FULL PAPER

Monoanionic N,P,S-Janus Head Tripods in s-Block Metal Coordination

Margret M. Meinholz[a] and Dietmar Stalke*[a]

Polyimido sulfur phosphanyl complexes of alkaline earth metals can be synthesised by transmetallation of a suitable lithium precursor. By the same route heterobimetallic complexes of lithium, potassium or rubidium are accessible. [(tmeda)Li{Ph$_2$PCH$_2$S(NSiMe$_3$)$_2$}] (**I**) is an excellent starting material for such reactions because the pendent phosphorus side arm is free to precoordinate with a second metal to bring this metal into close spatial proximity with the ligand's two nitrogen chelating claws. Lithium can then leave the complex as a stable tmeda/ligand adduct. Via this route several alkali and alkaline earth metal complexes such as [M{Ph$_2$PCH$_2$S(NSiMe$_3$)$_2$}$_2$] with M = Ca (**1**), Sr (**2**), and [(tmeda)M′{Ph$_2$PCH$_2$S(NSiMe$_3$)$_2$}$_2$Li] with M′ = Rb (**3**), K (**4**) were synthesized and structurally characterized. All compounds show interesting structural features both in the solid state and in solution.

Introduction

In recent publications we have reported alkali metal complexes of sulfur diimido phosphanyl[1] and aminyl[2] ligands and demonstrated the flexibility and versatility of this class of new hemilabile Janus head ligands. The complexes obtained so far are dimeric and monometallic. It is now of interest to promote metal exchange reactions to explore the full complexation potential of this new ligand type. In addition, the synthesis of heterobimetallic complexes is one of our main objectives, as the new ligands contain both hard and soft donor sites.

In the current study, we focus on alkali and alkaline earth metal complexes. Interest in heavy Grignard reagents has been growing steadily over the past years.[3] These aryl alkaline earth metal halides and hydrides[4] show increased reactivity in metallation reactions,[5] metathesis[6] and addition reactions[7] in comparison to their magnesium counterparts. Organocalcium compounds are used as initiators for ring-opening polymerisations of cyclic esters.[8] (β-diketiminato)calcium complexes are known to catalyse hydroamination[9] and hydrophosphination reactions of alkenes, alkynes and carbodiimides.[10] Benzyl alkaline earth metals are precatalysts for the hydrosilylation of alkenes.[11] Calcium has the advantage over many other metals by being readily available, cheap and non-toxic, which is most advantageous if it is to be used in polymerization reactions. The use of benzyl calcium as a precatalysis for the hydrosilylation of 2-vinylpyridine has been studied by Souter et al.[12]

[a] Institut für Anorganische Chemie, Georg-August-Universität Göttingen,
Tammannstr. 4, 37077 Göttingen, Germany
Fax: +49-551-39-3459
E-mail: dstalke@chemie.uni-goettingen.de

Heterobimetallic complexes have gained ever increasing attention in preparative chemistry,[9] above all for use in deprotonation reactions. Usually, lithium organic reagents like BuLi or LDA are used for such purposes. However, they suffer from insufficient functional group tolerance, low selectivity, and the reactions have to be conducted at low temperatures (usually below 0 °C) to avoid side reactions. This is why so-called complex metalators consisting of two or more metal components are used. In these compounds, the metal atoms interact synergistically because they are held in close spatial proximity by the ligands. Thereby, unusual (for lithium organics) deprotonation reactions are feasible and selectivities can greatly be enhanced. Prominent examples are the LiCKOR superbases developed by Lochmann and Schlosser,[13] zincate complexes,[14] turbo-Grignards,[15] and inverse crown reagents for alkali metal mediated metalations (AMMMs).[16]

Results and Discussion

In a previous studies we embarked on the direct transmetalation of [Li{Me$_2$PCH$_2$S(NR)$_2$}]$_2$ (R = *t*Bu, SiMe$_3$) with metal halides.[1] However, this reaction was only successful in the case of MgCl$_2$.[17] The futility of employing metal halides for such reactions with sulfur diimido compounds has already been discussed.[18] Sulfur ylides and other similar sulfur nitrogen compounds are too redox active, and the addition of metal halogenides leads to S–N and S–C bond cleavage reactions. This phenomenon was also reported in the 1980's for sulfur diimide derivatives.[19] The use of MgCl$_2$ in the above mentioned reaction was probably successful because of the diagonal relationship between magnesium and lithium in the periodic table of elements. The synthesis of the magnesium complexes [Mg{Me$_2$PCH$_2$S(NR)$_2$}$_2$] (R = *t*Bu, SiMe$_3$) involves two

NSCP ligands complexing with small dications in a hexadentate manner.[1] Consequently, it was of interest to determine what coordination geometry would be adopted by a larger dication. For comparison reasons the heavier homologues calcium and strontium were employed. However, another pathway for the transmetalation had to be found.

If the secondary metal is already precoordinated by an appropriate donor then this facilitates the transmetalation of the lithium diimido complexes. This principle is quite intuitive as the cation is not coordinated firmly to the ligand and can be removed easily. With this in mind, **I**[1] (Scheme 1) was identified as a good starting material, as the lithium atom is not only chelated by the diimido nitrogen atoms but also by a tmeda molecule.
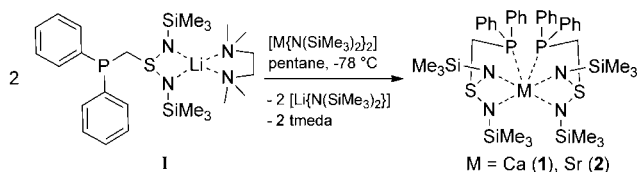
Scheme 1. General preparation procedure for the alkaline earth metal complexes.

