

Metal Complexes of Guanidine-Substituted Alkyl Ligands: An Unsolvated Monomeric Two-Coordinate Organolithium

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Summary: Single-crystal X-ray diffraction of $MC(SiMe_3)_2(SiMe_2hpp)$ ($M = Li, K$; $hppH = 1,3,4,6,7,8$, hexahydro-2H-pyrimido[1,2-a]pyrimidine) showed unsolvated organometallic compounds in which the iminonitrogen of the guanidine forms strong intramolecular bonds to generate six-membered metallacycles.

The organometallic chemistry of sterically demanding ‘trisyl’ ligands, derived from deprotonation of tris(trimethylsilyl)methane, has been greatly extended by the introduction of one or more donor groups (X) to afford ligands $[C(SiMe_3)_n(SiMe_2X)_{3-n}]^-$.¹ To date, examples involving lone-pair donation² are restricted to those in which intramolecular coordination generates either a four- (e.g., X = NMe_2 **A**,^{3–5} OMe **B**^{4,6}) or a five-membered (e.g., X = 2-pyridyl **C**,^{7,8} CH_2PPh_2 **D**⁹) metallacycle (Figure 1).¹ Access to transition-metal and lanthanide compounds has been predominantly via metathesis involving lithium and potassium salts, which themselves show diverse and interesting structural chemistry.^{3,9–12}

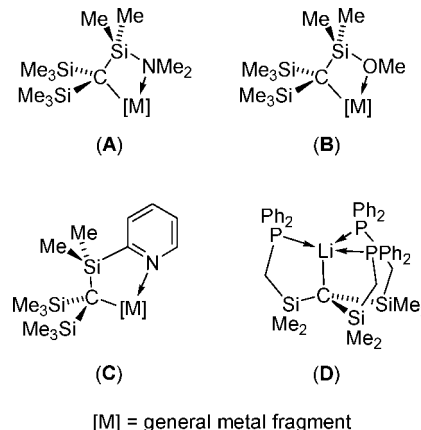


Figure 1

Donor-substituted trisyl-lithium compounds ($[M] = Li(solvent)_n$, Figure 1) most commonly crystallize as monomeric species in which there is room around the lithium atom for further coordination of solvent molecules.¹³ For example, dimethylamido derivative **A** has been characterized as both the bis-THF adduct¹⁴ and the TMEDA chelate,³ and the 2-pyridyl derivative **C** as the mono-THF adduct.¹¹ Similar structural fragments are found in the corresponding potassium reagents, **A**, **B**, and **C** ($M = K$), which are frequently isolated in the absence of donor solvents and crystallize as polymeric chains of alternating K^+ cations and planar carbanions.^{11,12,15} In this paper we describe the synthesis and structure of solvent-free lithium and potassium derivatives of the new precursor $HC(SiMe_3)_2(SiMe_2hpp)$, **1** ($hppH = 1,3,4,6,7,8$, hexahydro-2H-pyrimido[1,2-a]pyrimidine), which gives a ligand that is larger than those studied previously and has the potential to form six-membered metallacycles incorporating a strongly basic guanidine donor.¹⁶

Precursor **1** was obtained by a standard procedure from $hppH$, butyllithium, and $HC(SiMe_3)_2(SiMe_2Br)$ and isolated as a low-melting, colorless solid (Scheme 1). ¹H NMR spectra show that the compound is fluxional in solution, as there are only three sets of resonances for the annular methylene groups of the guanidine, indicating that the six-membered C_4N_2 -heterocycles are equivalent. This phenomenon has been noted previously in

(12) Bowman, L. J.; Izod, K.; Clegg, W.; Harrington, R. W.; Smith, J. D.; Eaborn, C. *Dalton Trans.* **2006**, 502–508.

(13) Tris(trimethylsilyl)methylolithium has been structurally characterized as the base-free salt. Hiller, W.; Layh, M.; Uhl, W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 324–326.

(14) Al-Juaid, S. S.; Eaborn, C.; El-Hamruni, S. M.; Hitchcock, P. B.; Smith, J. D. *Organometallics* **1999**, *18*, 45–52.

(15) Al-Juaid, S. S.; Eaborn, C.; El-Hamruni, S. M.; Farook, A.; Hitchcock, P. B.; Hopman, M.; Smith, J. D.; Clegg, W.; Izod, K.; O'Shaughnessy, P. *J. Chem. Soc., Dalton Trans.* **1999**, 3267–3273.

(16) Coles, M. P. *Dalton Trans.* **2006**, 985–1001.

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[†] University of Sussex. Fax: +44 (0)1273-876687. Tel: +44 (0)1273-877339.

