[27] AM1 calculations (AMPAC version 2.20) also clearly indicate the favored formation of intermediate TS2 (heat of formation 18.46 kcal) over TS1 (heat of formation 140.22 kcal).

[28] Previous investigations have been carried out on the sterochemical behavior of the four-membered oxyphosphoranes (1,2-oxaphosphetanes) having three P–C bonds: a) F. Ramirez, J. F. Pilot, O. P. Madan, C. P. Smith, *J. Am. Chem. Soc.* **1968**, *90*, 1275; b) F. Ramirez, C. P. Smith, J. F. Pilot, *J. Am. Chem. Soc.* **1968**, *90*, 6726; c) D. B. Denney, D. Z. Denney, C. D. Hall, K. L. Marsi, *J. Am. Chem. Soc.* **1972**, *94*, 245.

$[Ph_2P(NSiMe_3)]_2CLi_2$: A Dilithium Dianionic Methanide Salt with an Unusual Li_4C_2 Cluster Structure**

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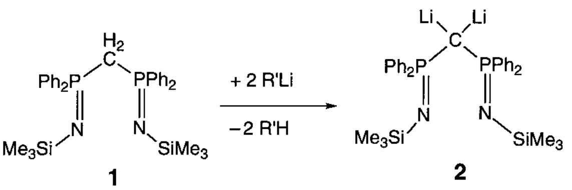
Bis(phosphane) ligands and their oxidized derivatives of the form $CH_2(R_2P{=}E)_2$ ($E = O, S, NR'$) have been widely used to form stable mono- and polymetallic complexes with both early and late transition metals.[1, 2] Generally the ligand retains its neutral character, and the methylene bridge between the two phosphorus atoms is preserved. However, these backbone protons are moderately acidic, and the ligand may be deprotonated by strong bases such as $LiN(SiMe_3)_2$, NaH, and alkyllithium reagents to generate monoanionic species. Many metal compounds have been derived from these monoanionic ligand precursors, and typically M–C bonds stabilized by additional coordination of the ligand are formed.[3–9] A few unexpected complexes have been reported in which double deprotonation of the P-CH_2-P backbone has been structurally established—namely, $[\{Pd(\mu\text{-}Cl)_2Pt[C(PPh_2)_2]\}_n]$,[10] $[Pt_2\{C(Ph_2P{=}S)_2\}(MeOcod)_2]$[11] (MeOcod = 8-methoxycyclooct-4-ene-1-yl), $[(AlR)\{C(Ph_2P{=}O)_2\}_2(AlR_2)_2]$ (R = Me,[12] Et[13]), and $[\{Al(C_4H_9)\}_2\{Ph_2P({=}S)CP(Ph)_2(S)_2\}\{Al(C_4H_9)_2\}_2]$[14]—but to date there has been no rational synthesis of a species with the doubly deprotonated P-C-P methanide moiety. Herein we report the first synthesis and crystal structure of a complex containing such a ligand formed by the double deprotonation of $CH_2(Ph_2P{=}NR)_2$. This represents the first example of a structurally characterized Group 1 metal complex of the $CH_2(R_2P{=}E)_2$ ($E = O, S, NR'$) ligand systems. In addition the structure is an unusual, highly symmetric dimer cluster of lithium and carbon.

Reaction of $CH_2(Ph_2P{=}NSiMe_3)_2$ (**1**) with two moles of PhLi or MeLi in toluene leads smoothly to the dilithium complex **2** as colorless air- and moisture-sensitive crystals [Eq. (1)].[15]



1 **2**

(1)

The ^{31}P NMR spectrum of the final reaction mixtures showed quantitative conversion of **1** into one single phosphorus-containing product. Complex **2** was isolated in only moderate yield due to its high solubility, and it was fully characterized by elemental analysis and spectroscopic methods. The ^{31}P NMR spectrum of **2** consists of one sharp singlet, indicating that the two phosphorus nuclei are equivalent. The ^{31}P resonance is shifted downfield by 19.1 ppm compared to that of the starting compound **1**. The ^{1}H NMR spectrum showed the absence of the methylene resonance of the P-CH_2-P backbone, indicating that the ligand has been doubly deprotonated. No $^{13}C\{^{1}H\}$ NMR signal was observed for the quaternary P-C-P carbon atom despite trials with long acquisition periods, possibly because the signal is very broad due to coupling with the lithium nuclei. However, the lack of suitable protons proximate to the methine carbon atoms provides minimal $^{1}H \rightarrow {}^{13}C$ magnetization transfer, so it is perhaps not too surprising that this signal is not observed.