The reaction of [Ca{N(SiMe₃)₂}₂] with **I** proceeded with a complete metal exchange, in accordance with Scheme 1. It could have been anticipated that the large calcium atom would be accommodated by the pendent phosphorus sidearm, and the smaller lithium cation would remain between the nitrogen atoms yielding a heterobimetallic complex like in [(thf)₂CaLi₂{(N*t*Bu)₃S}₂].[18] However, this was not observed and a dimer of the composition [Ca{Ph₂PCH₂S-(NSiMe₃)₂}₂] (**1**) was formed instead. The calcium dication is coordinated by the four nitrogen and two phosphorus atoms from two tridentate ligands in a facial manner (Figure 1). The coordination of the NSCP ligand resembles the coordination of S(N*t*Bu)₃²⁻ in [(thf)₂Li₂Ca-{(N*t*Bu)₃S}₂][18] and **1** could be regarded as a monometallic analogue of this complex. The coordination polyhedron should not be described as an octahedron as it is too distorted. One could envisage the structure as two CS-capped NNPCa tetrahedra fused at their common Ca apexes. The angles N1–Ca1–N2 63.47(6)° and N2–Ca1–P1 71.20(5)° around the calcium atom support this view. Both tetrahedra are twisted by 55° with respect to each other, inhibiting an alignment of the two phosphorus donor atoms. Despite the different ligands the structure is very similar to the already reported magnesium complex [Mg{Me₂PCH₂S-(N*t*Bu)₂}₂].[1] The bond lengths in **1** are all in the expected range and are comparable to other geometrically similar phosphorus–calcium and nitrogen–calcium complexes, although the phosphorus–calcium bonds are somewhat elongated.[20] This elongation is attributed to the side arm donation of a phosphanyl moiety[21] rather than a phosphanide anion. The S–N distances are shorter than single bonds and suit the concept of polar reinforced S^{δ+}–N^{δ−} bonds, which have been studied by experimental and theoretical charge density methods.[22]
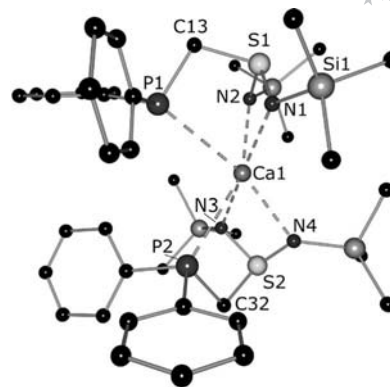

Figure 1. Molecular structure of **1**, hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: S1–N1 1.6078(19), S1–N2 1.6076(17), Ca1–N1 2.4198(18), Ca1–N2 2.3909(19), Ca1–P1 3.0815(7), N1–S1–N2 103.80(9), S1–C13–P1 107.70(11), N1–Ca1–N2 63.47(6), N2–Ca1–P1 71.20(5).

It is striking that the phosphorus atoms are on the same side of the molecule and not on opposite sides to reduce steric strain as one may expect. In the crystal structure of **1**, the four phenyl rings are twisted by approximately 90° with respect to each other to reduce steric strain. In a complementary explanation, it has already been established by theoretical investigations that the heavy alkaline earth metals show not only ionic but also covalent bonding properties. This is achieved by contribution of the *d*-orbitals to bonding, and the high polarisability of the sub-valence shells, which results in the atoms being non-spherical.[23] Therefore, the heavy alkaline earth metal halides, hydrides, and many other compounds like [Ca{C(SiMe₃)₃}₂][24] for instance, have bent rather than linear structures. The arrangement of the phosphorus atoms in **1** is also controlled by the same facts. Thus, the s-bonding character between the phosphorus *p*-orbital and the calcium *d*-orbital could be responsible for the *cis*-arrangement of the phosphorus side arms as well as the polarisation of Ca²⁺ by the ligand. A similar *cisoid* arrangement of ligands was found in [(thf)-Ca{(NSiMe₃)₂PPh₂}₂][25] and [(dme)₃Ba(*N*-carbazolyl)₂],[26] and was explained in the same way.

The reaction of **I** with [Sr{N(SiMe₃)₂}₂] afforded the strontium complex **2** as colourless crystals. Complex **2** is isostructural with the calcium complex **1**, and is depicted in Figure 2.

The nitrogen–strontium and phosphorus–strontium bond lengths are elongated in **2** in comparison to the calcium complex **1**, which is due to the larger ionic radius of strontium. However, they are in the range observed for the bonds in the bis(diphosphanylamido) complex [(thf)₃Sr-{(Ph₂P)₂N}₂],[27] which is to the best of our knowledge the only other reported example of phosphanyl donation in a strontium complex. The N1–S1–N2 angle is slightly widened in **2** in comparison to the calcium complex [104.73(7)° vs. 103.80(9)°] as is the S1–C13–P1 angle [108.20(8)° vs. 107.70(11)°]. On the other hand, the angles around the strontium dication are considerably more acute than in the calcium complex. This could be due to the fact that the
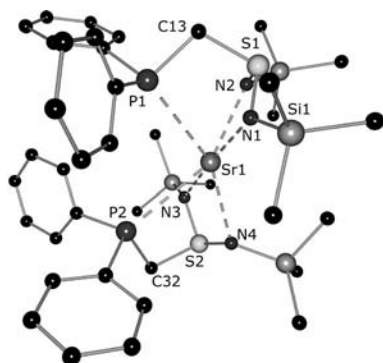
Figure 2. Molecular structure of $[Sr\{Ph_2PCH_2S(NSiMe_3)_2\}_2]$ (**2**), hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: S1–N1 1.6053(10), S1–N2 1.6139(10), Li1–N2 1.968(2), Li1–N3 2.193(2), Li2–N2 2.284(2), N1–S1–N2 104.73(7), S1–C13–P1 108.20(8), N1–Sr1–N2 59.71(4), N2–Sr1–P1 66.70(3).

