Synthesis and Characterization of a Sulfonyl- and Iminophosphoryl-Functionalized Methanide and Methandiide

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Abstract: The synthesis of $[H_2C(PPh_2=NSiMe_3)(SO_2Ph)]$ (**1**) and its mono- and dimetalation are reported. Due to the strong anion-stabilizing abilities of the iminophosphoryl and the sulfonyl group monometalation to **1-K** and dimetalation to **1-Li$_2$** proceed smoothly with potassium hydride and methyllithium, respectively. Both compounds could be isolated in high yields and were characterized by NMR spectroscopy as well as XRD analysis. The methanide **1-K** forms a coordination polymer in the solid state, while in case of the methandiide a tetrameric structure is observed. The latter features an unusual structural motif consisting of two $(SO_2Li)_2$ eight-membered rings, which are connected with each other via the methandiide carbon atoms and additional lithium atoms. With increasing metalation a contraction of the P–C–S linkage is observed, which is well in line with the increased charge at the central carbon atom and involved electrostatic interactions.

Keywords: methandiides; lithium; potassium; molecular structures

1. Background

In the past 20 years, methandiides with a doubly metalated carbon atom (R_2CM_2 with M mostly being Li) have attracted intense research interest in organometallic chemistry. This is mainly due to their applicability as ligands for the preparation of carbene-type complexes by simple salt metathesis reactions [1–3]. Thereby, methandiides revealed to be highly efficient ligand systems stabilizing a variety of carbene complexes with main group metals [4–7], early and late transition metals [8–12] as well as lanthanides and actinides [13–16]. The first dilithium compound, which was employed in this chemistry, was the bis(iminophosphorano) system $\{Li_2(bipm^{TMS})\}_2$ (**A**, $bipm^{TMS}=C(PPh_2NSiMe_3)_2$), which was simultaneously reported by the groups of Cavell and Stephan in 1999 (Figure 1) [17,18]. Unlike all other methandiides reported before [19–21], **A** was found to be conveniently accessible by double deprotonation and isolable in high yields, thus allowing its application in carbene complex synthesis [22]. The high stability and facile synthesis of **A** can be explained by the strong anion-stabilizing ability of the P(V) moieties as well as the additional nitrogen donor side-arms, which efficiently coordinate lithium to form stable complexes. Analogously, the corresponding thiophosphoryl system **B** reported by Le Floch also proved to be a stable and powerful ligand system [23–25]. More recently, our group has focused on non-DPPM derived methandiides, to expand the carbene chemistry of these compounds also to ligands with other substituents. The dilithium compound **C** with a sulfonyl functionality turned out to be easily accessible and similarly stable than the bis(phosphonium)-substituted systems [26]. The weaker coordination ability of the sulfonyl group also gave way to the formation of transition-metal complexes with open coordination-sides [27–29].
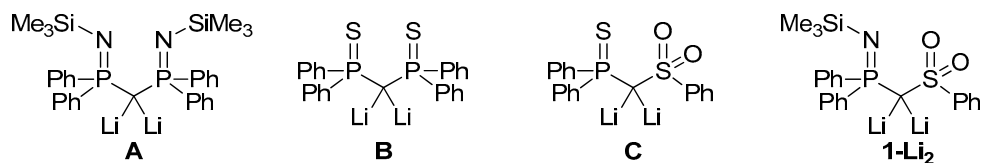
Figure 1. Isolated dilithiomethanes used as ligands for carbene complex formation.

Besides their applicability in carbene complex chemistry, methandiides are also interesting reagents because of their structural properties. Analogous to simple organolithium reagents [30–32], structure formation is dominated by the presence or absence of additional donor functions within the molecule. Non-functionalized methandiides typically form polymeric structures to complete the coordination sphere of lithium, such as in the case of parent dilithiomethane, H_2CLi_2 [33], or dilithiated fluorene **D** (Figure 2) [20]. In contrast, donor side-arms lead to the formation of defined cluster structures [19]. For instance, the DPPM-based systems **A** and **B** and derivatives thereof typically form dimeric structures with a central structural motif consisting of a Li_4 and Li_2C_2 four-membered ring perpendicular to each other [17,18,34–38]. This motif is also present in the structures of the heavier alkali metal derivatives [39,40]. An interesting monomeric structure was isolated by the introduction of the sterically demanding Dipp substitutents (Dipp = 2,6-Di(iso-propyl)phenyl) into the bipm framework together with TMEDA as additional Lewis base [41]. Most interestingly, this compound showed in contrast to the van't Hoff rule a planar rather than a tetrahedral geometry at the metalated carbon atom. Such a planar carbon environment was already predicted by Schleyer and coworkers on the basis of theoretical studies [42]. The unsymmetrical methandiide **C** was found to form a complex molecular structure, which however also showed a strong deviation from the ideal tetrahedral geometry of carbon [26].
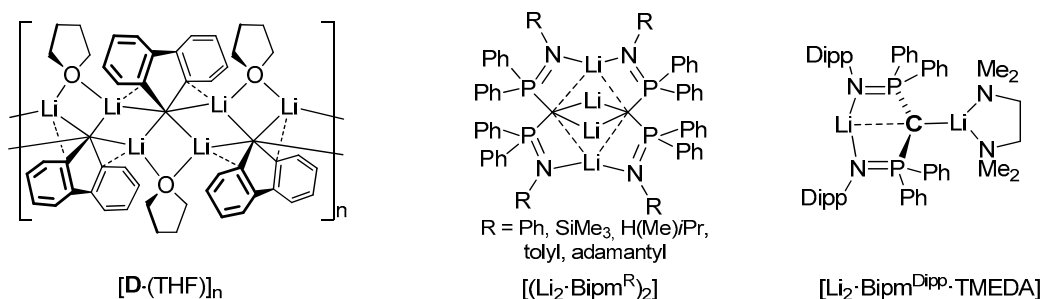

