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First Structurally Authenticated Heavier Alkali Metal Phosphinomethanide

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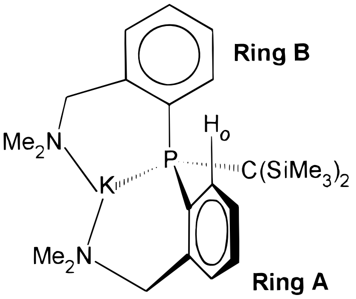
Summary: Metathesis between Li[C(SiMe$_3$)$_2${P(C$_6$H$_4$-2-CH$_2$NMe$_2$)$_2$}] **(1)** *and KO-t-Bu yields [{K[C(SiMe$_3$)$_2$-{P(C$_6$H$_4$-2-CH$_2$NMe$_2$)$_2$}]}$_2$]$_\infty$* **(2)**, *the first heavier alkali metal complex of a phosphorus-stabilized carbanion to be structurally characterized.*

The chemistry of phosphorus-stabilized carbanions (phosphinomethanides) has seen many developments over the last two decades, and a wide range of metal complexes have been isolated and crystallographically characterized.[1] The binding mode of such ligands is heavily dependent upon the metal center and the substituents at both phosphorus and carbon; examples of complexes in which phosphinomethanides bind as η^1-, η^2-, or η^3-ligands through phosphorus and/or carbon have been reported. However, despite the flexible nature of these ligands and the structural diversity displayed by heavier alkali metal derivatives of silicon-substituted carbanions,[2,3] there has been no previous structural study of complexes of the heavier alkali metals with phosphorus-stabilized carbanions. We now report the first such characterization of a potassium phosphinomethanide complex.[4]

Metathesis between the lithium complex **1,**[5] Li[C(SiMe$_3$)$_2${P(C$_6$H$_4$-2-CH$_2$NMe$_2$)$_2$}], and KO-*t*-Bu in diethyl ether gives the heavier alkali metal phosphinomethanide **2**, [{K[C(SiMe$_3$)$_2${P(C$_6$H$_4$-2-CH$_2$NMe$_2$)$_2$}]}$_2$]$_\infty$, in high yield.[6] The ^{1}H NMR spectrum of **2** at room temperature is extremely broad, with only one signal each for the NMe$_2$ and SiMe$_3$ groups. Below 269 K the Me$_3$Si and NMe$_2$ signals each separate into two peaks. The complex is therefore subject to a dynamic process in solution, for which line shape analysis yields $\Delta G^\ddagger$ = 51 kJ mol^{-1} at 269 K, $\Delta H^\ddagger$ = 37 kJ mol^{-1}, and $\Delta S^\ddagger$ = −71 J K^{-1}mol^{-1}, which may be attributed to either puckering of the chelate rings or reversible K−N bond cleavage by the strong donor solvent THF. At low temperature the relative positions of the two aromatic rings of the ligand cause one of the *ortho*-protons (H$_o$ in Scheme 1) in **2** to lie close to the other aromatic ring and hence to resonate at unusually low field in the proton NMR spectrum. The juxtaposition of the two rings causes all of the aromatic protons to be inequivalent at low temperature; the relative assignments of the protons on the A and B aromatic rings were obtained from 2D proton COSY experiments at 213 K.

Scheme 1



In contrast to the monomeric complex **1**, compound **2** crystallizes from toluene as solvent-free centrosymmetric dimers (Figure 1a).[7] Each potassium is bound by the phosphorus and two nitrogen atoms of one ligand in a manner similar to the lithium in **1**, with supplementary coordination via an intramolecular K···Me−Si(1) contact. This represents the first example of a complex in