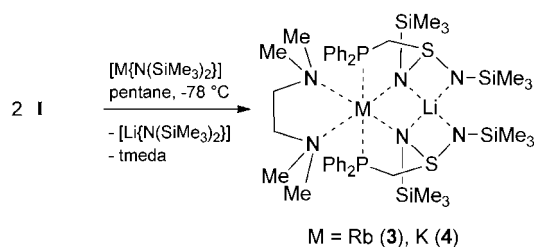Scheme 2. General preparation procedure for alkali mixed metal complexes.

bond lengths between the metal and donor atoms are longer because of the increased ionic radius of the metal, and therefore the ligand is located further away from the central metal atom. Consequently, the angles have to become more acute. The arrangement of the phosphorus side arms is the same as in the corresponding calcium complex, however the bending of the ligand is reduced [S1–Ca1–S2: 158.103(19)°, S1–Sr1–S2: 162.896(10)°], which might be due to the larger cation size.

In comparison it has been shown that the ligand $\{R_2PCH_2S(NSiMe_3)_2\}^-$ is very flexible and versatile as it can accommodate various alkaline earth metal dications. In the structures described so far, the ionic radii[28] range from 72 pm (Mg^{2+})[1] to 121 pm (Sr^{2+}), and the metals have coordination numbers equal to six. The connectivity is always the same with all nitrogen and phosphorus atoms taking part in the coordination, regardless of the hard and soft acid base (HSAB) hardness[29] of the central metal ion. There is no formation of aggregates, which is a known property of the heavy alkaline earth metals because of their very large ionic radii.[30] It can be concluded that the ligand employed in **1** and **2** is sterically demanding enough to block certain coordination sites and prevent the formation of aggregates, and hence soluble alkaline earth metal complexes are generated.

It was of further interest to prepare complexes of the ligand $\{Ph_2PCH_2S(NSiMe_3)_2\}^-$ and the heavy alkali metals to investigate the possible changes in coordination and to synthesize heterobimetallic complexes. Complex **3** was prepared by reacting **I** with $[Rb\{N(SiMe_3)_2\}]$ at –78 °C in pentane (Scheme 2).

As suspected because of the many coordination sites, the metal exchange was not complete and only half of the lithium ions were exchanged for rubidium, resulting in the formation of a heterobimetallic dimeric complex, with the molecular structure shown in Figure 3.

As anticipated, the lithium cation is coordinated to the four nitrogen atoms from both ligands. The rubidium cation is complexed by only two nitrogen atoms of the diimido moieties, but also by each of the phosphorus side arms and
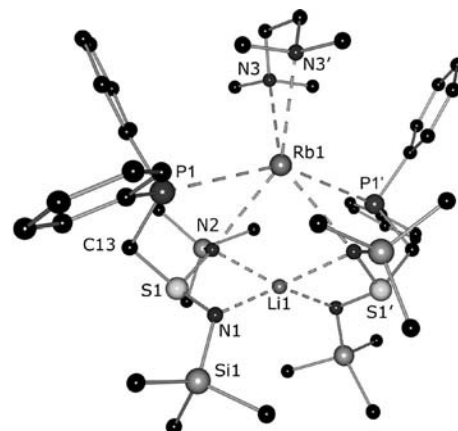
Figure 3. Molecular structure of $[(tmeda)Rb\{Ph_2PCH_2S-(NSiMe_3)_2\}_2Li]$ (**3**), hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: S1–N1 1.6024(15), S1–N2 1.6076(15), Li1–N1 2.053(2), Li1–N2 2.262(2), Rb1–N2 3.0646(15), Rb1–P1 3.5996(5), N1–S1–N2 103.69(8), N1–Li1–N2 71.43(6), N2–Rb1–P1 59.15(3), P1–Rb1–P1′ 150.818(18).

the tmeda molecule, which complete the coordination sphere. Consequently, both alkali metals have different coordination geometries and environments. The structure is bisected by a mirror plane that passes through both metal ions. Li1 has a distorted tetrahedral coordination geometry with Li–N bond lengths between 2.053(2) Å (Li1–N1) and 2.262(2) Å (Li1–N2). The Li1–N2 bond is slightly elongated because N2 is also coordinated to Rb1. The rubidium atom Rb1 is six fold coordinated in a severely distorted octahedral manner. It is interesting that one of the tmeda molecules remains in the complex, but switches its coordination to rubidium. The Rb–N and Rb–P bonds are above 3.0 Å, which is normal and can be found in other complexes like $[Rb(thf)P(SiMe_3)_2]_\infty$,[31] $[RbP(H)(dmp)]$[32] (dmp = 2,6-dimesitylphenyl) and $[Rb\{([Me_3Si]_2C)P(C_6H_4-2-CH_2-NMe_2)_2\}]_n$.[33]

A search of the Cambridge Structural Database (CSD) revealed that heterobimetallic complexes of lithium and rubidium are rare. There are only five examples of structurally characterized compounds of this type and none of them contains multifunctional ligands. Mulvey et al. describe a heptalithium tetrarubidium mixed alkoxide peroxide wherein the clusters are linked by Rb–(tmeda)–Rb bridges.[34] The reported mean Rb–N bond length of 3.197 Å is close to the value for Rb1–N3 [3.0458(16) Å] in **3**. Another compound with the composition $[(tBuO)_8Li_4Rb_4]$ contains

neither nitrogen nor phosphorus atoms, which is also the case with the other examples in the CSD.[35]

Interestingly, there are two signals in the $^7Li\{^1H\}$ NMR spectrum of **3**. The signal at $\delta = 1.81$ ppm can be associated with the Rb/Li heterobimetallic complex **3**; the other signal at $\delta = 1.02$ ppm seems to belong to the starting material **I**. This is certainly not due to contamination of the sample, as pure crystals of **3** were dissolved in C_6D_6 and the sample tube sealed airtight for the NMR data collections. In addition, the signal for the starting material **I** is quite high in intensity. An impurity of such a high concentration would have been detected in the elemental analysis, however this was not the case. When looking at the $^{31}P\{^1H\}$ spectrum of **3** the presence of starting material in the sample is even more obvious. There is a small broad signal at –39 ppm associated with **I**, whereas the heterobimetallic complex **3** shows a signal at –33 ppm. The integration reveals a ratio of 1 to 0.2 for these peaks. All these analytical results indicate that the Rb/Li complex is not retained completely in solution. The whole system seems to be flexible in solution like other sulfur diimido phosphanyl complexes.[1] Therefore, the tmeda molecule could switch positions and also bind to the lithium cation. The $^{31}P\{^1H\}$ NMR shifts related to this new compound would be very similar to **I**. However, this phenomenon is still under investigation.