**Figure 2.** Structures of dilithium methandiides.

Overall, small changes in the structure of methandiides can easily lead to big differences in their reactivity and the structure formation in the solid state. For example, replacement of the sulfonyl group in **C** by a sulfoximine moiety lead to an increased reactivity and decreased stability of the methandiide as well as the formation of a different structure in the solid state, which hampered its utilization as ligand in transition-metal chemistry [43]. However, due to the efficiency of methandiide **C** as ligand in carbene complexes, we became interested in the preparation of the iminophosphoryl derivative **1-Li₂** (Figure 1). Besides its syntheses we particularly addressed the elucidation of the molecular structures of the mono- and dimetallated compounds in comparison to the thiophosphoryl system.

2. Results

2.1. Synthesis of the Protonated Precursor **1**

In order to examine the influence of the electronic and steric properties of the iminophosphoryl group on the accessibility, reactivity and structure of methandiide **1-Li₂** we chose the protonated

precursor **1** with a sterically demanding trimethylsilyl (TMS) group at the imino nitrogen atom, since this group has most often been used in other methandiide systems. To this end, the synthetic strategy outlined in Figure 3 was used. At first, phenyl methyl sulfone was deprotonated with *n*-butyl lithium and reacted with chlorodiphenylphosphine, followed by a subsequent oxidation of the phosphine moiety with H_2O_2 [27]. Recrystallization from ethanol afforded phosphine oxide **2** as a colourless solid in 87% yield. Next, phosphine oxide **2** was treated with oxalyl bromide in DCM. After filtration, phosphine bromide **3** could be isolated as a colourless to slightly yellow solid in 91% yield [44]. Compound **3** shows a single signal in the $^{31}P\{^1H\}$ NMR spectrum at 18.7 ppm in deuterated DMSO and a characteristic doublet at 5.10 ppm with a coupling constant of $^2J_{PH} = 9.95$ Hz in the ^1H NMR spectrum. The formation of the iminophosphoryl moiety was achieved by treatment of phosphine bromide **3** with hexamethyldisilazane (HMDS) and subsequent deprotonation with NEt_3 [45]. Recrystallization from toluene/hexane yielded the α-iminophosphoryl-substituted sulfone **1** as colourless crystals in 88% yield. The $^{31}P\{^1H\}$ NMR spectrum exhibits a single signal at −12.7 ppm and the hydrogen atoms of the methylene bridge resonate as a doublet at 3.94 ppm with a coupling constant of $^2J_{PH} = 9.79$ Hz. The crystal structure of iminophosphoryl **1** is depicted in Figure 3. **1** crystallizes in the triclinic space group *P*-1 and shows typical bond lengths and angles compared to those in related compounds. Sole exception is the P1–N1–Si1 angle with an high value of 160.4(9)° [46–49]. In comparison, the symmetric bis(iminophosphoryl)methane, $(Me_3SiNPPh_2)_2CH_2$, featured an angle of 138.5(1)°.
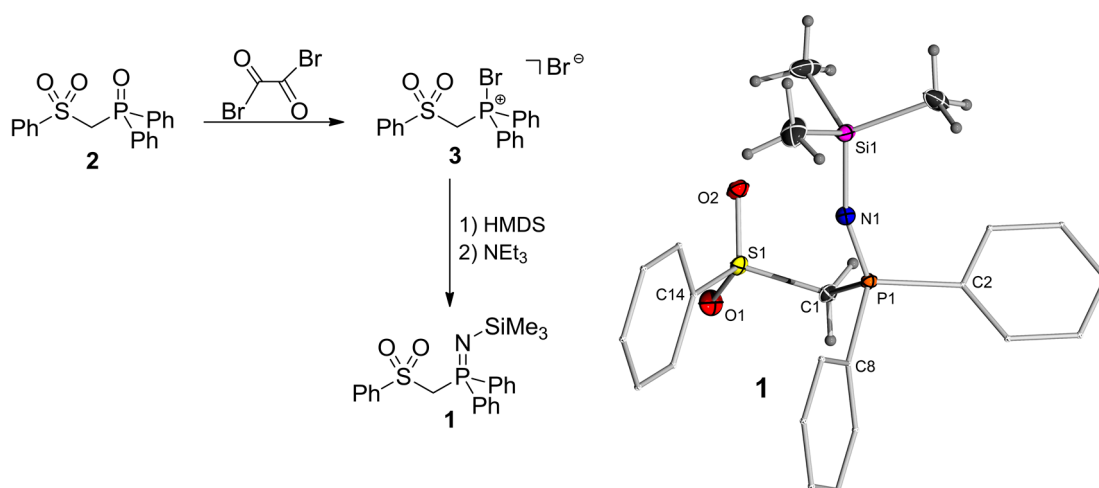
Figure 3. Synthesis of the α-iminophosphoryl-substituted sulfone **1** and molecular structure of **1**. Ellipsoids drawn at the 50% probability level. Hydrogen atoms (except for those at C1) omitted for clarity. Selected bond lengths (Å) and angles (°): C1–S1 1781(2), C1–P1 1844(2), S1–O1 1446(1), S1–O2 1.439(1), P1–N1 1.523(1), N1–Si1 1.681(1), S1–C14 1.763(2), P1–C2 1.819(2), P1–C8 1.816(2), S1–C1–P1 117.2(1), P1–N1–Si1 160.3(1).