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(1) For examples see: (a) Karsch, H. H. *Russ. Chem. Bull.* **1993**, *42*, 1937. (b) Karsch, H. H.; Zellner, K.; Mikulcik, P.; Lachmann, J.; Muller, G. *Organometallics* **1990**, *9*, 190. (c) Karsch, H. H.; Deubelly, B.; Hofmann, J.; Pieper, U.; Muller, G. *J. Am. Chem. Soc.* **1988**, *110*, 3654. (d) Karsch, H. H.; Grauvogl, G.; Mikulcik, P.; Bissinger, P.; Muller, G. *J. Organomet. Chem.* **1994**, *465*, 65. (e) Karsch, H. H.; Ferazin, G.; Bissinger, P. *Chem. Commun.* **1994**, 505. (f) Clegg, W.; Izod, K.; McFarlane, W.; O'Shaughnessy, P. *Organometallics* **1998**, *17*, 5231. (g) Denmark, S. E.; Swiss, K. A.; Wilson, S. R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2515. (h) Cramer, C. J.; Denmark, S. E.; Miller, P. C.; Dorow, R. L.; Swiss, K. A.; Wilson, S. R. *J. Am. Chem. Soc.* **1994**, *116*, 2437.

(2) For recent reviews of alkali metal organometallics see: (a) Schade, C.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1987**, *27*, 169. (b) Willard, P. G. In *Comprehensive Organic Synthesis, Vol. 1*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; pp 1−47. (c) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353. (d) Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1993**, *11*, 1501. (e) Smith, J. D. *Adv. Organomet. Chem.* **1998**, *43*, 267.

(3) (a) Hiller, W. G.; Layh, M.; Uhl, W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 324. (b) Eaborn, C.; Izod, K.; Smith, J. D. *J. Organomet. Chem.* **1995**, *500*, 89, and references therein. (c) Eaborn, C.; Clegg, W.; Hitchcock, P. B.; Hopman, M.; Izod, K.; O'Shaughnessy, P. N.; Smith, J. D. *Organometallics* **1997**, *16*, 4728 (d) Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P.; Diansheng, L.; Shun, T. *Chem. Commun.* **1993**, 1386.

(4) A potassium phosphinomethanide has been reported as an intermediate in the synthesis of a lanthanide phosphinomethanide complex but was not isolated. Karsch, H. H.; Appelt, A.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 823.

(5) Clegg, W.; Doherty, S.; Izod, K.; O'Shaughnessy, P. *Chem. Commun.* **1998**, 1129.

(6) A solution of **1** (1.15 g, 2.31 mmol) in diethyl ether (10 mL) was added to a suspension of KO-*t*-Bu (0.26 g, 2.31 mmol) in the same solvent (15 mL). The reaction mixture was stirred for 12 h, and then solvent was removed in vacuo. The solid was washed with light petroleum ether (bp 40−60 °C, 3 × 10 mL), and crystals of **2** suitable for an X-ray crystallographic study were obtained from toluene solution at room temperature. Yield: 0.82 g, 71.4%, Anal. Calcd for C$_{25}$H$_{42}$KN$_2$PSi$_2$: C, 60.31; H, 8.71; N, 5.63. Found: C, 60.19; H, 8.57; N, 5.16. ^{1}H NMR (500 MHz, THF-*d*$_8$, 213 K): δ −0.50 (s, 9H, SiMe$_3$), −0.02 (s, 9H, SiMe$_3$), 1.96 (s, 6H, NMe$_2$), 2.29 (s, 6H, NMe$_2$), 2.87 (d, ^2J(H,H) 14.8 Hz, 1H, CH$_2$N), 3.50 (dd, ^2J(H,H) 14.8 Hz, J(H,P) 6.5 Hz, 1H, CH$_2$N), 3.97 (d, ^2J(H,H) 15.5 Hz, 1H, CH$_2$N), 4.22 (dd, ^2J(H,H) 15.5 Hz, J(H,P) 6.5 Hz, 1H, CH$_2$N), 6.54 (m, 1H, *p*-Ar^{B}H), 6.65 (m, 1H, *m*-Ar^{B}H), 6.79 (m, 1H, *m*-Ar^{B}H), 6.89 (m, 1H, *p*-Ar^{A}H), 7.00 (m, 1H, *m*-Ar^{A}H), 7.31 (m, 1H, *m*-Ar^{A}H), 7.36 (m, 1H, *o*-Ar^{B}H), 8.26 (m, 1H, *o*-Ar^{A}H). ^{31}P{^{1}H} NMR (121 MHz, THF-*d*$_8$, 297 K): δ −7.9.