A reaction, according to Scheme 2, conducted with $[K\{N(SiMe_3)_2\}]$ yields colourless crystals belonging to the space group *C2/c*. The compound that was synthesized in this reaction is the heterobimetallic lithium/potassium complex **4**, which is isostructural with **3**. The molecular structure of **4** is shown in Figure 4. Unfortunately, the crystals were of too poor a quality to enable the crystal structure to be fully refined, and the final refinement model contained some unaccounted for residual electron density. Although the structural model is reasonable, the bond lengths and angles should be discussed with caution.
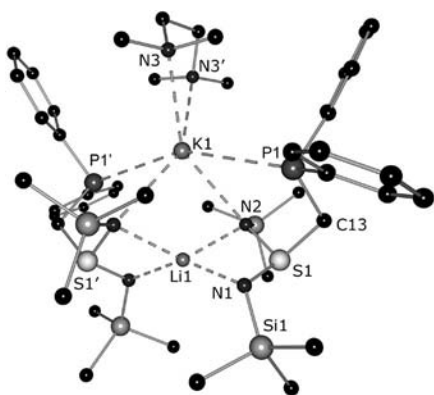

Figure 4. Molecular structure of [(tmeda)K{Ph$_2$PCH$_2$S-(NSiMe$_3$)$_2$}$_2$Li] (**4**), hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: S1–N1 1.602(2), S1–N2 1.604(2), Li1–N1 2.063(4), Li1–N2 2.263(5), K1–N2 2.934(2), K1–P1 3.5613(7), N1–S1–N2 103.62(12), N1–Li1–N2 71.07(9), N2–K1–P1 60.43(5), P1–K1–P1′ 156.23(4).

The Li–N bond lengths are 2.069(4) Å (Li1–N1) and 2.254(4) Å (Li1–N2). Remarkably, the K1–P1 bond length

of 3.5613(7) Å in **4** is almost the same as the Rb1–P1 distance in **3** [3.5996(5) Å]. This is probably due to the fact that the rigid coordination of the lithium cation serves as a structural anchor, and predetermines the position of the phosphorus side arms. The potassium-nitrogen bond lengths have almost the same values [K1–N2: 2.933(2) Å, K1–N3: 2.937(2) Å]. The angles in **4** differ very little from the rubidium derivative. It is striking though that the P1–K1–P1′ angle of 156.23(4)° is almost six degrees wider in **4** than it is in **3**. The lithium atom is disordered with a second potassium cation, which has an occupancy factor of 6%.

There are only a few examples of lithium/potassium heterobimetallic complexes. Several examples with butoxy ligands are supposed to be novel superbases, and there are even Li/Na/K heterotrimetallic compounds[36] and mixed phosphanediide/silanolate heterotrimetallic aggregates containing Li/K/Sr and Li/K/Ba.[37] In 1998, we presented a lithium/potassium heterobimetallic complex based on the {S(N*t*Bu)$_3$}$^{2–}$ ligand.[38] The compound [(thf)$_2$Li$_4$K$_2$(O*t*Bu)$_2$\{(N*t*Bu)$_3$S\}$_2$] was the first example of a complex with a triazasulfite dianion. The metal ions are sandwiched between two {S(N*t*Bu)$_3$}$^{2–}$ caps and have different coordination geometries, obviously the arrangements are very different to those in **3** and **4** because there is no side arm donation in [(thf)$_2$Li$_4$K$_2$(O*t*Bu)$_2$\{(N*t*Bu)$_3$S\}$_2$].

Conclusions

The formation of the above mentioned complexes demonstrates that sulfur diimido phosphanyl ligands are valuable multidentate chelating ligands due to the intramolecular phosphane donor site that is held in close spatial proximity to the functional imido groups.

During the course of our research, it became obvious that the loose coordination of the lithium atom in **I** is essential for various transmetalation reactions. It is an excellent starting material for such reactions because the pendent phosphorus side arm is free to precoordinate with the secondary metal and bring it into close spatial proximity with the two nitrogen chelating claws. Lithium can then leave the complex as a stable tmeda/ligand adduct. Via this route several alkali and alkaline earth metal complexes were synthesized. The ligand is able to adapt to different ionic radii, which makes it a valuable tool in coordination chemistry. With divalent metals, a monomeric soluble complex is formed with two ligands acting as tridentate facial chelates. When monovalent metals are employed, heterobimetallic complexes **3** and **4** are generated, showing the great potential of this class of ligand. In essence, **3** represents the first heterobimetallic lithium/rubidium complex containing nitrogen and phosphorus donor atoms. The coordination mode of phosphorus in such complexes is unprecedented. **1–4** are soluble in polar and apolar organic solvents, which is a great advantage and is due to the periphery groups of the ligand. Complexes of the heavy alkali and alkaline earth metals tend to form large aggregates that are poorly soluble. However, in the cases presented herein this is averted by the ligand.

Experimental Section

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 with appropriate alkali metals, and were distilled and degassed prior to use. [(tmeda)Li{Ph$_2$PCH$_2$S(NSiMe$_3$)$_2$}] (**I**) was synthesized according to literature reports.[1] All NMR spectra were either recorded on a Bruker Avance DPX 300 MHz or Bruker Avance DRX 500 MHz spectrometer with TMS (^{1}H, ^{13}C and ^{29}Si), LiCl (^{7}Li) and H$_3$PO$_4$ (^{31}P) as external references and the protons of the deuterated solvents as internal standards. The spectra were measured at room temperature if not otherwise stated. Elemental analyses (C, H, N and S) were carried out at the Mikroanalytisches Labor, Institut für Anorganische Chemie, Universität Göttingen.