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(1) Eaborn, C.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **2001**, 1541–1552.

(2) Intramolecular coordination by phenyl and vinyl groups has also been observed.

(3) Al-Juaid, S. S.; Avent, A. G.; Eaborn, C.; El-Hamruni, S. M.; Hawkes, S. A.; Hill, M. S.; Hopman, M.; Hitchcock, P. B.; Smith, J. D. *J. Organomet. Chem.* **2001**, *631*, 76–86.

(4) (a) Al-Juaid, S. S.; Eaborn, C.; El-Hamruni, S. M.; Hitchcock, P. B.; Smith, J. D.; Sözerli-Can, S. E. *J. Organomet. Chem.* **2002**, *649*, 121–127. (b) Bowman, L. J.; Izod, K.; Clegg, W.; Harrington, R. W. *Organometallics* **2006**, *25*, 2999–3006.

(5) (a) Azarifar, D.; Coles, M. P.; El-Hamruni, S. M.; Eaborn, C.; Hitchcock, P. B.; Smith, J. D. *J. Organomet. Chem.* **2004**, *689*, 1718–1722. (b) Lund, C. L.; Schachner, J. A.; Quail, J. W.; Müller, J. *Organometallics* **2006**, *25*, 5817–5823. (c) Lund, C. L.; Schachner, J. A.; Quail, J. W.; Müller, J. *J. Am. Chem. Soc.* **2007**, *129*, 9313–9320.

(6) (a) Izod, K.; Liddle, S. T.; Clegg, W. *J. Am. Chem. Soc.* **2003**, *125*, 7534–7535. (b) Bowman, L. J.; Izod, K.; Clegg, W.; Harrington, R. W. *J. Organomet. Chem.* **2007**, *692*, 806–812.

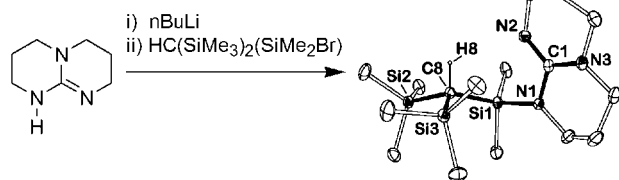
(7) (a) Howson, J.; Eaborn, C.; Hitchcock, P. B.; Hill, M. S.; Smith, J. D. *J. Organomet. Chem.* **2005**, *690*, 69–75. (b) Stanga, O.; Lund, C. L.; Liang, H.; Quail, J. W.; Müller, J. *Organometallics* **2005**, *24*, 6120–6125. (c) Al-Juaid, S. S.; Avent, A. G.; Eaborn, C.; Hill, M. S.; Hitchcock, P. B.; Patel, D. J.; Smith, J. D. *Organometallics* **2001**, *20*, 1223–1229. (d) Eaborn, C.; Hill, M. S.; Hitchcock, P. B.; Smith, J. D.; *J. Chem. Soc., Dalton Trans.* **2002**, 2467–2472. (e) Schachner, J. A.; Lund, C. L.; Quail, J. W.; Müller, J. *Organometallics* **2005**, *24*, 785–787. (f) Schachner, J. A.; Lund, C. L.; Quail, J. W.; Müller, J. *Organometallics* **2005**, *24*, 4483–4488.

(8) Asadi, A.; Avent, A. G.; Coles, M. P.; Eaborn, C.; Hitchcock, P. B.; Smith, J. D. *J. Organomet. Chem.* **2004**, *689*, 1238–1248.

(9) Avent, A. G.; Bonafoux, D.; Eaborn, C.; Hill, M. S.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **2000**, 2183–2190.

(10) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sözerli, S. E. *Organometallics* **1998**, *17*, 4322–4325.

(11) Al-Juaid, S. S.; Eaborn, C.; Hitchcock, P. B.; Hill, M. S.; Smith, J. D. *Organometallics* **2000**, *19*, 3224–3231.

Scheme 1. Synthesis of Ligand Precursor 1^a

^a Selected bond lengths (Å) and angles (deg): C1–N1 1.397(3), C1–N2 1.287(3), C1–N3 1.381(3), N1–Si1 1.772(2); Si1–C8–Si2 115.08(11), Si1–C8–Si3 114.66(12), Si2–C8–Si3 113.77(11).

silyl-substituted hpp-derivatives¹⁷ and likely involves interchange of the dimethyl-substituted silicon atom between N1 and N2. An X-ray structure determination showed the presence of discrete molecules with a unidentate guanidine coordinated to the SiMe₂ group, in contrast to some recently reported five-coordinate silicon derivatives of the [hpp][−] anion.¹⁸ Refinement of the hydrogen atom H8 attached to the central carbon allowed the distance to N2 to be determined as 2.75 Å, showing that there was no intramolecular hydrogen bond.