The molecular structure of **2**,[16] determined by X-ray diffraction, is unusual and interesting. Figure 1 shows an ORTEP[17] plot of the central cluster structure. The complex is a dimer, with four lithium atoms forming a square plane which is capped above and below by carbon atoms C(1) and C(2) of the two P-C-P frames. The bridging atoms C(1) and C(2) lie 1.67 Å above and below the Li_4 square plane to form a near perfect octahedron of atoms in the center of the cluster, which deviates only slightly from a regular octahedron because of the presence of the different axial atoms. The ligand N-P-C-P-N units are approximately planar, and there is only a small displacement (0.16–0.30 Å) of the Si atoms from the P-N-C planes. The N-P-C-P-N ligand planes are orthogonal to each other (the dihedral angle between the two planes is 88.12(11)°) and in turn

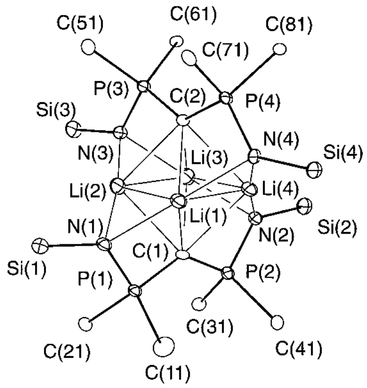


Figure 1. ORTEP[17] view of the central core of **2** showing the atom labeling scheme. All of the hydrogen atoms, the methyl carbon atoms on the silicon atoms, and all phenyl-ring carbon atoms (except the *ipso*-carbon atoms) have been removed for clarity. The atoms are represented by Gaussian ellipsoids at the 20% probability level. The thin lines serve to emphasize the geometrical relationship between the carbon and lithium atoms and are not to be considered normal bonds. Selected interatomic distances [Å] and angles [°]: P(1)–N(1) 1.619(4), P(1)–C(1) 1.695(5), P(2)–C(1) 1.681(5), C(1)–Li 2.33(1)–2.42(1), C(2)–Li 2.312(9)–2.45(1), N(1)–Li(2) 2.128(9), N(2)–Li(4) 2.108(9); P(1)-C(1)-P(2) 132.6(3), N(1)-P(1)-C(1) 104.4(2), N(2)-P(2)-C(1) 103.9(2).

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orthogonal to the plane formed by the four lithium atoms (the dihedral angle is 89.81(19)° between planes N(1)-P(1)-C(1)-P(2)-N(2) and Li(1)-Li(2)-Li(3)-Li(4), and 88.6(2)° between planes N(3)-P(3)-C(2)-P(4)-N(4) and Li(1)-Li(2)-Li(3)-Li(4)).

There are no solvent molecules coordinated to the lithium atoms in **2**, rather the lithium atoms are intramolecularly solvated by the silylated imine groups. A similar internal solvation was observed for the lithiated monophosphane imines $[\{LiCH_2P(Me)_2(NSiMe_3)\}_4]$ and $[\{LiCMe_2P(i\text{Pr})_2(NSiMe_3)\}_2]$.[18] In the central core of **2** each lithium atom is close to two other lithium, two carbon, and two imine nitrogen atoms. The essence of the structure is the central cluster core, an octahedron of four lithium and two carbon atoms supported by four nitrogen atoms which bridge opposite pairs of lithium atoms. The Li–C distances (av 2.38(1) Å) are comparable to those in the oligomeric aggregates $[\{PhLi(tmeda)\}_2]$ (tmeda = *N,N,N',N'*-tetramethylethylenediamine) and $[\{PhLi\cdot OEt_2\}_4]$.[19] The Li–N distances for the N atoms bridging the Li atoms are in the range observed for lithiated monophosphanylimines (2.052(10) – 2.151(9) Å)[18, 20, 21] The Li–Li distances fall within a narrow range (2.393 – 2.410 Å) and shorter than those found in the alkyllithium aggregates $[(LiR)_n]$ (R = Me, Et, Bu).[22–24]