[Ca{Ph$_2$PCH$_2$S(NSiMe$_3$)$_2$}$_2$] (1): To a slurry of [Ca{N(SiMe$_3$)$_2$}$_2$] (0.10 g, 0.29 mmol, 1.0 equiv.) in pentane (25 mL) a solution of **I** (0.30 g, 0.57 mmol, 2.0 equiv.) in pentane (10 mL) was slowly added at –78 °C. After warming to room temp. and stirring overnight, the light yellow suspension was filtered through celite, reduced in volume and stored at 4 °C. Colourless crystals formed after one day; yield (crystals): 0.12 g, 0.14 mmol, 48%. C$_{38}$H$_{60}$CaN$_4$P$_2$S$_2$Si$_4$ (851.40): found C 53.49, H 7.13, N 7.19, S 8.19; calcd. C 53.61, H 7.10, N 6.58, S 7.53. ^{1}H NMR (300.13 MHz, C$_6$D$_6$): δ = 0.19 [s, 36 H, NSi(CH$_3$)$_3$], 3.39 (d, $^2J_{P,H}$ = 5.01 Hz, 4 H, PCH$_2$S), 6.99–7.07 (m, 12 H, o-H, p-H), 7.51–7.57 (m, 8 H, m-H) ppm. ^{13}C{^{1}H} NMR (125.76 MHz, C$_6$D$_6$): δ = 2.39 [NSi(CH$_3$)$_3$], 70.09 (PCH$_2$S), 128.75 (pseudo-t, o-C), 128.00 (p-C), 133.00 (m, $^3J_{P,C}$ = 18.25 Hz, m-C), 137.29 (i-C) ppm. ^{29}Si{^{1}H} NMR (99.36 MHz, C$_6$D$_6$): δ = –3.67 ppm. ^{31}P{^{1}H} NMR (121.49 MHz, C$_6$D$_6$): δ = –39.31 ppm.

[Sr{Ph$_2$PCH$_2$S(NSiMe$_3$)$_2$}$_2$] (2): To a slurry of [Sr{N(SiMe$_3$)$_2$}$_2$] (0.15 g, 0.37 mmol, 1.0 equiv.) in pentane (5 mL) a solution of **I** (0.39 g, 0.73 mmol, 2.0 equiv.) in pentane (10 mL) was slowly added at –78 °C. After warming to room temp. and stirring over-

night, the light yellow suspension was filtered through celite, reduced in volume and stored at 4 °C. Colourless crystals formed after two days; yield (crystals): 0.15 g, 0.17 mmol, 45%. C$_{38}$H$_{60}$SrN$_4$P$_2$S$_2$Si$_4$ (898.94): found C 50.73, H 7.04, N 6.34, S 7.44; calcd. C 50.77, H 6.73, N 6.23, S 7.13. ^{1}H NMR (300.13 MHz, C$_6$D$_6$): δ = 0.21 [s, 36 H, NSi(CH$_3$)$_3$], 3.41 (d, $^2J_{P,H}$ = 5.15 Hz, PCH$_2$S), 6.99–7.05 (m, 12 H, p-H, o-H), 7.47–7.50 (m, 8 H, m-H) ppm. ^{13}C{^{1}H} NMR (125.76 MHz, C$_6$D$_6$): δ = 2.42 [NSi(CH$_3$)$_3$], 70.08 (d, $^1J_{P,C}$ = 5.55 Hz, PCH$_2$S), 128.76 (m, o-C), 128.95 (p-C), 133.66–133.88 (m, m-C), 137.46 (m, i-C) ppm. ^{29}Si{^{1}H} NMR (99.36 MHz, C$_6$D$_6$): δ = –4.53 ppm. ^{31}P{^{1}H} NMR (121.49 MHz, C$_6$D$_6$): δ = –36.07 ppm.

[(tmeda)Rb{Ph$_2$PCH$_2$S(NSiMe$_3$)$_2$}$_2$Li] (3): To a slurry of [Rb{N(SiMe$_3$)$_2$}] (0.14 g, 0.57 mmol, 1.0 equiv.) in pentane (5 mL) a solution of **I** (0.30 g, 0.57 mmol, 1.0 equiv.) in pentane (10 mL) was slowly added at –78 °C. After warming to room temp. and stirring overnight, the light brown suspension was filtered through celite, reduced in volume and stored at 4 °C. Yellow crystals formed after two hours; yield (crystals): 0.26 g, 0.26 mmol, 45%. C$_{44}$H$_{76}$LiN$_6$P$_2$RbS$_2$Si$_4$ (1019.94): found C 51.60, H 7.60, N 8.32, S 6.55; calcd. C 51.81, H 7.51, N 8.24, S 6.55. ^{1}H NMR (300.13 MHz, C$_6$D$_6$): δ = 0.30 [s, 36 H, NSi(CH$_3$)$_3$], 2.08 [s, 12 H, N(CH$_3$)$_2$], 3.43 (s, 4 H, PCH$_2$S), 7.02–7.13 (m, 12 H, o-H, p-H), 7.56 (br. s, 8 H, m-H) ppm; the N(CH$_2$)$_2$N protons were not resolved from the baseline. ^{7}Li{^{1}H} NMR (194.37 MHz, C$_6$D$_6$): δ = 1.81 (br. s) ppm. ^{13}C{^{1}H} NMR (125.76 MHz, C$_6$D$_6$): δ = 3.37 [NSi(CH$_3$)$_3$], 45.85 [N(CH$_3$)$_2$], 57.53 [br, N(CH$_2$)$_2$N], 67.99 (br, PCH$_2$S), 128.29 (o-C), 128.65 (br, p-C), 132.47 (d, $^3J_{P,C}$ = 18.71 Hz, m-C), 133.53 (d, $^1J_{P,C}$ = 18.35 Hz, i-C) ppm. ^{29}Si{^{1}H} NMR (99.36 MHz, C$_6$D$_6$): δ = –5.63 (br. s) ppm. ^{31}P{^{1}H} NMR (202.46 MHz, C$_6$D$_6$): δ = –33.03 (br. s) ppm; beside these signals that are assigned to the product **3**, signals due to the starting material **I** were detected with batch-dependent intensity relationships: ^{1}H NMR (300.13 MHz, C$_6$D$_6$): δ = 0.28 [s, 18 H, Si(CH$_3$)$_3$], 1.77 [br. s, 4 H, N(CH$_2$)$_2$N], 2.07 [s, 12 H, (CH$_3$)$_2$N], 3.47 (br. s, 2 H, SCH$_2$P), 6.99–7.12 (m, 6 H, o-H, p-H), 7.59–7.70 (m, 4 H, m-H)