Treatment of **1** with methyl lithium in THF and extraction of the oily yellow product into pentane yielded a clear solution from which colorless crystals of the lithium salt LiC(SiMe₃)₂(SiMe₂hpp) (**2**) were obtained. These were unsuitable for an X-ray structure determination but from integration of the ¹H NMR spectrum were consistent with the formulation **2**·THF, analogous to the previously described LiC(SiMe₃)₂-(SiMe₂C₅H₄N-2)(THF).¹¹ Metalation of **1** with butyllithium in hexanes at −78 °C, however, gave compound **2** as colorless, air-sensitive crystals that were shown to be the unsolvated compound by NMR spectroscopy and elemental analysis.

Numerous alkyllithium compounds have been crystallographically characterized showing a diverse range of bonding types and modes of aggregation.^{19,20} Compound **2** is a rare example of a monomeric unsolvated organolithium compound and the first, as far as we are aware, with two-coordinate lithium (Figure 2a). The carbanionic ligand is bidentate, generating a six-membered metallacycle in which the metal occupies one vertex, with a C8–Li–N2 angle of 115.91(14)° and a Li–C bond length that falls within the expected range.¹⁹ The N2–Li distance (1.926(3) Å) is, however, considerably shorter than those in other examples where the N_{imine} atom of hppH coordinates as a neutral donor, e.g., [Li(hpp)(hppH)]₂ (2.029(6) Å)²¹ and [Li(OSiPh₃)(THF)(hppH)]₂ (2.054(4) Å).²² There is a considerable distortion toward planarity at the central carbon in **2** (Σ_{Si–C–Si}: **1**, 343.5°; **2** 350.0°) and a contraction in the C8–Si distances (av **1**, 1.888 Å; **2**, 1.820 Å). The remaining silicon–methyl bond lengths in **2** are normal (av 1.888 Å), showing that delocalization of negative charge is largely confined to the CSi₃ unit.

In contrast to the previously described unsolvated organolithium derivative [LiC(SiMe₃)₂(C₅H₄N-2)]₂, which is dimeric,²³ and other neutral, two-coordinate alkyllithium species that are

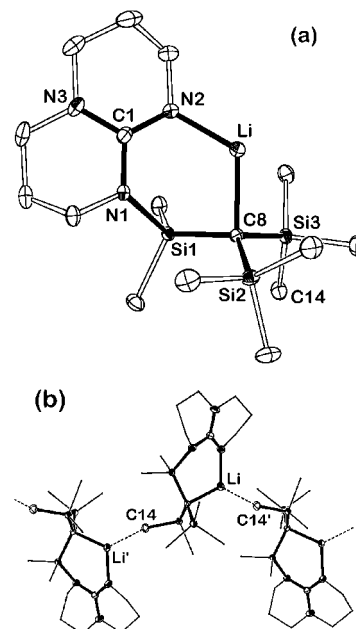


Figure 2. (a) ORTEP of LiC(SiMe₃)₂(SiMe₂hpp), **2** (ellipsoids at 30% probability; hydrogens omitted; [−] −x+1, y+1/2, −z+1/2; ⁺ −x+1, y−1/2, −z+1/2). Selected bond lengths (Å) and angles (deg): Li–C8 2.094(3), Li–N2 1.926(3), C1–N1 1.375(2), C1–N2 1.310(2), C1–N3 1.371(2), N1–Si1 1.8050(13); N2–Li–C8 115.91(14), Si1–C8–Si2 115.24(8), Si1–C8–Si3 117.38(8), Si2–C8–Si3 117.41(8). (b) Intermolecular Li···C interactions in **2**: Li···H 2.13, 2.15, 2.43 Å.

either oligomeric/polymeric,^{13,24–26} or solvated,^{26,27} compound **2** is monomeric in the solid state.²⁸ Weak interactions between Li and the methyl group of an adjacent molecule, which link the molecules of **2** into a chain along the *b* axis (Li···C 2.387(3) Å, Figure 2b), are of a similar strength to those in crystalline LiBH₄²⁹ and between (LiMe)₄ tetramers in methyl lithium [Li···C 2.36(1) Å in both cases].³⁰ Refinement of the hydrogen atoms on C14 shows no apparent distortion from normal geometry, indicating an almost symmetrical interaction with the three hydrogen atoms. The ¹H and ¹³C NMR spectra show that, in contrast to **1**, there are six distinct signals attributed to the CH₂ groups of the hpp fragment. These data indicate that the amido and imine nitrogen atoms are inequivalent, suggesting the latter is strongly coordinated to the metal and that the molecular structure is preserved in benzene solution.

