Carbene-Lithium Interactions

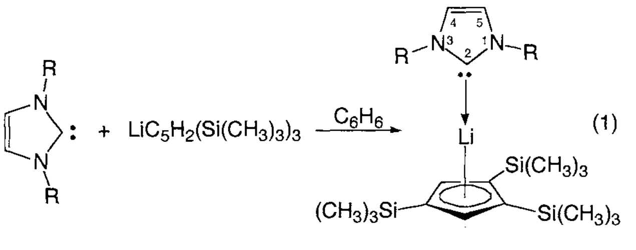
Anthony J. Arduengo, III,* Matthias Tamm,†,†† Joseph C. Calabrese,† Fredric Davidson,† and William J. Marshall†
Institut für Anorganische und Analytische Chemie der Technischen Universität, Postfach 3329, D-38023 Braunschweig, Germany
†DuPont Central Research, Experimental Station, Wilmington, Delaware 19880, U.S.A.

(Received June 8, 1999; CL-990486)

The syntheses and characterizations are described for carbene•lithium complexes in which the lithium center is ligated only by carbon atoms. A single crystal X–ray diffraction structure determination on one adduct confirms the coordination environment. The C–Li distance at the carbene center is 215.5 pm. All other coordination to the lithium center originates from a substituted η^5–cyclopentadienyl ligand with an average C–Li distance of 225.4 (7) pm.

Carbene•lithium complexes were among the first metal complexes to be formed directly from isolated stable imidazol–2–ylidenes and a variety of structural types have been reported.[1,2] Except for hydrogen[3] and to some extent lithium, the heavier alkali metals (Na–Cs) have not readily yielded crystalline carbene–main group 1 adducts. Only very recently has conclusive evidence emerged for complexation between Na^+ or K^+ and stabilized carbenes.[4] Among the alkali metals, even the more "carbon friendly" lithium has resisted attempts to produce homoleptic carbene complexes such as those observed for its transition group relatives (group 11 metals; Cu, Ag, Au).[5] We now report the first examples of carbene–lithium complexes in which the lithium center is coordinated only to carbon centers.

The stable carbenes **1a–c** react readily in benzene solution with lithium 1,2,4–tris(trimethylsilyl)cyclopentadienide to form the 1:1 complexes **2a–c** (Eq. 1).[6]



1 a: R = *tert.*-butyl **2**
b: R = 1-adamantyl
c: R = 2,4,6-trimethylphenyl

The carbene•lithium adducts **2a–c** are isolated as colorless solids that can be recrystallized from hexane. Both **2b** and **2c** have melting points over 200 °C while **2a** melts slightly lower at 170–4 °C. In C_6D_6 solution at room temperature the imidazole ^{13}C–2 centers in **2a–c** resonate at δ 190.7, δ 188.7 and δ 198.13 respectively. These resonances are all upfield of those for the corresponding carbenes and are similar to the previously reported carbene–lithium adducts in which heteroatoms (N, P, or O) are also coordinated to the lithium center.[1,2,4] The ^{1}H NMR spectra of **2a–c** in C_6D_6 solution reveal resonances for the imidazole $H^{4(5)}$ protons at δ 6.32, δ 6.54 and δ 6.57. The adamantyl substituted adduct **2b** shows a significant Δδ for these ring protons (0.37 ppm upfield) relative to the free carbene. The ^{7}Li NMR spectra of these adducts exhibit resonances upfield (δ –7.78, –7.63 and –9.01 for **2a–c** resp.) of the standard saturated lithium chloride in D_2O.

Crystals of **2a** suitable for X–ray crystallographic structure determination were grown by cooling a saturated hexane solution to –25 °C.[7] The solid state structure of **2a** is depicted by the KANVAS[8] drawing in Figure 1 and representative bond lengths and angles are presented in Table 1.

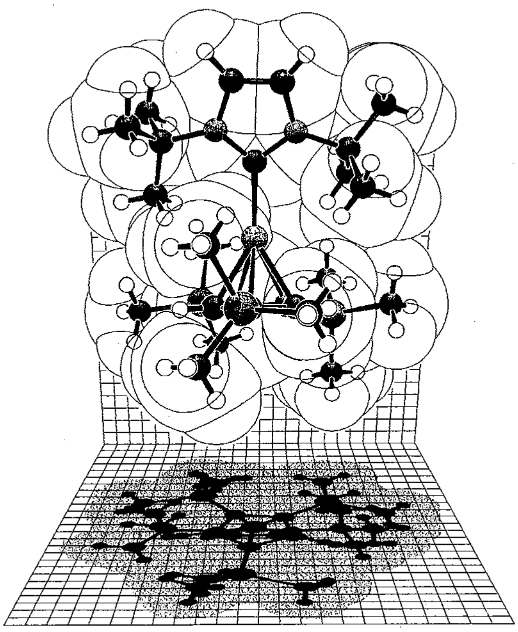


Figure 1. KANVAS drawing of the adduct **2a**.

Table 1. Selected bond lengths and angles in **1a** and **2a**

Property	**1a**[a]	**2a**
r(C^2–Li)	–	215.5 (4)
r(C^2–$N^{1(3)}$)	136.7 (7), 135.7 (7)	137.3 (3), 136.5 (3)
r($N^{1(3)}$–$C^{5(4)}$)	139.1 (7), 138.2 (7)	138.9 (3), 138.7 (3)
r(C^4–C^5)	134.1 (8)	133.2 (4)
$\bar{r}$ (C^{Cp}–Li)	–	225.4 (7)
r($Cp^{(centroid)}$–Li)	–	190.0
θ(C^2–Li– $Cp^{(centroid)}$)	–	167.5
θ(N^1–C^2–N^3)	102.2 (5)	102.7 (2)
θ(C^2–$N^{1(3)}$–$C^{5(4)}$)	112.1 (5), 113.1 (4)	111.3 (2), 112.2 (2)
θ($N^{1(3)}$–$C^{5(4)}$– $C^{4(5)}$)	106.5 (6), 106.1 (5)	107.4 (2), 106.4 (2)
θ(Li–C^2–$N^{1(3)}$)	–	126.6 (2), 129.7 (2)

[a] Ref. 9.