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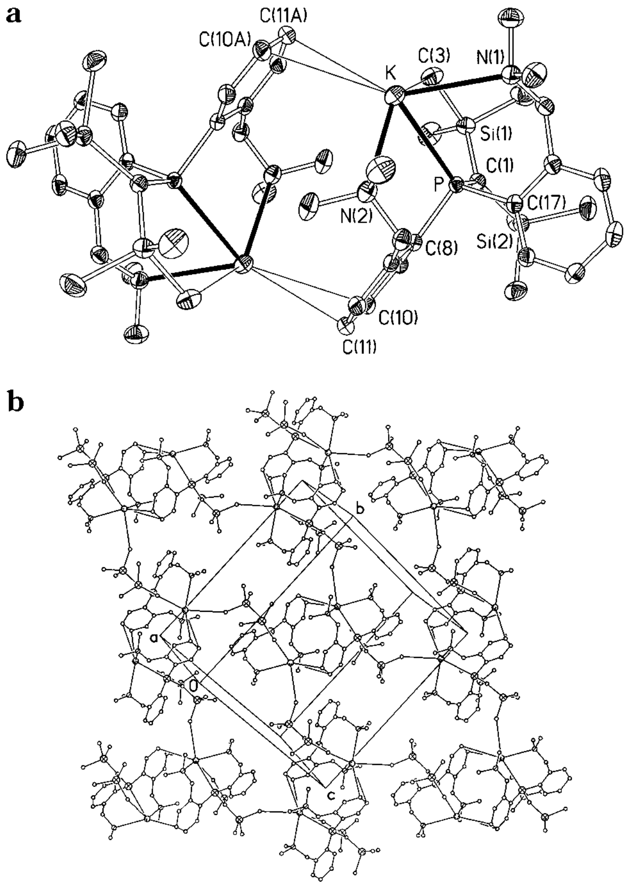

Figure 1. (a) Structure of the dimeric subunits of **2** with 50% probability ellipsoids. (b) Sheet arrangement of the dimers in **2**. Selected bond lengths (Å) and angles (deg): K−P 3.2227(5), K−N(1) 2.9454(12), K−N(2) 2.8067(13), K···C(3) 3.4646(17), K···C(10A) 3.5137(14), K···C(11A) 3.2513(15), K···C(5B) 3.3981(16), P−C(1) 1.7524(14), P−C(8) 1.8712(13), P−C(17) 1.8652(14), C(1)−Si(1) 1.8202(14), C(1)−Si(2) 1.8264(13), Si−C(Me) 1.891 (average), P−K−N(1) 72.30(2), P−K−N(2) 76.74(3).

which there is a direct K−P contact where the phosphorus is not bound in the form of a phosphide anion;[8] there have been no reports of structurally characterized complexes in which potassium is bound to phosphorus either as a neutral phosphine or as a phosphinomethanide.[9] The K−P distance (3.2227(5) Å) in **2** is at the lower end of the range of K−P distances reported,[8] with the only shorter reported distance occurring in the ladder polymer $[\{(2,4,6\text{-}t\mathrm{Bu}_3\text{−}\mathrm{C}_6\mathrm{H}_2)\mathrm{HP}\}\mathrm{K}]_x$ (K−P = 3.181(2), 3.271(2), and 3.357(2) Å).[8f] The short M−P distance in **2** is consistent with a significant degree of charge delocalization from the carbanion center to phosphorus and the formation of two chelate rings. The K−N distances of 2.8067 and 2.9454 Å are typical of such contacts.[2]