Table 1. Crystallographic data for **1** to **4**.

	1	2	3	4
Empirical formula	C$_{38}$H$_{60}$CaN$_4$P$_2$S$_2$Si$_4$	C$_{38}$H$_{60}$N$_4$P$_2$S$_2$Si$_4$Sr	C$_{44}$H$_{76}$LiN$_6$P$_2$RbS$_2$Si$_4$	C$_{44}$H$_{76}$K$_{1.06}$Li$_{0.94}$N$_6$P$_2$S$_2$Si$_4$
Formula weight	851.40	898.94	1019.94	975.50
Crystal size [mm]	0.16 × 0.02 × 0.02	0.2 × 0.15 × 0.1	0.2 × 0.15 × 0.1	0.1 × 0.1 × 0.02
Symmetry setting	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	P2$_1$2$_1$2$_1$	P2$_1$2$_1$2$_1$	C2/c	C2/c
a [Å]	10.2753(11)	10.4329(17)	18.0553(17)	18.2492(11)
b [Å]	20.867(2)	20.842(3)	13.6709(13)	13.4012(8)
c [Å]	22.261(2)	22.140(4)	22.639(2)	22.8301(14)
β [°]	90	90	97.149(2)	96.4140(10)
V [Å^3]	4773.1(9)	4814.3(13)	5544.6(9)	5548.4(6)
$\rho_{calcd.}$ [g cm^{-3}]	1.185	1.240	1.222	1.168
Z	4	4	4	4
GoF	1.050	1.053	1.036	1.066
θ range [°]	1.34–26.02	1.34–26.77	1.81–26.02	1.80–25.68
Reflections measured	46417	120179	40145	39141
Independent reflections	9409	10269	5449	5267
μ [mm^{-1}]	0.416	1.402	1.147	0.354
F(000)	1816	1888	2160	2092
R_{int}/R_σ	0.0462/0.0305	0.0262/0.0105	0.0393/0.0245	0.0389/0.0228
Max./min. transmission	0.9422/0.8075	0.9422/0.8426	0.942/0.8952	0.9422/0.8605
Restraints/parameters	0/472	0/472	0/280	10/280
$R1$, $wR2$ (all data)	0.0340, 0.0691	0.0181, 0.0445	0.0361, 0.0641	0.0585, 0.1199
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0291, 0.0668	0.0173, 0.0442	0.0281, 0.0612	0.0495, 0.1146
Flack parameter[44]	0.04(3)	0.066(2)		
Diff. peak/hole [e Å^{-3}]	0.295/–0.193	0.255/–0.142	0.536/–0.241	1.470/–0.691

ppm. ^{7}Li{^{1}H} NMR (194.37 MHz, C$_6$D$_6$): δ = 1.00 ppm. ^{13}C{^{1}H} NMR (125.76 MHz, C$_6$D$_6$): δ = 3.19 [Si(CH_3)$_3$], 45.82 [(CH_3)$_2$N], 56.66 [N(CH_2)$_2$], 70.84 (d, $^1J_{P-C}$ = 23.99 Hz, PCH_2S), 128.46 (d, $^3J_{P-C}$ = 6.02 Hz, m-C), 132.48 (d, $^4J_{P-C}$ = 18.74 Hz, p-C), 133.90 (d, $^2J_{P-C}$ = 19.50 Hz, o-C), 142.04 (d, $^1J_{P-C}$ = 14.98 Hz, i-C) ppm. ^{29}Si{^{1}H} NMR (99.36 MHz, C$_6$D$_6$): δ = –8.29 ppm. ^{31}P{^{1}H} NMR (202.46 MHz, C$_6$D$_6$): δ = –38.78 (br. s, PCH_2S) ppm. The temperature and solvent dependency of the **I/3** ratio has not been studied yet.

[(tmeda)K{Ph$_2$PCH$_2$S(NSiMe$_3$)$_2$}$_2$Li] (4): To a slurry of [K{N(SiMe$_3$)$_2$}] (0.11 g, 0.57 mmol, 1.0 equiv.) in pentane (5 mL) a solution of **I** (0.30 g, 0.57 mmol, 1.0 equiv.) in pentane (10 mL) was slowly added at –78 °C. After warming to room temp. and stirring overnight, the yellow suspension was filtered through celite, reduced in volume and stored at –25 °C. Yellow crystals formed after four days; yield (crystals): 0.16 g, 0.16 mmol, 29%. C$_{44}$H$_{76}$LiN$_6$P$_2$KS$_2$Si$_4$ (973.57), a satisfactory elemental analysis could not be obtained for **4**, which might be due to the potassium present in the sample. ^{1}H NMR (300.13 MHz, C$_6$D$_6$): δ = 0.23 [s, 18 H, NSi(CH_3)$_3$], 0.30 [s, 18 H, NSi(CH_3)$_2$], 2.04 [br. s, 16 H, (CH_3)$_2$N, N(CH_2)$_2$N], 3.40 (br. s, 4 H, PCH_2S), 6.98–7.13 (m, 12 H, o-H, p-H), 7.46–7.68 (m, 8 H, m-H) ppm. ^{7}Li{^{1}H} NMR (116.64 MHz, C$_6$D$_6$): δ = 1.90 (br. s) ppm. ^{31}P{^{1}H} NMR (121.49 MHz, C$_6$D$_6$): δ = –33.99 (br. s) ppm.