2.2. Preparation of Methanide **1-K** and Methandiide **1-Li₂**

To evaluate the effects of the sulfonyl and the iminophosphoryl group on the deprotonation behavior of compound **1** we next aimed at the synthesis of the corresponding mono- and dimetallated species (Figure 4). Single deprotonation was selectively achieved with a series of different metal bases, as evidenced by a single new signal in the $^{31}P\{^1H\}$ NMR spectrum at −1.18 ppm and the signal of the methanide hydrogen at 2.38 ppm with a coupling constant of $^2J_{PH} = 10.8$ Hz in the ^1H NMR spectrum. Convenient isolation of the methanide could be achieved by employment of KH, which allowed the isolation of **1-K** as a colourless solid in 89% yield. **1-K** is stable over weeks under inert gas atmosphere and exhibits—despite the TMS functionalization—a remarkably low solubility in common organic solvents. Thus all NMR studies had to be performed in deuterated DMSO. Crystals suitable for X-ray

diffraction analysis could be obtained by diffusion of pentane into a saturated solution of compound **1-K** in THF.
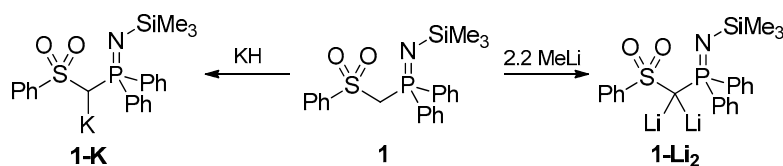

Figure 4. Synthesis of **1-K** and **1-Li$_2$**.

1-K crystallizes as a coordination polymer in the triclinic space group *P*-1. This observation is well in line with the poor solubility of monoanion **1-K**. The asymmetric unit contains a dimeric structural motif with one non-coordinating THF molecule (not shown in Figure 5). The two monomeric subunits of this *pseudo* C_2-symmetric dimer ($K_1 - K_2 = C_2$ axis) are connected via two potassium atoms. Both show a slightly different coordination environment: While potassium atom K1 is coordinated by the nitrogen atoms of both iminophosphoryl substituents, the oxygen and the phenyl group of the sulfonyl moieties and two protons of a TMS-group, potassium atom K2 is solely coordinated by the oxygens of the sulfonyl moieties and the iminophosphoryl phenyl rings. Completion of the coordination sphere of K2 is finally achieved through coordination of the sulfonyl groups of two adjacent dimers, thus leading to the polymeric structure in the solid state. The potassium atoms show no contacts to the carbon atoms of the methylene groups which leads to a planar geometry with sums of angles of 359(4)° and 360(6)° with slightly widened P–C–S angles of 120.09(18)° and 123.05(18)°, respectively, compared to the neutral compound **1** (from 117.17(8)). The most important feature of the molecular structure of **1-K** is the shortening of the C–P bonds (from 1.8441(15) Å to 1.727(3) Å) and the C–S bond lengths (from 1.7808(16) Å to 1.638(3) Å) in the P–C–S backbone compared to the protonated precursor **1**. This can be explained with electrostatic interactions between the negativ charge at the methylene carbon and the positive charges at the phosphorous and the sulfur. At the same time, an elongation of the P–N bond from 1.5229(13) Å to 1.569(2) Å and 1.562(2) Å, respectively, can be observed which is due to negative hyperconjugation of the lone pair of the methanide carbon into the antibonding σ* orbitals of the P–N bonds.

