bond lengths of methyl(diimido)sulfonic acid H(N'Bu)₂SMe and methylene-bis(triimido)sulfonic acid H₂C{S(N'Bu)₂(NH'Bu)}₂, which have S–N bond distances of 1.52 and 1.68 Å.^{31,35} Looking at the packing of the molecules in the crystal, it is apparent that H1 is interacting with the π -system of the phenyl ring of the next adjacent molecule (C7–C12). Both six-membered rings are inclined by 99.1° with respect to each other. This is due to the interaction of H14 with the π -system of the second ring (C1–C6).

Interestingly, after stirring the reaction mixture for 20 h, there was evidence of a compound which gave a very broad signal at –39 ppm in the ³¹P{¹H} NMR spectrum. From this intermediate compound the reaction to the final product ($\delta_{31\text{P}} = -28.8$ ppm) then proceeded very slowly at –25 °C. From the NMR spectrum it was concluded that the intermediate compound is some kind of lithium complex. When the same reaction (according to Scheme 3) was carried out in pentane instead of toluene it was possible to crystallize the lithium complex **6** (Fig. 9). The ³¹P{¹H} NMR spectrum of the crystals shows a very broad signal at –39 ppm. This undoubtedly proves **6** to be the intermediate in the accrual of **9**. With the free ligand at hand it should now be much easier to obtain a great variety of mono- and bimetallic complexes directly rather than following the metathesis or salt elimination route. The reaction of **9** with metal amides or metal hydrides will hopefully give new metal complexes. Compound **9** will prove to be an excellent starting material for such reactions as it can be prepared in nearly quantitative yield and great purity.

Conclusion

With this work we have widened the area of multifunctional ligands and the scope of the Janus head ligands as well. The multifunctionality could easily be achieved just by linking the reactivity of sulfur-diimides and phosphane species. Modification in the ligands is feasible by using different substituents on the phosphane, diimido and C-bridgehead moieties. Compounds **1–5** are dimeric and the main core of the system consists of a (LiN)₂ ring in which both the lithium atoms are four-coordinated by the donor atoms of each ligand. It seems that the R₂PCH(X)S(NR')₂[–] anions are indeed tridentate ligands containing hard nitrogen and soft phosphorus donor sites. The synthesis of complexes **7** and **8** provided evidence of the coordination versatility of these newly synthesized ligands. This also indicates that the ligands with podand topology are endowed with intrinsically distinct coordination geometries leading to fascinating bonding and reactivity patterns. Transmetalation of **1–5** as well as protonation (**9**) and metal coordination (**6**) opens a wide synthetic route to introduce a variety of different metals and organometallic residues to the tripodal Janus head ligand. The intrinsic topology of intramolecularly coordinated tridentate ligands may introduce interesting reactivity and electronic properties to the metal complexes. These results are even more significant if we take into account that these were obtained by a simple reaction between the sulfur-diimide and corresponding lithiated phosphane. In addition, the formation of

these new ligands also opens up the route to create multimetallic complexes, which is becoming a rather important field nowadays and further developments are anticipated. In essence we succeeded in synthesizing new types of promising Janus head ligands that show interesting hemilabile complexation properties both in the solid state and in solution. Further investigations are under way and open questions are to be addressed to fully understand the stereochemistry of compounds **1–5** in solution and the protonation of the anions by toluene. This will be achieved *e.g.* by variable temperature NMR labeling studies.

Experimental

General

All manipulations were performed either in an inert gas atmosphere of purified dry nitrogen or argon with standard Schlenk techniques or in an argon glove box. The glassware was dried at 130 °C, assembled hot and cooled under vacuum. All solvents were dried over appropriate alkali metals, distilled and degassed prior to use. The reactants were synthesized according to the literature reports: S(NSiMe₃)₂,³⁶ (S(N'Bu)₂)³⁷ and [Ph₂PCH₂Li·TMEDA].³⁸ ^tBuLi and ⁿBuLi were supplied by Chemetall GmbH. All NMR spectra were either recorded on a Bruker Avance DPX 300 MHz or Bruker Avance DRX 500 MHz spectrometer using TMS (¹H, ¹³C and ²⁹Si), H₃PO₄ (85%) (³¹P) and LiCl (⁷Li) as the external reference and the protons of the deuterated solvents as the internal standard. Elemental analyses (C, H, N and S) were carried out at the Mikroanalytisches Labor, Institut für Anorganische Chemie, Universität Göttingen.