The two halves of the dimer are linked by η^2-interactions between one of the aromatic rings in the ligand and a potassium atom in the adjacent K-$\{C(SiMe_3)_2P(C_6H_4CH_2NMe_2)_2\}$ moiety. The K−C(ring) distances of 3.5137(14) and 3.2513(15) Å are typical of such multihapto interactions between potassium and an aromatic ring.[2,8a,f,10] These dimeric units are further linked into a two-dimensional sheet arrangement (Figure 1b) via intermolecular contacts between a methyl of the second Me_3Si group and a potassium atom in an adjacent dimer [K(1B)···Me-Si(2)]. Thus the two Me_3Si groups of each ligand are involved in distinct Si−Me···K interactions, one *intra*molecular and one *inter*molecular. The intramolecular contact, C(3)···K (3.4646(17) Å), is somewhat longer than the intermolecular contact, C(5B)···K (3.3981(16) Å), but both are within the typical range of distances for K···Me contacts.[2e] A similarly short distance between the potassium atom and one of the methyls of one NMe_2 group (K···C(16) = 3.2585(19) Å) gives each potassium an effective coordination number of seven.

The carbanion center C(1) is almost perfectly planar (sum of angles at C(1) = 358.3°), with no short inter- or intramolecular contacts to K. The P−C(1) distance (1.7524(14) Å) is slightly longer than the same distance in **1** (1.735(3) Å), but is still significantly shorter than that expected for a P−C single bond, consistent with significant multiple-bond character due to charge delocalization from the carbanion center to phosphorus.

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Supporting Information Available: Details of data collection, refinement, atom coordinates, anisotropic displacement parameters, and bond lengths and angles. This material is available free of charge via the Internet at http://www.pubs.acs.org.

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(7) Crystal data for **3**: $C_{25}H_{42}KN_2PSi_2$ (monomer formula), fw = 496.9, monoclinic, space group $P2_1/n$, $a = 9.9165(4)$ Å, $b = 17.7521(8)$ Å, $c = 15.8600(7)$ Å, $\beta = 92.514(2)°$, $V = 2789.3(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.183$ g cm^{-3}, $\mu = 0.35$ mm^{-1}, $T = 160$ K, crystal size 0.54 × 0.30 × 0.26 mm; Bruker SMART CCD diffractometer, structure solution by direct methods, refinement on F^2, ($2\theta < 29.1°$); $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2} = 0.0838$ (all data), conventional $R = 0.0324$ on F values of 5417 reflections with $F_o^2 > 2\sigma(F_o^2)$, goodness of fit = 1.043, final difference synthesis within ±0.35 e Å^{-3}.

(8) For leading references to potassium phosphide complexes see: (a) Frenzel, C.; Jörchel, P.; Hey-Hawkins, E. *Chem. Commun.* **1998**, 1363. (b) Englich, U.; Hassler, K.; Ruhlandt-Senge, M.; Uhlig, F. *Inorg. Chem.* **1998**, *37*, 3532. (c) Fermin, M.; Ho, J.; Stephan, D. W. *Organometallics* **1995**, *14*, 4247. (d) Beswick, M. A.; Hopkins, A. D.; Kerr, L. C.; Mosquera, M. E. G.; Palmer, J. S.; Raithby, P. R.; Rothenberger, A.; Stalke, D.; Wheatley, A. E. H.; Wright, D. S. *Chem. Commun.* **1998**, 1527. (e) Andrianarison, M.; Stalke, D.; Klingebiel, U. *Chem. Ber.* **1990**, *123*, 71. (f) Rabe, G. W.; Yap, G. P. A.; Rheingold, A. L. *Inorg. Chem.* **1997**, *36*, 1990.

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(10) For examples see: (a) Eaborn, C.; Hitchcock, P. B.; Izod, K.; Smith, J. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2679. (b) Eaborn, C.; Hitchcock, P. B.; Izod, K.; Jaggar, A. J.; Smith, J. D. *Organometallics* **1994**, *13*, 753.