The preparation of the dianionic species **1-Li$_2$** was achieved by reaction with a slight excess of MeLi in Et$_2$O. Addition of MeLi to a suspension of **1** in Et$_2$O led to a complete solvation followed by the formation of a colourless solid after a few minutes. Removal of the supernatant solution and drying of the obtained solid in vacuo gave dianionic species **1-Li$_2$** in 78% yield. The ^{31}P{^{1}H} NMR spectrum shows a single signal at 7.63 ppm. The ^{1}H NMR spectrum confirms the successful double deprotonation through the absence of the protons of the methylene bridge and shows additional coordinating diethyl ether. The ^{7}Li NMR spectrum shows two signals at 0.19 and 1.67 ppm thus indicating the formation of an unsymmetrical structure with different coordination spheres of the two lithium atoms. This assumption is further supported by the presence of two separate sets of signals for the two phosphorous bound phenyl rings speaking for a diastereotopic behavior. X-ray quality crystals could be obtained by performing the reaction without stirring in a larger volume of solvent leading to the direct crystallization of the product. The crystal structure of methandiide **1-Li$_2$** is shown in Figure 6.
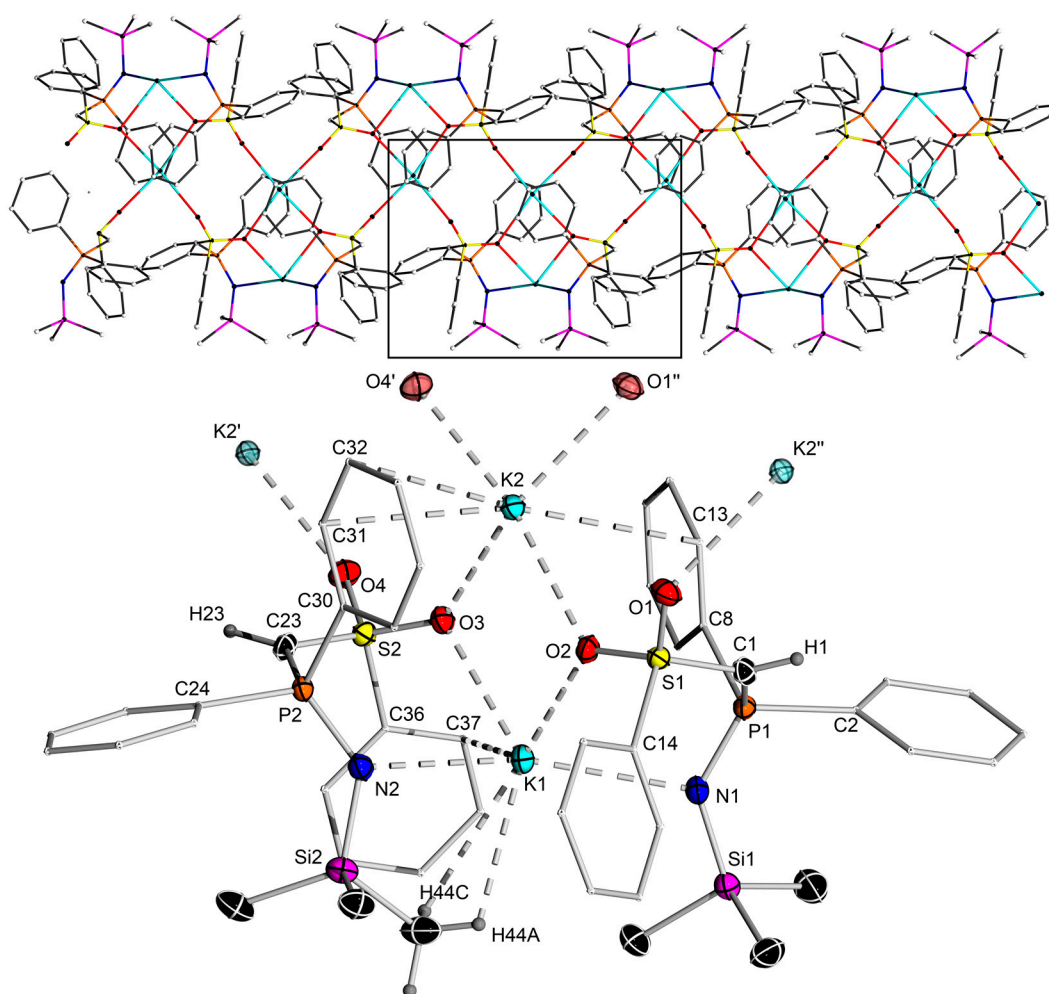
Figure 5. Polymeric structure of monometalated system **1-K** (**top**); and highlighted asymmetric unit (**bottom**). Ellipsoids drawn at the 50% probability level. Hydrogen atoms (except for the methylene bridge) and solvent molecule omitted for clarity. Connecting atoms of neighboring asymmetric units shown for clarity. Selected bond lengths (Å) and angles (°): C1–P1 1728(3), C1–S1 1.637(3), P1–N1 1.569(2), P1–C2 1.820(3), P1–C8 1.823(3), N1–Si2 1.691(2), S1–O1 1.446(2), S1–O2 1.4602(19), S1–C14 1.787(3), C23–P2 1.726(3), C23–S2 1.639(3), P2–C24 1.813(3), P2–C30 1.820(3), P2–N2 1.562(2), N2–Si2 1.683(2), S2–O3 1.462(2), S2–O4 1.444(2), S2–C36 1.790(3), K1–N1 2.843(2), K1–N2 2.817(2), K1–O2 2.611(2), K1–O3 2.704(2), K1–C37 3.262(3), K1–H44A 2.84(3), K1–H44C 2.94(4), K2–O2 2.6907(19), K2–O3 2.711(2), K2–C13 3.354(3), K2–C31 3.223.(3), K2–C32 3.321(3), K2–O1″ 2.703(2), K2–O4′ 2.593(2), P1–C1–S1 123.05(18), P1–N1–Si1 134.44(15), P1–C1–H1 120(2), H1–C1–S1, 116(2), P2–C23–S2 120.09(18), P2–N2–Si2 133.31(15), P2–C23–H23 119(3), H23–C23–S2 121(3).
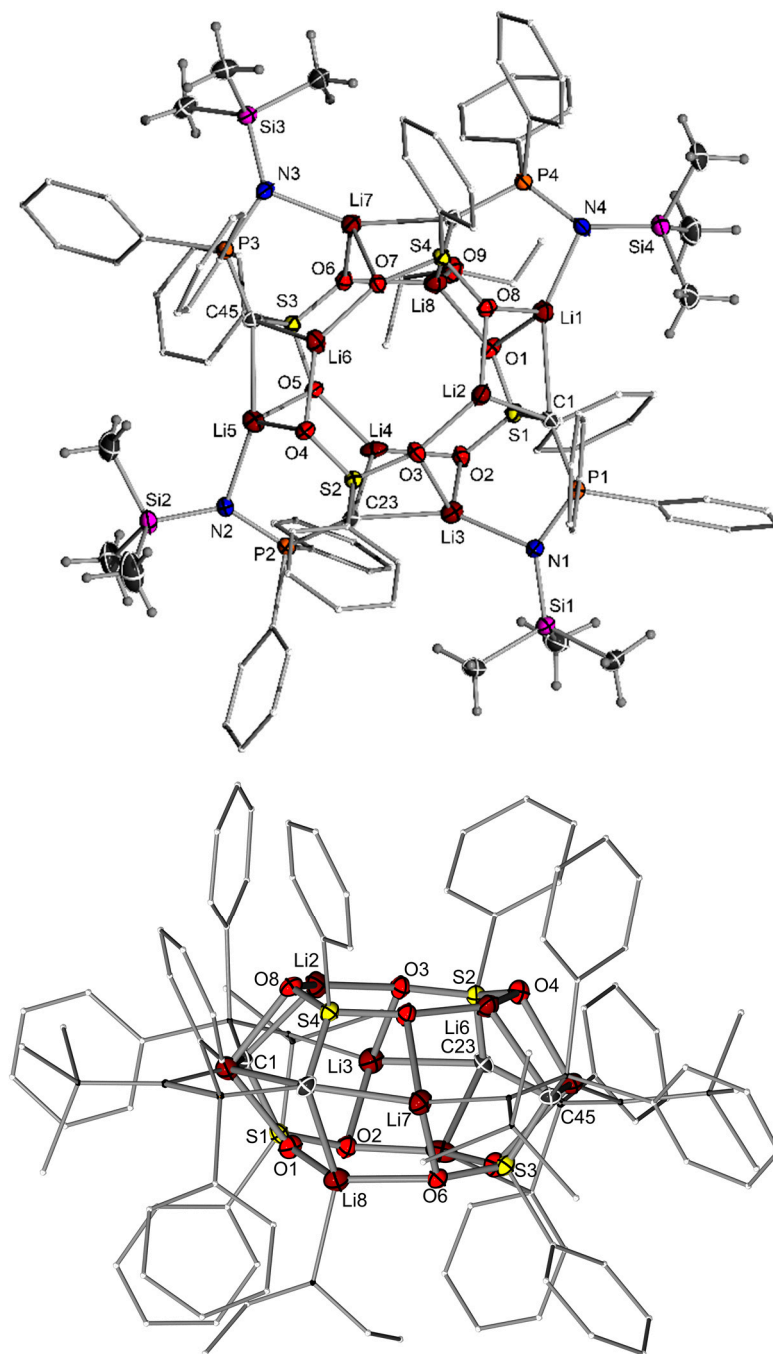
Figure 6. Displays of the crystal structure of methandiide **1-Li₂**. Ellipsoids drawn at the 50% probability level. Non-coordinating diethyl ether molecules and hydrogen atoms omitted for clarity. For bond lengths and angles, see Figure 7.