General preparation of lithiated phosphanes

^tBuLi (1.38 M) was reduced to half of its volume and the corresponding phosphane (PMe₃, PEt₃, Me₂PPh) was added very slowly at room temperature. After stirring for 14 h and refluxing for 2 h in the case of PEt₃, the white to light yellow precipitates were filtered, washed with *n*-pentane (3 × 5 mL) and dried *in vacuo*.

[Li{Me₂PCH₂S(N'Bu)₂}]₂ (1). 1.67 g (9.60 mmol, 2.0 eq.) S(N'Bu)₂ were slowly added to a slurry of 0.79 g (9.60 mmol, 2.0 eq.) Me₂PCH₂Li in 60 mL *n*-pentane at –78 °C. The mixture was yellow at first and became light orange after stirring overnight at room temperature. The clear solution was reduced to half of its volume *in vacuo*. Storage at –25 °C for 5 days yielded colorless crystals. Yield: 1.65 g (3.20 mmol) 67%; mp 143 °C (from pentane, decomposition); Found: C, 51.6; H, 10.9; N, 10.8; S, 12.3. C₂₂H₅₂N₄P₂S₂Li₂ requires C, 51.6; H, 10.2; N, 10.9; S 12.5%; δ ¹H (500.13 MHz; C₆D₆): 0.896 (6 H, d, ²J_{P-H} = 0.55 Hz, P(CH₃)₂), 0.898 (6 H, d, ²J_{P-H} = 0.55 Hz, P(CH₃)₂), 1.44 (36 H, s, C(CH₃)₃), 2.676 (2 H, d, ²J_{P-H} = 0.92 Hz, PCH₂S), 2.678 (2 H, d, ²J_{P-H} = 0.92 Hz, PCH₂S); δ ¹³C (125.76 MHz; C₆D₆): 13.70 (d, ¹J_{P-C} = 1.65 Hz, PCH₃), 13.73 (d, ¹J_{P-C} = 1.65 Hz, PCH₃), 33.76 (s, C(CH₃)₃), 54.02 (s, C(CH₃)₃), 64.83 (d, ¹J_{P-C} = 2.99 Hz, PCH₂S), 64.92 (d, ¹J_{P-C} = 2.99 Hz, PCH₂S); δ ³¹P (202.46 MHz; C₆D₆): –67.0 (sept, ¹J_{P-Li} = 18.5 Hz, LiPLi); δ ⁷Li (194.37 MHz; C₆D₆): 2.22 ppm (t, ¹J_{P-Li} = 18.5 Hz, PLiP).

[Li{Me₂PCH₂S(NSiMe₃)₂}]₂ (2). To a suspension of Me₂PCH₂Li (0.60 g, 7.32 mmol, 2.0 eq) in *n*-pentane (40 mL) S(NSiMe₃)₂ (1.51 g, 7.32 mmol, 2.0 eq) was added very slowly