The phosphorus atoms in complex **2** also lie very close to the lithium atoms, but probably only as a result of the tight cluster structure. Surprisingly, however, these phosphorus–lithium distances fall within the range of a P–Li single bond (2.64 – 2.69 Å) and are comparable with those reported for $[LiCH(PPh_2)_2]$ and related compounds.[8, 25, 26] The P=N bond lengths in **2** (av 1.621(4) Å) are slightly elongated relative to those found in $CH_3CH\{Ph_2P{=}N(Tol)\}_2$[27] and $H_2C(Cy_2P{=}NSiMe_3)_2$.[28] The exocylic P–C bonds are of normal length. The endocyclic P–C bond distances are, however, significantly shortened and the N–Li distances are also shorter than the C–Li distances, suggesting that there is a considerable delocalization of the π electron density over the N-P-C-P-N backbone. The P-C-P bond angles in **2** (av 132.4(3)°) are significantly expanded compared to the corresponding angles in $CH_3CH\{Ph_2P{=}N(Tol)\}_2$ (112.39(19°)[27] and $H_2C(Cy_2P{=}NSiMe_3)_2$ (117.41(12)°),[28] where the carbon has a more sp^3 geometry.

The successful synthesis of this doubly deprotonated dilithiated salt can be attributed to the enhanced acidity of the P-CH_2-P backbone protons in the bisimine system.[29]

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[1] F. A. Cotton, B. Hong, *Prog. Inorg. Chem.* **1992**, *40*, 179 – 289.

[2] R. J. Puddephatt, *Chem. Soc. Rev.* **1983**, *12*, 99 – 127.

[3] M. W. Avis, K. Vrieze, J. M. Ernsting, C. J. Elsevier, N. Veldman, A. L. Spek, K. V. Katti, C. L. Barnes, *Organometallics* **1996**, *15*, 2376 – 2392.

[4] H. H. Karsch, G. Grauvogl, M. Kawecki, P. Bissinger, O. Kumberger, A. Schier, G. Müller, *Organometallics* **1994**, *13*, 610 – 618.

[5] S. Hao, J.-I. Song, H. Aghabozorg, S. Gambarotta, *J. Chem. Soc. Chem. Commun.* **1994**, 157 – 158.

[6] P. Imhoff, R. van Asselt, J. M. Ernsting, K. Vrieze, C. J. Elsevier, W. J. J. Smeets, A. L. Spek, A. P. M. Kentgens, *Organometallics* **1993**, *12*, 1523 – 1536.

[7] I. G. Phillips, R. G. Ball, R. G. Cavell, *Inorg. Chem.* **1988**, *27*, 4038 – 4045.

[8] D. J. Brauer, S. Hietkamp, O. Stelzer, *J. Organomet. Chem.* **1986**, *299*, 137 – 142.

[9] H. Schmidbaur, E. Weiss, B. Zimmer-Gasser, *Angew. Chem.* **1979**, *91*, 848-850; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 782 – 784.

[10] S. I. Al-Resayes, P. B. Hitchcock, J. F. Nixon, *J. Chem. Soc. Chem. Commun.* **1986**, 1710 – 1711.

[11] J. Browning, K. R. Dixon, R. W. Hilts, *Organometallics* **1989**, *8*, 552.

[12] G. H. Robinson, B. Lee, W. T. Pennington, S. A. Sangokoya, *J. Am. Chem. Soc.* **1988**, *110*, 6260 – 6261.

[13] B. Lee, S. A. Sangokoya, W. T. Pennington, G. H. Robinson, *J. Coord. Chem.* **1990**, *21*, 99 – 105.

[14] G. H. Robinson, M. F. Self, W. T. Pennington, S. A. Sangokoya, *Organometallics* **1988**, *7*, 2424 – 2426.