Methandiide **1-Li₂** crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit consists of a *pseudo*-tetrameric complex, whose S4 symmetry however is broken due to the coordination of only one additional diethyl ether molecule (to Li8). The central structural motif is formed by two almost planar $(SO_2Li)_2$ eight-membered rings, which are connected with each other via the methandiide carbon atoms and additional four lithium atoms. The four lithium atoms of the $(SO_2Li)_2$ rings are solely coordinated by the sulfonyl moieties and the methanide carbon atoms. These lithium atoms are only three-fold coordinated, except for Li8, which is also coordinated by the ether molecule. The other four lithium atoms (Li1, Li3, Li5 and Li7) are coordinated by the sulfonyl oxygen atoms, the methanide

atom and the nitrogen atom of the iminophosphoryl group, thus having a coordination number of four. Overall, this complexation formally leads to two different types of lithium atoms bound to each methandiide carbon atom, which is well in line with the two signals observed in the ^{7}Li NMR spectrum. A detailed view of a monomeric subunit can be seen in Figure 7.
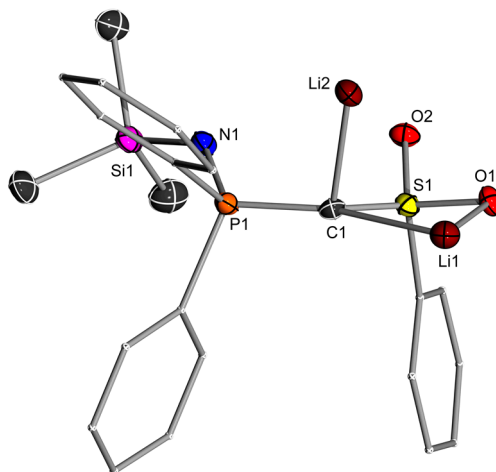
Figure 7. Monomeric subunit of methandiide **1-Li$_2$**. Ellipsoids drawn at the 50% probability level. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): C1–S1 1.601(3), C1–P1 1.714(3), C1–Li1 2.337(6), C1–Li2 2.200(6), S1–O1 1.490(2), S1–O2 1.499(2) S1–C14 1.788(3), P1–N1 1.583(3), P1–C2 1.831(3), P1–C8 1.827(3), N1–Si1 1.700(3), O1–Li1 2.050(6), O1–Li8 1.898(6), O2–Li4 1.885(6), Li2–O8 1.889(6), Li2–O3 1.862(6), S1–C1–P1 121.98(19), P1–N1–Si1 137.57(17).