Single Crystal Structural Analysis: X-ray data sets were collected at 100(2) K with an INCOATEC Mo microfocus source[39] with mirror-monochromated Mo-K_α radiation (λ = 0.71073 Å) in omega scan mode. The single crystals were mounted, while cooled, in inert oil under argon with a XTEMP-2 device.[40] An absorption correction was applied to the data with SADABS.[41] The structures were solved by direct methods with SHELXS, and they were refined by full-matrix least-squares on F^2, with all data, with SHELXL.[42,43] Non-hydrogen atoms were refined with anisotropic displacement parameters. All H atoms were placed in calculated positions and refined with a riding model. Crystallographic data can be found in Table 1.

CCDC-828833 (for **1**), -828834 (for **2**), -828835 (for **3**) and -828835 (for **4**) 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.

Acknowledgments

[1] M. M. Meinholz, S. K. Pandey, S. M. Deuerlein, D. Stalke, *Dalton Trans.* **2011**, *40*, 1662.

[2] M. M. Meinholz, M. Klemmer, E. Kriemen, D. Stalke, *Chem. Eur. J.* **2011**, *17*, 9415.

[3] a) M. Westerhausen, *Angew. Chem.* **2001**, *113*, 3063; *Angew. Chem. Int. Ed.* **2001**, *40*, 2975; b) J. S. Alexander, K. Ruhlandt-Senge, *Eur. J. Inorg. Chem.* **2002**, 2761; c) M. Westerhausen, M. Gärtner, R. Fischer, J. Langer, L. Yu, M. Reiher, *Chem.*

[4] *Eur. J.* **2007**, *13*, 6292; d) M. Westerhausen, *Coord. Chem. Rev.* **2008**, *252*, 1516.

[4] J. P. Dunne, M. Tacke, C. Selinka, D. Stalke, *Eur. J. Inorg. Chem.* **2003**, 1416.

[5] a) M. Gärtner, H. Görls, M. Westerhausen, *Synthesis* **2007**, 725; b) R. Fischer, M. Gärtner, H. Görls, L. Yu, M. Reiher, M. Westerhausen, *Angew. Chem.* **2007**, *119*, 1642; *Angew. Chem. Int. Ed.* **2007**, *46*, 1618.

[6] a) M. Gärtner, H. Görls, M. Westerhausen, *Inorg. Chem.* **2007**, *46*, 7678; b) M. Gärtner, R. Fischer, J. Langer, H. Görls, D. Walther, M. Westerhausen, *Inorg. Chem.* **2007**, *46*, 5118.

[7] a) M. Westerhausen, C. Gückel, H. Piotrowski, M. Vogt, *Z. Anorg. Allg. Chem.* **2002**, *628*, 735; b) M. Westerhausen, C. Gückel, T. Habereder, M. Vogt, M. Warchhold, H. Nöth, *Organometallics* **2001**, *20*, 893.

[8] a) F. Feil, C. Müller, S. Harder, *J. Organomet. Chem.* **2003**, *683*, 56; b) M. Westerhausen, S. Schneiderbauer, A. N. Kneifel, Y. Söltl, P. Mayer, H. Nöth, Z. Zhong, P. J. Dijkstra, J. Feijen, *Eur. J. Inorg. Chem.* **2003**, 3432; c) S. Harder, S. Müller, E. Hübner, *Organometallics* **2004**, *23*, 178; d) M. H. Chisholm, J. C. Gallucci, K. Phomphrai, *Inorg. Chem.* **2004**, *43*, 6717.

[9] A. Mukherjee, S. Nembenna, T. K. Sen, S. P. Sarish, P. K. Ghorai, H. Ott, D. Stalke, S. K. Mandal, H. W. Roesky, *Angew. Chem.* **2011**, *123*, 4054; *Angew. Chem. Int. Ed.* **2011**, *50*, 3968.

[10] a) M. R. Crimmin, I. J. Casely, M. S. Hill, *J. Am. Chem. Soc.* **2005**, *127*, 2042; b) M. R. Crimmin, A. G. M. Barrett, M. S. Hill, P. B. Hitchcock, P. A. Procopiou, *Organometallics* **2007**, *26*, 2953; c) M. R. Crimmin, A. G. M. Barrett, M. S. Hill, P. B. Hitchcock, P. A. Procopiou, *Organometallics* **2008**, *27*, 497.

[11] F. Buch, J. Brettar, S. Harder, *Angew. Chem.* **2006**, *118*, 2807; *Angew. Chem. Int. Ed.* **2006**, *45*, 2741.

[12] W. E. Lindsell, F. C. Robertson, I. Souter, *Eur. Polym. J.* **1983**, *19*, 115.

[13] a) L. Lochmann, J. Pospíšil, D. Lim, *Tetrahedron Lett.* **1966**, *7*, 257; b) M. J. Schlosser, *J. Organomet. Chem.* **1967**, *8*, 9.

[14] a) Y. Kondo, M. Shilai, M. Uchiyama, T. Sakamoto, *J. Am. Chem. Soc.* **1999**, *121*, 3539; b) T. Imahori, M. Uchiyama, T. Sakamoto, Y. Kondo, *Chem. Commun.* **2001**, *23*, 2450; c) S. Merkel, D. Stern, J. Henn, D. Stalke, *Angew. Chem.* **2009**, *121*, 6468; *Angew. Chem. Int. Ed.* **2009**, *48*, 6350.