[15] Preparation of **2**: All work was done in an inert atmosphere box filled with argon. Solid PhLi (0.30 g, 3.59 mmol) was added at room temperature to a stirred solution (20 mL) of **1** (1.0 g, 1.79 mmol) in toluene, and the mixture was stirred for three days. A small quantity of a colorless solid was filtered out. The mother liquor was reduced to nearly half of the original volume and then allowed to stand at room temperature for 48 h. Colorless crystals of **2** deposited which desolvated readily on isolation (yield: 0.62 g, 60.7 %). ^{1}H NMR (400.1 MHz, [D$_6$]benzene, 25 °C): δ = 7.53 – 7.49 (m, phenyl), 7.04 – 6.93 (m, phenyl), 0.04 (s, CH_3Si); $^{13}C\{^1H\}$ NMR (100.6 MHz, [D$_6$]benzene, 25 °C): δ = 139.0 (m, 4 C, *ipso*-phenyl), 131.0 (t, $^2J(P,C)$ = 4.5 Hz, 8 C, *ortho*-phenyl), 129.0 (s, 4 C, *para*-phenyl), 127.8 (s, 8 C, *meta*-phenyl), 4.4 (s, 6 C, CH_3Si); $^{31}P\{^1H\}$ NMR (161.9 MHz, [D$_6$]benzene, 25 °C): δ = 13.7 (2 P); IR (Nujol mull): $\tilde{\nu}$ = 1434 (m), 1244 (s), 1190 (s), 1174 (m), 1101 (s), 1067 (s), 852 (s), 832 (s), 764 (m), 747 (m), 725 (m), 709 (m), 696 (s), 675 (w), 663 (w), 646 (s), 618 (w), 606 (w), 539 (s), 512 cm^{-1} (m); elemental analysis calcd for $C_{31}H_{38}Li_2N_2P_2Si_2$: C 65.25, H 6.71, N 4.91; found: C 65.27, H 6.69, N 4.60.

[16] Crystallographic data for **2** (obtained as solvated crystals which contained one benzene and one toluene molecule per molecular dimer): triclinic, space group $P\bar{1}$ (no. 2), a = 12.5041(6), b = 17.1185(7), c = 19.2928(12) Å, α = 98.128(5), β = 102.994(4), γ = 105.667(3)°, Z = 2. The structure was solved by direct methods and refined by full-matrix least-squares procedures: R_1 = 0.0688 and 0.0976 (wR_2 = 0.1683 and 0.1919) for 7313 reflections with $F_o^2 > 2\sigma(F_o^2)$ and all data, respectively. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114415. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[17] C. K. Johnson, ORTEP, Report ORNL No. 5138, Oak Ridge National Labs, Oak Ridge, TN, USA, **1976**.

[18] A. Müller, B. Neumüller, K. Dehnicke, *Chem. Ber.* **1996**, *129*, 253 – 257.

[19] H. Hope, P. P. Power, *J. Am. Chem. Soc.* **1983**, *105*, 5320 – 5324.

[20] A. Müller, B. Neumüller, K. Dehnicke, *Angew. Chem.* **1997**, *109*, 2447 – 2449; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2350 – 2352.

[21] A. Steiner, D. Stalke, *Angew. Chem.* **1995**, *107*, 1908 – 1910; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1752 – 1755.

[22] H. Dietrich, *J. Organomet. Chem.* **1981**, *205*, 291 – 299.

[23] E. Weiss, T. Lambertsen, B. Schubert, J. K. Cockcroft, A. Wiedenmann, *Chem. Ber.* **1990**, *123*, 79 – 81.

[24] T. Kottke, D. Stalke, *Angew. Chem.* **1993**, *105*, 619-621; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 580 – 582.

[25] H. H. Karsch, G. Müller, *J. Chem. Soc. Chem. Commun.* **1984**, 569.

[26] H. H. Karsch, G. Grauvogl, P. Mikulcik, P. Bissinger, G. Müller, *J. Organomet. Chem.* **1994**, *465*, 65 – 71.

[27] M. W. Avis, C. J. Elsevier, N. Veldman, H. Kooijman, A. L. Spek, *Inorg. Chem.* **1996**, *35*, 1518 – 1528.

[28] The structure of $CH_2(Cy_2P{=}NSiMe_3)_2$ (R. G. Cavell, R. P. Kamalesh Babu, R. McDonald, University of Alberta Structure Report RGC 9802) will be published elsewhere.

[29] Editorial note: The structure of **2** was recently published: C. M. Ong, D. W. Stephan, *J. Am. Chem. Soc.* **1999**, *121*, 2939 – 2940.