The Li–C bond lengths with an average value of 2.235(6) Å are in the expected range compared to known methandiides featuring sulfonyl or iminophosphoryl groups [3,17,26]. The Li–N contacts are (with an average bond length of 2.006 Å) a bit shorter than those found in other iminophosphoryl stabilized geminal dianions, while the Li–O bonds (with an average length of 1.973(6) Å) are well in line with reported data [3,17]. The central P–C–S backbone shows an even stronger contraction than in the monoanionic species **1-K**, with an average P–C bond length of 1.714(3) Å and an average S–C bond length of 1.608(3) Å speaking for even stronger electrostatic interactions (for a comparison of all bond length, see Table 1). The same strengthening can be observed for the negative hyperconjugation effects, which lead to even further elongated bond lengths for the P–N and especially S–O bonds with average values of 1.586(3) Å and 1.494(2) Å respectively. These observations are consistent with those reported for other mono- and dimetallated systems [14–20]. For example, the bond length changes in **1-Li$_2$** are similar to those found in the corresponding thiophosphoryl compound **C** (Table 1), despite of the different structures formed in the solid state [26].

Table 1. Comparison of structural parameters (average values for S–O bonds, **1-K** and **1-Li$_2$**).

Bond	1	1-K	1-Li$_2$	C
C–S (Å)	1.7807(16)	1.638(3)	1.608(3)	1.613(3)
C–P (Å)	1.8441(15)	1.727(3)	1.714(3)	1.710(3)
P–N (Å)	1.5229(13)	1.566(2)	1.586(3)	-
S–O (Å)	1.4427(11)	1.453(2)	1.494(2)	1.501(2)

Another interesting feature of the crystal structure of **1-Li$_2$** concerns the coordination environments of the methandiide carbon atoms which strongly deviate from an ideal tetrahedron. As shown in Figure 7, C(1), S(1), P(1) and Li(1) are almost in one plane, while Li(2) is coordinating almost orthogonally to that plane with an Li–C–Li angle of 72.9(2)°. This has also been observed in the

crystal structure of methandiide **C**. On the basis of theoretical methods [26] this coordination mode can be explained by the two methandiide lone pairs populating two different orbitals, one of sp^2- and the other of p-symmetry.

3. Experimental Section

3.1. General Procedures

All experiments were carried out under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Solvents were dried over sodium or potassium (or over P_4O_{10}, CH_2Cl_2) and distilled prior to use. H_2O is distilled water. Organolithium reagents were titrated against diphenylacetic acid prior use. ^1H, ^7Li, ^{13}C, ^{31}P NMR spectra were recorded on Avance-500, Avance-400 or Avance-300 spectrometers (Bruker Biospin GmbH, Rheinstetten, Germany) at 22 °C if not stated otherwise. All values of the chemical shift are in ppm regarding the δ-scale. All spin-spin coupling constants (J) are printed in Hertz (Hz). To display multiplicities and signal forms correctly the following abbreviations were used: s = singulet, d = doublet, t = triplet, m = multiplet, br = broad signal. Signal assignment was supported by DEPT and HMQC experiments. Elemental analyses were performed on an Elementar vario MICRO-cube elemental analyzer. All reagents were purchased from Sigma-Aldrich (Munich, Germany), ABCR (Karlsruhe, Germany)) or Acros Organics/Fisher Scientific GmbH (Nidderau, Germany) and used without further purification. Phosphine oxide **2** was, synthesized according to literature procedure [27].

3.2. Syntheses

Synthesis of Bromide 3. Compound **3** was prepared in analogues fashion to literature procedure [44]. Phosphine oxide **2** (5.00 g, 14.0 mmol) was dissolved in 40 mL DCM. Oxalyl bromide (6.06 g, 28.0 mmol) was slowly added via syringe and the resulting suspension stirred at room temperature over night until no further gas evolution could be observed. The reaction mixture was filtrated and the resulting solid washed three times with DCM (10 mL) giving phosphine bromide **3** as an off white solid (6.39 g, 12.7 mmol, 91%). **^{1}H NMR**: (400.1 MHz, d_6-DMSO): δ = 5.11 (d, $^2J_{HP}$ = 9.91 Hz, 2H; SCH_2P), 7.46–7.56 (m, 8H; C$H_{Ph,meta,para}$), 7.64–7.68 (m, 1H; C$H_{Ph,meta,para}$), 7.77–7.88 (m, 6H; C$H_{Ph,ortho}$). **^{13}C{^{1}H} NMR**: (75.5 MHz, d_6-DMSO): δ = 54.6 (d, $^1J_{CP}$ = 57.4 Hz; SCP), 127.8 (C$H_{SPh,meta}$), 128.4 (d, $^3J_{CP}$ = 12.3 Hz; C$H_{PPh,meta}$), 128.8 (C$H_{SPH,ortho}$), 130.6 (d, $^2J_{CP}$ = 9.93 Hz; C$H_{PPh,ortho}$), 131.9 (d, $^4J_{CP}$ = 2.54 Hz; C$H_{PPh,para}$), 132.62 (d, $^1J_{CP}$ = 104.66 Hz; $C_{PPh,ipso}$), 133.6 (C$H_{SPh,para}$), 141.1 ($C_{SPh,ipso}$). **^{31}P{^{1}H} NMR**: (162.0 MHz, d_6-DMSO): δ = 18.7. See also Figures S1 and S2 in the Supplementary Materials.