[15] A. Krasovskiy, P. Knochel, *Angew. Chem.* **2004**, *116*, 3396; *Angew. Chem. Int. Ed.* **2004**, *43*, 3333.

[16] a) P. C. Andrikopoulos, D. R. Armstrong, D. V. Graham, E. Hevia, A. R. Kennedy, R. E. Mulvey, C. T. O'Hara, C. Talmard, *Angew. Chem.* **2005**, *117*, 3525; *Angew. Chem. Int. Ed.* **2005**, *44*, 3459; b) R. E. Mulvey, *Acc. Chem. Res.* **2009**, *42*, 743.

[17] S. Freitag, W. Kolodziejski, F. Pauer, D. Stalke, *J. Chem. Soc., Dalton Trans.* **1993**, 3479.

[18] R. Fleischer, D. Stalke, *Organometallics* **1998**, *17*, 832.

[19] D. Hänssgen, R. Steffens, *Z. Anorg. Allg. Chem.* **1983**, *507*, 178.

[20] a) S. Blair, K. Izod, W. Clegg, *Inorg. Chem.* **2002**, *41*, 3886; b) P. W. Roesky, *Inorg. Chem.* **2006**, *45*, 798; c) S. Datta, M. T. Gamer, P. W. Roesky, *Dalton Trans.* **2008**, 2839.

[21] a) H. H. Karsch, M. Reisky, *Eur. J. Inorg. Chem.* **1998**, 905; b) V. Knapp, G. Müller, *Angew. Chem.* **2001**, *113*, 187; *Angew. Chem. Int. Ed.* **2001**, *40*, 183; c) T. K. Panda, M. T. Gamer, P. W. Roesky, *Inorg. Chim. Acta* **2006**, *359*, 4765; d) J. Langer, K. Wimmer, H. Görls, M. Westerhausen, *Dalton Trans.* **2009**, 2951.

[22] a) D. Leusser, J. Henn, N. Kocher, B. Engels, D. Stalke, *J. Am. Chem. Soc.* **2004**, *126*, 1781; b) J. Henn, D. Leusser, D. Ilge, D. Stalke, B. Engels, *J. Phys. Chem. A* **2004**, *108*, 9442.

[23] a) M. Kaupp, P. v. R. Schleyer, H. Stoll, H. Preuss, *J. Chem. Phys.* **1991**, *94*, 1360; b) M. Kaupp, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1992**, *114*, 491.

[24] C. Eaborn, S. A. Hawkes, P. B. Hitchcock, J. D. Smith, *Chem. Commun.* **1997**, 1961.

[25] R. Fleischer, D. Stalke, *Inorg. Chem.* **1997**, *36*, 2413.

[26] G. Mösges, F. Hampel, M. Kaupp, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1992**, *114*, 10880.

[27] P. W. Roesky, *Inorg. Chem.* **2006**, *45*, 798.

[28] R. D. Shannon, *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

[29] a) R. G. Pearson, *J. Am. Chem. Soc.* **1963**, *85*, 3553; b) R. G. Parr, R. G. Pearson, *J. Am. Chem. Soc.* **1983**, *105*, 7512; c) R. G. Pearson, *J. Am. Chem. Soc.* **1985**, *107*, 6801.

[30] T. P. Hanusa, *Chem. Rev.* **1993**, *93*, 1023.

[31] U. Englich, K. Hassler, K. Ruhlandt-Senge, F. Uhlig, *Inorg. Chem.* **1998**, *37*, 3532.

[32] G. W. Rabe, S. Kheradmandan, L. M. Liable-Sands, I. A. Guzei, A. L. Rheingold, *Angew. Chem.* **1998**, *110*, 1495; *Angew. Chem. Int. Ed.* **1998**, *37*, 1404.

[33] K. Izod, W. Clegg, S. T. Liddle, *Organometallics* **2001**, *20*, 367.

[34] W. Clegg, A. M. Drummond, R. E. Mulvey, S. T. Liddle, *Chem. Commun.* **1998**, 2391.

[35] D. R. Armstrong, W. Clegg, A. M. Drummond, S. T. Liddle, R. E. Mulvey, *J. Am. Chem. Soc.* **2000**, *122*, 11117.

[36] a) F. M. Mackenzie, R. E. Mulvey, *J. Am. Chem. Soc.* **1996**, *118*, 4721; b) X. Wei, Q. Dong, H. Tong, J. Chao, D. Liu, M. F. Lappert, *Angew. Chem.* **2008**, *120*, 4040; *Angew. Chem. Int. Ed.* **2008**, *47*, 3976; c) R. E. Mulvey, *Chem. Soc. Rev.* **1998**, *27*, 339.

[37] M. Westerhausen, S. Weinrich, G. Kramer, H. Piotrowski, *Inorg. Chem.* **2002**, *41*, 7072.

[38] D. Ilge, D. S. Wright, D. Stalke, *Chem. Eur. J.* **1998**, *4*, 2275.

[39] T. Schulz, K. Meindl, D. Leusser, D. Stern, J. Graf, C. Michaelsen, M. Ruf, G. M. Sheldrick, D. Stalke, *J. Appl. Crystallogr.* **2009**, *42*, 885.

[40] a) D. Stalke, *Chem. Soc. Rev.* **1998**, *27*, 171; b) T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615.

[41] a) G. M. Sheldrick, *SADABS 2008/1*, University of Göttingen, Germany, **2008**; b) G. M. Sheldrick, *SADABS 2008/2*, University of Göttingen, Germany, **2008**.

[42] P. Müller, R. Herbst-Irmer, A. L. Spek, T. R. Schneider, M. R. Sawaya, in: *Crystal Structure Refinement - A Crystallographer's Guide to SHELXL*, in: *IUCr Texts on Crystallography*, vol. 8 (Ed.: P. Müller), Oxford University Press, Oxford, U.K., **2006**.

[43] a) G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112; b) G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

[44] H. D. Flack, *Acta Crystallogr., Sect. A* **1983**, *39*, 876.