at $-78\text{ }^{\circ}\text{C}$. The suspension was allowed to warm to room temperature after 20 min and stirred for 24 h. The green-yellow solution was filtered, reduced to half of its volume and stored at $-25\text{ }^{\circ}\text{C}$. Colourless crystals, suitable for structural analysis were obtained after two days. Yield: 1.64 g, 2.85 mmol, 78%; mp $147.3\text{ }^{\circ}\text{C}$ (from pentane, decomp.); Found: C, 37.21; H, 9.00; N, 9.92; S, 11.14. $\text{C}_{18}\text{H}_{52}\text{N}_4\text{Si}_4\text{P}_2\text{S}_2\text{Li}_2$ requires C, 37.21; H, 9.08; N, 9.71; S, 11.12%; $\delta\text{ }^1\text{H}$ (500.13 MHz, C_6D_6): 0.32 (36 H, s, $\text{Si}(\text{CH}_3)_3$), 0.83 (12 H, s, $\text{P}(\text{CH}_3)_2$), 2.65 (4 H, s, PCH_2S); $\delta\text{ }^{13}\text{C}$ (125.77 MHz, C_6D_6): 2.92 ($\text{Si}(\text{CH}_3)_3$), 12.92 (d, $\text{P}(\text{CH}_3)_2$), $^1J_{\text{P-C}} = 3.31$ Hz), 66.51 (d, PCH_2S , $^1J_{\text{P-C}} = 10.94$ Hz); $\delta\text{ }^{31}\text{P}$ (202.46 MHz, C_6D_6): -67.87 (hept, $^1J_{\text{P-Li}} = 20.84$ Hz); $\delta\text{ }^7\text{Li}$ (194.37 Hz, C_6D_6): 2.19 (t, $^1J_{\text{P-Li}} = 20.84$ Hz); $\delta\text{ }^{29}\text{Si}$ (99.36 MHz, C_6D_6): -2.71 (s, $^1J_{\text{N-Si}} = 27.55$ Hz).

[Li{Ph₂PCH₂S(N^tBu)₂}]₂ (3). 1.74 g (10.0 mmol, 2.0 eq.) $\text{S}(\text{N}^t\text{Bu})_2$ were slowly added to a slurry of 2.06 g (10.0 mmol, 2.0 eq.) $[\text{Li}(\text{H}_2\text{CPPh}_2)\cdot\text{TMEDA}]$ in 60 mL *n*-pentane at $-78\text{ }^{\circ}\text{C}$. After stirring overnight at room temperature, the white precipitate was filtered, washed with pentane and dissolved in toluene. The light yellow solution was kept at $-25\text{ }^{\circ}\text{C}$ for three days, yielding colourless crystals. Yield: 2.05 g (2.88 mmol) 78%; mp $123\text{ }^{\circ}\text{C}$ (from toluene, decomp.); Found: C, 64.6; H, 7.7; N, 6.5; S, 8.1. $\text{C}_{42}\text{H}_{60}\text{N}_4\text{P}_2\text{S}_2\text{Li}_2$ requires C, 66.3; H, 8.0; N, 7.4; S, 8.4%; $\delta\text{ }^1\text{H}$ (500.13 MHz, C_6D_6): 1.37 (36 H, s, $\text{C}(\text{CH}_3)_3$), 3.64 (4 H, s, PCH_2S), 6.98–7.01 (4 H, m, *p*-H), 7.04–7.07 (8 H, m, *m*-H), 7.56–7.59 (8 H, m, *o*-H); $\delta\text{ }^{13}\text{C}$ (125.76 MHz, C_6D_6): 33.60 (s, $\text{C}(\text{CH}_3)_3$), 54.31 (s, $\text{C}(\text{CH}_3)_3$), 62.26 (d, $^1J_{\text{P-C}} = 17.49$ Hz, PCH_2S), 128.63–128.76 (m, *i*-C), 128.92 (s, *p*-C), 133.45–133.63 (m, $^2J_{\text{P-C}} = 18.30$ Hz, *o*-C), 137.79–137.82 (m, $^3J_{\text{P-C}} = 3.76$ Hz, *m*-C); $\delta\text{ }^{31}\text{P}$ (202.46 MHz, C_6D_6): -32.57 (br s, LiPLi); $\delta\text{ }^7\text{Li}$ (194.37 MHz, C_6D_6): 2.63 ppm (t, $^1J_{\text{P-Li}} = 12.8$ Hz, PLiP).