Synthesis of Compound 1. Compound **1** was prepared in analogues fashion to literature procedure [45]. 6.73 g (13.4 mmol) of Bromide **3** were suspended in 40 mL MeCN and cooled to −40 °C. 2.89 g (17.9 mmol) HMDS were added under light exclusion and the reaction mixture slowly warmed to room temperature and stirred overnight. The solvent was removed in vacuo and the residue suspended in 30 mL toluene. 2.72 g (26.9 mmol) Triethylamine were added and the reaction mixture stirred overnight. The solution was filtered and the solvent removed under reduced pressure. Recrystallization of the crude product in toluene/hexane (1:2) gave way to the product as a white crystalline solid (5.5 g, 11.7 mmol, 88%). **^{1}H NMR:** (300.2 MHz, C_6D_6): δ = 0.31 (d, $^4J_{HP}$ = 0.48 Hz, 9H; Si(CH_3)$_3$), 3.94 (d, $^2J_{HP}$ = 9.79 Hz, 2H; SCH_2P), 6.80–7.05 (m, 9H; C$H_{SPh,meta,para}$/C$H_{PPh,meta,para}$), 7.46–7.53 (m, 4H; C$H_{PPh,ortho}$), 7.75–7.78 (m, 2H; C$H_{,SPh,ortho}$). **^{13}C{^{1}H} NMR:** (75.5 MHz, C_6D_6): δ = 4.13 (d, $^4J_{CP}$ = 3.38 Hz; Si(CH_3)$_3$), 58.9 (d, $^1J_{CP}$ = 57.8 Hz; SCH_2P), 128.35 (C$H_{SPh,para}$), 128.5 (C$H_{SPh,meta}$), 128.7 (d, $^3J_{CP}$ = 8.73 Hz; C$H_{PPh,meta}$), 131.3 (d, $^4J_{CP}$ = 2.96 Hz; C$H_{PPh,para}$), 131.5 (d, $^2J_{CP}$ = 10.6 Hz; C$H_{PPh,ortho}$), 133.1 (C$H_{SPh,ortho}$), 134.6 (d, $^1J_{CP}$ = 104.4 Hz; $C_{PPh,ipso}$), 142.1 ($C_{SPh,ipso}$). **^{31}P{^{1}H} NMR:** (121.5 MHz, C_6D_6): δ = −12.7. Anal. Calc. for $C_{19}H_{17}Br_2O2PS$: C, 61.80; H, 6.13; N, 3.28. Found: C, 62.06; H, 6.10; N, 3.20. See also Figures S3–S5 in the Supplementary Materials.

Synthesis of 1-K. 1.00 g (2.35 mmol) iminophosphorane **1** and 94.0 mg KH were suspended in 20 mL Et_2O and the reaction mixture stirred at room temperature until no further gas formation could be observed. The resulting suspension was filtrated and removal of the solvent gave Monoanion **1-K** as a colourless solid (974 mg, 2.09 mmol, 89%). **^{1}H NMR:** (300.2 MHz, d_6-DMSO): δ = −0.19 (9H; Si(CH_3)$_3$), 2.38 (d, $^2J_{HP}$ = 10.8 Hz, 1H; SC*H*KP), 7.17–7.25 (m, 9H; C$H_{Ph,meta,para}$), 7.63–7.74 (m, 6H; C$H_{Ph,ortho}$). **^{13}C{^{1}H} NMR:** (75.5 MHz, d_6-DMSO): δ = 4.86 (d, $^3J_{CP}$ = 3.40 Hz; Si(CH_3)$_3$), 46.3 (d, $^1J_{CP}$ = 127.1 Hz), 124.8 (C$H_{SPh,meta}$), 126.7 (d, $^3J_{CP}$ = 11.5 Hz; C$H_{PPh,meta}$), 127.2 (C$H_{SPh,ortho}$), 127.6 (C$H_{SPh,para}$), 128.2 (d, $^4J_{CP}$ = 1.69 Hz; C$H_{PPh,para}$), 131.3 (d, $^2J_{CP}$ = 9.86 Hz; C$H_{PPh,ortho}$), 142.4 (d, $^1J_{CP}$ = 105.6 Hz; $C_{PPh,ipso}$) 153.5 ($C_{SPh,ipso}$). **^{31}P{^{1}H} NMR:** (121.5 MHz, d_6-DMSO): δ = −1.18. Anal. Calcd. for $C_{22}H_{25}KNO_2PSSi$: C, 56.75; H, 5.41; N, 3.01; S, 6.88. Found: C, 57.01; H, 5.42; N, 3.22; S, 6.69. See also Figures S6 and S7 in the Supplementary Materials.