The alkyllithium compound KC(SiMe₃)₂(SiMe₂hpp) (**3**) was synthesized by treatment of **1** with MeLi in the presence of potassium *tert*-butoxide⁸ and isolated as colorless crystals.

(24) Atwood, J. L.; Fjeldberg, T.; Lappert, M. F.; Luong-Thi, N. T.; Shakir, R.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1163–1165.

(25) (a) Schmidt, G.; Baum, G.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1111–1112. (b) Karsch, H. H.; Zellner, K.; Mikulcic, P.; Lachmann, J.; Müller, G. *Organometallics* **1990**, *9*, 190–194. (c) Ruhlandt-Senge, K.; Ellison, J. J.; Wehmschulte, R. J.; Pauer, F.; Power, P. P. *J. Am. Chem. Soc.* **1993**, *115*, 11353–11357. (d) Hardman, N. J.; Twamley, B.; Stender, M.; Baldwin, R.; Hino, S.; Schiemenz, B.; Kaulzlarich, S. M.; Power, P. P. *J. Organomet. Chem.* **2002**, *643*, 461–467.

(26) Eaborn, C.; Clegg, W.; Hitchcock, P. B.; Hopman, M.; Izod, K.; O'Shaughnessy, P. N.; Smith, J. D. *Organometallics* **1997**, *16*, 4728–4736.

(27) (a) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 1390–1391. (b) Viehhaus, T.; Walz, A.; Niemeyer, M.; Schwarz, W.; Weidlein, J. *Z. Anorg. Allg. Chem.* **2000**, *626*, 2040–2042.

(28) The molecular structure of LiCH(SiMe₃)₂ is monomeric in the gas phase. See ref 24.

(29) Rhine, W. E.; Stucky, G.; Peterson, S. W. *J. Am. Chem. Soc.* **1975**, *97*, 6401–6406.

(30) Weiss, E.; Hencken, G. *J. Organomet. Chem.* **1970**, *21*, 265–268.

(17) Oakley, S. H.; Coles, M. P.; Hitchcock, P. B. *Dalton Trans.* **2004**, 1113–1114.

(18) Maaranen, J.; Andell, O. S.; Vanne, T.; Mutikainen, I. *J. Organomet. Chem.* **2006**, *691*, 240–246.

(19) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353–451.

(20) Mulvey, R. E. *Chem. Soc. Rev.* **1998**, *27*, 339–346.

(21) Coles, M. P.; Hitchcock, P. B. *Chem. Commun.* **2005**, 3165–3167.

(22) Oakley, S. H.; Soria, D. B.; Coles, M. P.; Hitchcock, P. B. *Polyhedron* **2006**, *25*, 1247–1255.

(23) Papisergio, R. I.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1983**, 1419–1420.

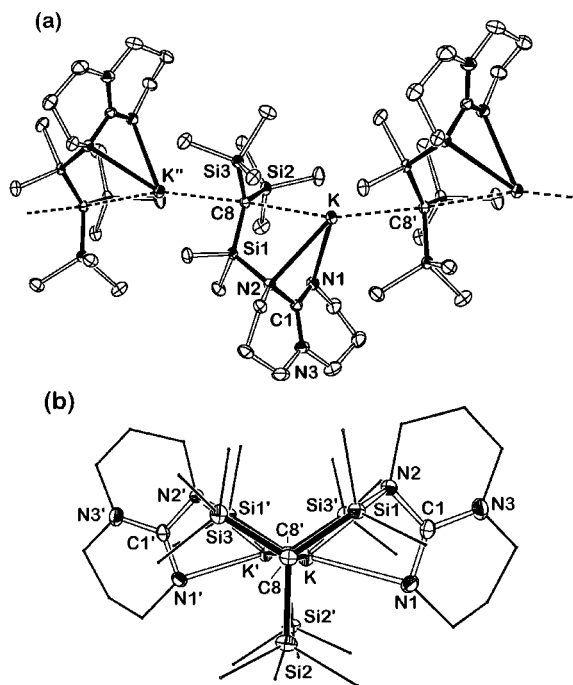


Figure 3. ORTEP of a section of the chain formed by $\text{KC}(\text{SiMe}_3)_2(\text{SiMe}_2\text{hpp})$, **3** (ellipsoids at 30% probability; hydrogens omitted; $'x+1/2, y, -z+3/2$; $''x-1/2, y, -z+3/2$). Selected bond lengths (Å) and angles (deg): K–C8 3.1727(19), K–C8' 3.3197(19), K–N1 2.7179(17), K–N2 2.9691(16), C1–N1 1.294(2), C1–N2 1.395(2), C1–N3 1.369(3), N2–Si1 1.8258(16); C8–K–C8' 164.699(16), K–C8–K'' 176.66(7), Si1–C8–Si2 124.71(11), Si1–C8–Si3 116.23(10), Si2–C8–Si3 118.99(10).