[Li{Et₂PCH(Me)S(NSiMe₃)₂}]₂ (4). To a suspension of $\text{Et}_2\text{PCH}(\text{Me})\text{Li}$ (0.13 g, 0.81 mmol, 2.0 eq.) in *n*-pentane (10 mL) $\text{S}(\text{NSiMe}_3)_2$ (0.17 g, 0.81 mmol, 2.0 eq.) was added very slowly at $-78\text{ }^{\circ}\text{C}$. After 20 min the suspension was allowed to warm to room temperature and stirred for 24 h. The yellow solution was reduced to 1/2 of its volume and stored at $-25\text{ }^{\circ}\text{C}$. After one week, colourless crystals, suitable for structural analysis, were obtained. Yield: 0.21 g, 0.32 mmol, 80%; mp $138.9\text{ }^{\circ}\text{C}$ (from pentane, decomp.); Found: C, 42.96; H, 9.58; N, 8.70; S, 9.83. $\text{C}_{24}\text{H}_{64}\text{N}_4\text{Si}_4\text{P}_2\text{S}_2\text{Li}_2$ requires C, 43.60; H, 9.76; N, 8.47; S, 9.70%; $\delta\text{ }^1\text{H}$ (500.13 MHz, C_6D_6): 0.36–0.37 (72 H, m, $2\times\text{Si}(\text{CH}_3)_3$), 0.92–1.02 (24 H, m, $2\times\text{PCH}_2\text{CH}_3$), 1.17–1.22 (24 H, m, $2\times\text{PCH}_2\text{CH}_3$), $1/3\times\text{PCH}(\text{CH}_3)\text{S}$, 1.43–1.54 (4 H, m, $2/3\times\text{PCH}(\text{CH}_3)\text{S}$), 2.59–2.68 (4 H, m, $2\times\text{PCH}(\text{CH}_3)\text{S}$); $\delta\text{ }^{13}\text{C}$ (125.77 MHz, C_6D_6): 3.09–3.42 (m, $\text{Si}(\text{CH}_3)_3$), 10.46–11.21 (m, PCH_2CH_3 , PCH_2CH_3), 14.10 (dd, $^2J_{\text{P-C}} = 111.5$ Hz, $^4J_{\text{P-C}} = 8.81$ Hz, $\text{PCH}(\text{CH}_3)\text{S}$), 17.24 (dd, $^2J_{\text{P-C}} = 72.57$ Hz, $^4J_{\text{P-C}} = 6.60$ Hz, $\text{PCH}(\text{CH}_3)\text{S}$), 63.34 (d, $^1J_{\text{P-C}} = 13.48$ Hz, $\text{PCH}(\text{CH}_3)\text{S}$), 64.87 (d, $^1J_{\text{P-C}} = 14.34$ Hz, $\text{PCH}(\text{CH}_3)\text{S}$); $\delta\text{ }^{31}\text{P}$ (202.46 MHz, C_6D_6): -30.74 (hept, $^1J_{\text{P-Li}} = 18.81$ Hz, LiPLi), -27.34 (hept, $^1J_{\text{P-Li}} = 19.16$ Hz, LiPLi); $\delta\text{ }^7\text{Li}$ (194.37 Hz, C_6D_6): 2.27 (t, $^1J_{\text{P-Li}} = 18.81$ Hz, PLiP), 2.37 (t, $^1J_{\text{P-Li}} = 19.16$ Hz, PLiP); $\delta\text{ }^{29}\text{Si}$ (99.36 MHz, C_6D_6): -4.19 (s, $^1J_{\text{N-Si}} = 26.61$ Hz, $\text{NSi}(\text{CH}_3)_3$), -3.65 (s, $^1J_{\text{N-Si}} = 27.16$ Hz, $\text{NSi}(\text{CH}_3)_3$), -1.05 (s, $^1J_{\text{N-Si}} = 27.61$ Hz, $\text{NSi}(\text{CH}_3)_3$), -0.55 (s, $^1J_{\text{N-Si}} = 27.61$ Hz, $\text{NSi}(\text{CH}_3)_3$).