Preparation of 1-Li$_2$. 600 mg (1.40 mmol) of precursor **1** were suspended in 4 mL Et_2O. 1.80 mL (3.09 mmol, 1.59 M solution in Et_2O) MeLi were added and the reaction mixture stirred at room temperature until no further gas evolution could be observed giving a colourless suspension. The supernatant solvent was removed via cannula and the colourless product dried under reduced pressure (501 mg, 1.09 mmol, 78%). **^{1}H NMR:** (500.1 MHz, C_6D_6): δ = 0.25 (9H; Si(CH_3)$_3$), 1.11 (t, $^3J_{HH}$ = 5.00 Hz, 3H; C$H_{3,Et2O}$), 3.26 (q, $^3J_{HH}$ = 5.00 Hz, 2H; C$H_{2,Et2O}$), 6.83–6.94 (m, 4H; C$H_{SPh,meta,para}$/C$H_{PPh,meta,para}$), 7.10–7.23 (m, 7H; C$H_{SPh,meta,para}$/C$H_{PPh,ortho,meta,para}$), 8.02–8.04 (m, 2H; C$H_{SPh,ortho}$), 8.23–8.27 (m, 2H; C$H_{PPh,ortho}$). **^{13}C{^{1}H} NMR:** (125.8 MHz, C_6D_6): δ = 4.74 (d, $^3J_{CP}$ = 3.69 Hz; Si(CH_3)$_3$), 15.6 (C$H_{3,Et2O}$), 52.4 (d, $^1J_{CP}$ = 53.3 Hz; SCP), 65.9 (C$H_{2,Et2O}$), 126.0 (C$H_{SPh,meta}$), 127.4 (d, $^3J_{CP}$ = 11.8 Hz; C$H_{PPh,meta}$), 128.4 (d, $^3J_{CP}$ = 11.5 Hz; C$H_{PPh,meta}$), 128.5 (C$H_{SPh,para}$), 129.0 (br, C$H_{PPh,para}$), 129.5 (C$H_{SPh,ortho}$), 130.4 (br; C$H_{PPh,para}$), 131.2 (d, $^2J_{CP}$ = 7.25 Hz; C$H_{PPh,ortho}$), 131.3 (d, $^2J_{CP}$ = 10.73 Hz; C$H_{PPh,ortho}$), 141.2 (d, $^1J_{CP}$ = 64.4 Hz; $C_{PPh,ipso}$), 142.0 (d, $^1J_{CP}$ = 81.7 Hz; $C_{PPh,ipso}$), 151.5 (d, $^3J_{CP}$ = 2.36 Hz; $C_{SPh,ipso}$). **^{31}P{^{1}H} NMR:** (202.5 MHz, C_6D_6): δ = 7.63. **^{7}Li{^{1}H} NMR:** (194.4 MHz, C_6D_6): δ = 0.19, 1.67. Anal. Calcd. for $C_{24}H_{29}Li_2N_1O_{2.5}P_1S_1Si_1$: C, 60.49; H, 6.13; N, 2.94; S, 6.73. Found: C, 60.27; H, 5.93; N, 3.1 2; S, 6.59. See also Figures S8–S10 in the Supplementary Materials.

3.3. X-ray Crystallography

General. Data collection of the compound was conducted with a Bruker APEX2-CCD (D8 three-circle goniometer). The structures were solved using direct methods, refined with the Shelx software package [50] and expanded using Fourier techniques. The crystal of the compound was mounted in an inert oil (perfluoropolyalkylether). Crystal structure determination were effected at 100 K. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1514516–1514518. Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; (fax: (+44)-1223-336-033; email: deposit@ccdc.cam.ac.uk).

Crystal data for compound 1. $C_{22}H_{26}NO_2PSSi$; M_r = 427.56; colourless block; 0.40 × 0.30 × 0.29 mm^3; triclinic; space group P-1; a = 99.2087(4), b = 10.5543(4), c = 12.6990(5) Å; V = 1079.35(8) Å^3; Z = 2; $ρ_{calcd}$ = 1.316 g·cm^{-3}; μ = 0.298 mm^{-1}; $F(000)$ = 452; T = 100(2) K; R_1 = 0.0290 and wR^2 = 0.1137; 3796 unique reflections (θ < 25.00) and 262 parameters. See also Tables S1–S3 in the Supplementary Materials.

Crystal data for compound 1-K. $C_{48}H_{58}K_2N_2O_5P_2S_2Si_2$; M_r = 1003.40; colourless needle; 0.15 × 0.05 × 0.04 mm^3; triclinic; space group P-1; a = 11.2841(10), b = 15.3705(14), c = 16.8163(15) Å; V = 2489.2(4) Å^3; Z = 2; $ρ_{calcd}$ = 1.339 g·cm^{-3}; μ = 0.433 mm^{-1}; $F(000)$ = 1056; T = 100(2) K; R_1 = 0.0408 and wR^2 = 0.0917; 8770 unique reflections (θ < 24.998) and 605 parameters. See also Tables S1, S4 and S5 in the Supplementary Materials.

Crystal data for compound 1-Li$_2$. $C_{98}H_{121}Li_8N_4O_{10.50}P_4S_4Si_4$; M_r = 1942.98; colourless needle; 0.15 × 0.06 × 0.06 mm^3; monoclinic; space group $P2_1/c$; a = 25.265(3), b = 18.972(2), c = 24.452(3) Å; V = 10,485(2) Å^3; Z = 4; $ρ_{calcd}$ = 1.231 g·cm^{-3}; μ = 0.254 mm^{-1}; $F(000)$ = 4100; T = 100(2) K; R_1 = 0.0494 and

$wR^2 = 0.0947$; 18,468 unique reflections ($\theta < 24.997$) and 1254 parameters. See also Tables S1, S6 and S7 in the Supplementary Materials.

4. Conclusions

In summary, we reported on the synthesis and metalation of the iminophosphoryl and sulfonyl-functionalized methane **1**. The corresponding potassium methanide **1-K** and dilithium compound **1-Li₂** are easily accessible by standard deprotonation reactions and isolable in high-yields as solid materials. XRD analysis allowed the elucidation of their molecular structures, showing typical bond length changes reflecting the electronic structure. **1-K** formed a coordination polymer in solid state, while the methandiide was found to crystallize as well-defined *pseudo*-tetrameric complex with an unusual structural motif. The facile synthesis of **1-Li₂** and the formation of a well-defined structure in solid state are both advantageous for its application as ligand in carbene complex chemistry.

Supplementary Materials: The following are available online at www.mdpi.com/2304-6740/4/4/40/s1, NMR spectra of all isolated compounds (Figures S1–S10) as well as crystallographic details for the compounds **1**, **1-K** and **1Li₂** (Tables S1–S7, Figures S11–S13).

Author Contributions: Kai-Stephan Feichtner synthesized and characterized all compounds, Kai-Stephan Feichtner and Viktoria H. Gessner prepared the manuscript and planned the research.

Conflicts of Interest: The authors declare no conflict of interest.

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