Spectroscopic and analytical data showed that the compound was solvent-free, as reported for the related dimethylamido-,¹⁵ methoxy-,¹² and 2-pyridyl-substituted¹¹ potassium salts ($\text{A}-\text{C}$, $[\text{M}] = \text{K}$, Figure 1). X-ray crystallography showed that the repeating unit of **3** is similar to that of **2** but that the coordination at the carbanionic center is planar ($\sum_{\text{Si}-\text{C}-\text{Si}} 359.9^\circ$). Compound **3** comprises slightly puckered chains of alternating potassium cations and carbanions with $\text{K}\cdots\text{C}\cdots\text{K} = 176.66(7)^\circ$ and $\text{C}\cdots\text{K}\cdots\text{C} = 164.699(16)^\circ$ (Figure 3a). The $[\text{CSi}_3]^-$ units are eclipsed (max. $\text{Si}-\text{C}\cdots(\text{K})\cdots\text{C}-\text{Si}$ torsion = 4.8°) with the hpp groups of adjacent units located on opposite sides of the $\cdots\text{C}\cdots\text{K}\cdots\text{C}\cdots$ backbone (Figure 3b).

The potassium–carbon distances (3.1727(19) and 3.3197(19) Å) are in the range found in related polymeric systems³¹ and in

(31) Smith, J. D. *Adv. Organomet. Chem.* **1999**, *43*, 267–348.

the parent potassium trisyl compound $[\text{KC}(\text{SiMe}_3)_3]_\infty$. $\text{K}\cdots\text{C} = 3.090(11)$ and $3.104(11)$ Å.³² Additional $\text{K}\cdots\text{C}$ distances < 3.5 Å, the shortest being to the central carbon of the hpp group ($\text{K}\cdots\text{C1} = 3.120$ Å), are associated with the tilt of the guanidine toward potassium that enhances the steric protection of the cation. As in **2**, the C8–Si bonds are short (av 1.813 Å) compared with the corresponding bonds in **1** and the remaining Si–Me bonds in **3** (av 1.891 Å).

In contrast to **2**, both the N1 and N2 atoms of the guanidine interact with the metal (K–N distances: 2.7179(17) and 2.9691(16) Å to N1 and N2, respectively), probably reflecting the greater ionic character of the metal–carbanion interaction. The ¹H and ¹³C NMR spectra of **3** in C_6D_6 at 25 °C indicate that exchange of Si between N2 and N1 is not sufficiently fast to give average signals for the CH_2 groups of the guanidine.

The increasing size of the ligands $\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{X})$ is shown by the C–Li–N bite angles, viz., 80° ($\text{X} = \text{NMe}_2$), 102° ($\text{X} = 2\text{-Py}$), 116° ($\text{X} = \text{hpp}$). The consequence is that the lithium derivative **2**, as well as the potassium compound **3**, can be isolated as an unsolvated crystalline solid. This significantly increases the potential of **2** and **3** as ligand transfer reagents in the synthesis of organometallic compounds, such as derivatives of alkaline earth metals³³ and lanthanides³⁴ known to cleave C–O bonds of ethers. We are currently studying how the greater bulk of the novel $\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{hpp})$ ligand and the strong basicity of the nitrogen donor can be exploited in the synthesis of kinetically stabilized low-coordinate organometallic compounds that are not available with previously described ligands.

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Supporting Information Available: Details of synthetic procedures and characterization details for compounds **1–3**; X-ray crystallographic data for compounds **1–3** as CIF files. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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(32) Eaborn, C.; Hitchcock, P. B.; Izod, K.; Jaggard, A. J.; Smith, J. D. *Organometallics* **1994**, *13*, 753–754.

(33) Eaborn, C.; Hawkes, S. A.; Hitchcock, P. B.; Smith, J. D. *Chem. Commun.* **1997**, 1961–1962.

(34) Eaborn, C.; Hitchcock, P. B.; Izod, K.; Lu, Z.-R.; Smith, J. D. *Organometallics* **1996**, *15*, 4783–4790.