[Li{Me(Ph)PCH₂S(N^tBu)₂}]₂ (5). To a suspension of $\text{Me}(\text{Ph})\text{PCH}_2\text{Li}$ (1.50 g, 11.4 mmol, 2.0 eq.) in *n*-pentane (30 mL)

$\text{S}(\text{N}^t\text{Bu})_2$ (1.98 g, 11.4 mmol, 2.0 eq.) was added very slowly at $-78\text{ }^{\circ}\text{C}$. After 20 min the suspension was allowed to warm to room temperature and stirred for 24 h. The yellow-orange solution was reduced to 2/3 of its volume and stored at $-25\text{ }^{\circ}\text{C}$. After three days, colourless crystals suitable for structural analysis, were obtained. Yield: 2.65 g, 4.16 mmol, 73%; mp $125.5\text{ }^{\circ}\text{C}$ (from pentane, decomp.); Found: C, 59.33; H, 8.75; N, 8.79; S, 10.26. $\text{C}_{32}\text{H}_{56}\text{N}_4\text{P}_2\text{S}_2\text{Li}_2$ requires C, 60.36; H, 8.86; N, 8.80; S, 10.07%; $\delta\text{ }^1\text{H}$ (500.13 MHz, C_6D_6): 1.20 (3 H, s, PCH_3), 1.32 (3 H, s, PCH_3), 1.37 (9 H, s, $\text{C}(\text{CH}_3)_3$), 1.38 (9 H, s, $\text{C}(\text{CH}_3)_3$), 1.43 (9 H, s, $\text{C}(\text{CH}_3)_3$), 1.45 (9 H, s, $\text{C}(\text{CH}_3)_3$), 2.96–3.12 (4 H, m, PCH_2S), 7.02–7.05 (2 H, m, *p*-H), 7.08–7.12 (4 H, m, *m*-H), 7.47–7.51 (4 H, m, *o*-H); $\delta\text{ }^{13}\text{C}$ (125.76 MHz, C_6D_6): 13.43 (dd, $^1J_{\text{P-C}} = 4.73$ Hz, $^3J_{\text{P-C}} = 3.01$ Hz, PLiPCH_3), 13.60 (dd, $^1J_{\text{P-C}} = 5.02$ Hz, $^3J_{\text{P-C}} = 2.44$ Hz, PLiPCH_3), 33.51–33.67 (m, $\text{C}(\text{CH}_3)_3$), 53.94–54.40 (m, $\text{C}(\text{CH}_3)_3$), 64.10–64.27 (m, PCH_2S), 128.56–128.70 (m, *o*-C), 131.89–132.27 (m, *p*-C), 139.65 (dd, $^3J_{\text{P-C}} = 3.49$ Hz, $^5J_{\text{P-C}} = 1.99$ Hz, *m*-C), 139.97 (dd, $^1J_{\text{P-C}} = 3.16$ Hz, $^3J_{\text{P-C}} = 2.24$ Hz, *i*-C); $\delta\text{ }^{31}\text{P}$ (202.46 MHz, C_6D_6): -51.98 – -51.51 (m, LiPLi); $\delta\text{ }^7\text{Li}$ (194.37 Hz, C_6D_6): 2.41 (t, $^1J_{\text{P-Li}} = 13.43$ Hz, PLiP).

[TMEDA·Li{Ph₂PCH₂S(NSiMe₃)₂}] (6). To a slurry of $\text{Ph}_2\text{PCH}_2\text{Li}\cdot\text{TMEDA}$ (3.01 g, 9.30 mmol, 1.0 eq.) in *n*-pentane (50 mL) $\text{S}(\text{NSiMe}_3)_2$ (1.92 g, 9.30 mmol, 1.0 eq.) was slowly added at $-78\text{ }^{\circ}\text{C}$. After stirring at room temperature overnight, the solution was filtered over celite, reduced in volume and stored at $-25\text{ }^{\circ}\text{C}$, yielding colourless crystals after 2 days.

Yield: 4.44 g, 8.40 mmol, 90%; Found: C, 56.08; H, 8.48; N, 10.37; S, 6.28. $\text{C}_{25}\text{H}_{46}\text{N}_4\text{Si}_2\text{PSLi}$ requires C, 56.78; H, 8.77; N, 10.59; S, 6.06%; $\delta\text{ }^1\text{H}$ (300.13 MHz, C_6D_6): 0.28 (18 H, s, $\text{Si}(\text{CH}_3)_3$), 1.77 (4 H, s br, $\text{N}(\text{CH}_2)_2\text{N}$), 2.07 (12 H, s, $(\text{CH}_3)_2\text{N}$), 3.47 (2 H, s br, SCH_2P), 6.99–7.12 (6 H, m, *o*-H, *p*-H), 7.59–7.70 (4 H, m, *m*-H); $\delta\text{ }^{13}\text{C}$ (125.76 MHz, C_6D_6): 3.19 ($\text{Si}(\text{CH}_3)_3$), 45.82 ($(\text{CH}_3)_2\text{N}$), 56.66 ($\text{N}(\text{CH}_2)_2$), 70.84 (d, $^1J_{\text{P-C}} = 23.99$ Hz, PCH_2S), 128.46 (d, $^3J_{\text{P-C}} = 6.02$ Hz, *m*-C), 132.48 (d, $^4J_{\text{P-C}} = 18.74$ Hz, *p*-C), 133.90 (d, $^2J_{\text{P-C}} = 19.50$ Hz, *o*-C), 142.04 (d, $^1J_{\text{P-C}} = 14.98$ Hz, *ipso*-C); $\delta\text{ }^{31}\text{P}$ (121.49 MHz, C_6D_6): -38.78 (s br, PCH_2S); $\delta\text{ }^7\text{Li}$ (194.37 MHz, C_6D_6): 1.00(s); $\delta\text{ }^{29}\text{Si}$ (99.36 MHz, C_6D_6): -8.29 (s).

[Mg{Me₂PCH₂S(N^tBu)₂}]₂ (7). 0.50 g (0.98 mmol, 1.0 eq.) **1** and 0.90 g (0.98 mmol, 1.0 eq.) MgCl_2 were combined in an argon drybox and dissolved in 40 mL *n*-pentane/thf at room temperature. After stirring overnight, the solvent was removed *in vacuo* and the resulting yellow powder suspended in 20 mL *n*-pentane. The suspension was filtered over celite and the volume of the filtrate was reduced. Colourless crystals were obtained after storing the yellow solution for 3 days at $4\text{ }^{\circ}\text{C}$. Yield: 0.33 g (0.63 mmol) 64%; mp $165.5\text{ }^{\circ}\text{C}$ (from pentane, decomp.); Found: C, 49.9; H, 10.0; N, 11.0; S, 12.2. $\text{C}_{22}\text{H}_{52}\text{N}_4\text{P}_2\text{S}_2\text{Mg}$ requires C, 50.5; H, 10.0; N, 10.7; S, 12.3; $\delta\text{ }^1\text{H}$ (500.13 MHz, C_6D_6): 0.98 (12 H, t, $^2J_{\text{P-H}} = 1.15$ Hz, $\text{P}(\text{CH}_3)_2$), 1.39 (36 H, s, $\text{C}(\text{CH}_3)_3$), 2.21 (4 H, t, $^2J_{\text{P-H}} = 1.65$ Hz, PCH_2S); $\delta\text{ }^{13}\text{C}$ (125.76 MHz, C_6D_6): 14.67 (d, $^1J_{\text{P-C}} = 4.06$ Hz, $\text{P}(\text{CH}_3)_2$), 14.71 (d, $^1J_{\text{P-C}} = 4.06$ Hz, $\text{P}(\text{CH}_3)_2$), 33.67 (s, $\text{C}(\text{CH}_3)_3$), 53.08 (s, $\text{C}(\text{CH}_3)_3$), 65.92 (d, $^1J_{\text{P-C}} = 1.92$ Hz, PCH_2S), 65.94 (d, $^1J_{\text{P-C}} = 1.92$ Hz, PCH_2S); $\delta\text{ }^{31}\text{P}$ (202.46 MHz, C_6D_6): -82.69 ppm (s br, $\text{P}(\text{CH}_3)_2$).

[Mg{Me₂PCH₂S(NSiMe₃)₂}]₂ (8). **2** (0.54 g, 0.94 mmol, 1.0 eq.) and MgCl_2 (0.13 g, 1.4 mmol, 1.5 eq.) were combined in an argon drybox and dissolved in thf (10 mL). After stirring for

24 h at room temperature, the solvent was evaporated *in vacuo* and the resulting powder was suspended in pentane (10 mL). The suspension was filtered and reduced in volume. After storing the colourless solution at 4 °C for four days, crystals suitable for structural analysis were obtained. Yield: 0.53 g, 0.90 mmol, 96%; mp 206.5 °C (from pentane, decomp.); Found C, 36.92; H, 9.27; N, 9.75; S, 11.11. C₁₈H₅₂N₄Si₄P₂S₂Mg requires C, 36.81; H, 8.92; N, 9.54; S, 10.92%; δ¹H (500.13 MHz, C₆D₆): 0.29 (36 H, s, Si(CH₃)₃), 0.91 (12 H, s, P(CH₃)₂), 2.398 (2 H, d, ²J_{P-H} = 1.93 Hz, PCH₂S), 2.402 (2 H, d, ²J_{P-H} = 1.93 Hz, PCH₂S); δ¹³C (125.77 MHz, C₆D₆): 2.75 (s, Si(CH₃)₃), 13.77 (d, ¹J_{P-C} = 2.30 Hz, P(CH₃)₂), 13.79 (d, ¹J_{P-C} = 2.30 Hz, P(CH₃)₂), 67.57 (s, PCH₂S); δ²⁹Si (99.36 MHz, C₆D₆): -4.05 (s, ¹J_{N-Si} = 27.91 Hz, Si(CH₃)₃); δ³¹P (202.46 MHz, C₆D₆): -84.63 (s, PCH₂S).

[Ph₂PCH₂(SNSiMe₃)(HNSiMe₃)] (9). To a slurry of Ph₂PCH₂Li-TMEDA (0.88 g, 2.72 mmol, 1.0 eq.) in pentane (30 mL) S(NSiMe₃)₂ (0.56 g, 2.72 mmol, 1.0 eq.) was slowly added at -78 °C. After stirring at room temperature overnight, the solution was filtered over celite and the solvent evaporated *in vacuo*. The precipitate was dissolved in toluene, reduced in volume, layered with pentane and stored at -25 °C. After 2 months, crystals suitable for structural analysis were obtained. Yield: 1.07 g, 2.63 mmol, 97%; mp 138.3 °C (from pentane, decomp.); Found: C, 55.94; H, 7.66; N, 7.00; S, 8.00. C₁₉H₃₁Si₂N₂PS requires C, 56.11; H, 7.68; N, 6.89; S, 7.88%; δ¹H (500.13 MHz, C₆D₆): 0.22 (18 H, s, Si(CH₃)₃), 4.09 (2 H, d, ²J_{P-H} = 0.80 Hz, PCH₂S), 7.00–7.04 (2 H, m, *p*-H), 7.06–7.10 (4 H, m, *m*-H), 7.49–7.52 (2 H, m, *o*-H); δ¹³C (125.76 MHz, C₆D₆): 1.89 (Si(CH₃)₃), 63.59 (d, ¹J_{P-C} = 24.61 Hz, PCH₂S), 128.76 (d, ³J_{P-C} = 6.65 Hz, *m*-C), 129.00 (*p*-C), 133.34 (d, ²J_{P-C} = 19.71 Hz, *o*-C), 138.43 (d, ¹J_{P-C} = 14.76 Hz, *ipso*-C); δ³¹P (202.46 MHz, C₆D₆): -28.81 (s, PCH₂S); δ²⁹Si (99.36 MHz, C₆D₆): 2.59 (s, ¹J_{N-Si} = 28.35 Hz); EI-MS *m/z*: 406 (M⁺, 17%), 318 (14, M – HNSiMe₃), 286 (19, Ph₂PCH₂SNSiMe₃), 272 (19, Ph₂PCH₂SiMe₃), 207 (15, M – Ph₂PCH₂), 199 (100, Ph₂PCH₂), 121 (44, SN(HSiMe₃) + H), 73 (20, SiMe₃).

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