The X–ray structure of **2a** reveals that the lithium center is coordinated in an η^5–fashion to the cyclopentadienyl ring and that there is a single σ–interaction between the lithium and the carbene center. The lithium is positioned symmetrically over the Cp–ring so that the lithium is only 0.7° off a vector that is normal to the Cp–plane and passes through its centroid. The Li–Cp$^{(\text{centroid})}$ distance is 190 pm and the average C–Li distance to the Cp ring atoms is 225.4 (7) pm. The lithium is not symmetrically positioned with respect to the imidazole ring. The lithium center lies 215.5 pm from the carbene center but the C–Li bond vector is 8.9° away from the idealized imidazole C_2–axis. Most of this distortion occurs out of the imidazole plane so that the lithium resides 33.4 pm out of the plane of the five imidazole ring atoms. There is also a bending at the lithium center such that the C^2–Li–Cp$^{(\text{centroid})}$ angle is 167.5°. These deformations at lithium and C^2 give rise to an angle between the imidazole and Cp planes that is only 68.6° rather than the 90° that would be expected for ideal, symmetrical orientations. The overall geometry of **2a** is similar that observed for a related quinuclidine•lithium cyclopentadienide complex.[10]

The shortest lithium–carbon interaction is to the σ–bonded carbene center. This bond distance (215.5 pm) is within the range of distances observed for aryl–lithium compounds but lies at the longer extreme.[11,12] In complex **2a**, the anionic ligand (Cp) on lithium is bonded in a π–fashion while the neutral (carbene) ligand forms the C–Li σ–interaction. This arrangement is the reverse of the situation reported by Power *et al.* for the arene solvates of various aryl–lithiums.[11,12] Even though there is this difference in charge–type between the π– and σ–bonded ligands for the Power complexes and **2a**, the C–Li distances appear to depend more on whether C–Li interaction is of a σ– or π–nature rather that the charge–type (neutral or anionic) of the ligands involved. The Li–C distance in **2a** is similar to that reported for carbene adducts in which the lithium bears additional non–carbon ligands.[1,2] Another type of imidazole anion–lithium complex reported by Boche *et al.* shows a preference for strong N–Li interactions and longer C^2–Li distances.[13]

Finally, we should comment on the high field positions of the lithium NMR shifts for **2a–c**. These high field shifts are the result of positioning of the lithium cation in the shielding region of the anionic Cp ligand. Such shieldings have been observed for other lithium cyclopentadienyls and closely related structures.[10,14] The benzene solvated aryl–lithium of Schiemenz and Power shows this shielding effect to a lesser extent.[11] The highest field position for a lithium–carbene adduct is observed for **2c** (δ –9.01) in which it is possible that the mesityl substituents also contribute to magnetic shielding of the lithium center.

References and Notes

†† DuPont Visiting Research Scientist 1993-4.

1 a) A. J. Arduengo, Graduierten Kolleg der Technischen Universität und Freien Universität Berlin, Synthese und Strukturuntersuchung Niedermolekularer Verbindungen, December 1992. b) A. J. Arduengo, 2nd Heron Island Conference on Reactive Intermediates, Recent Advances in the Chemistry of Stable Nucleophilic Carbenes, Queensland Australia, July 1994. c) A. J. Arduengo; '96 ORCHEM (Bad Nauheim, Germany) Seminar Nucleophile Carbene: Gestern, heute und morgen, September 1996.

2 A. Wacker, H. Pritzkow, and W. Siebert, *Eur. J. Inorg. Chem.*, 843 (**1998**).

3 A. J. Arduengo, III, S. F. Gamper, M. Tamm, J. C. Calabrese, F. Davidson, and H. A. Craig, *J. Am. Chem. Soc.*, **117**, 572 (1995).

4 R. W. Alder, M. E. Blake, C. Bortolotti, S. Bufali, C. P. Butts, E. Linehan, J. M. Oliva, A. G. Orpen, and M. J. Quayle, *Chem. Commun. (Cambridge)*, 241 (**1999**).

5 A. J. Arduengo, III, H. V. R. Dias, J. C. Calabrese, and F. Davidson, *Organometallics*, **12**, 3405 (1993).

6 Preparation of **2a**. At 23 °C, a solution of [$(Me_3Si)_3C_5H_2$]Li (320 mg, 1.1 mmol) in 20 ml of benzene was treated with a solution of carbene **1a** (200 mg, 1.1 mmol) in 20 ml of benzene. After stirring for 2 h the solvent was removed in vacuo to afford a white solid. NMR analysis showed only pure **2a**. Recrystallization from hexane at –26 °C gave 372 mg (72%) as colorless needles. mp 170–174 °C; ^{1}H NMR (C_6D_6) δ 0.38 (s, 4–SiC*H*$_3$, 9 H), 0.56 (s, 1,2–SiC*H*$_3$, 18 H), 1.19 (s, CC*H*$_3$, 18 H), 6.31 (s, NC*H*, 2 H), 7.00 (s, 3,5–C*H*, 2 H); ^{13}C NMR (C_6D_6) δ 1.47 (s, Si*C*H$_3$), 2.72 (s, Si*C*H$_3$), 31.75 (s, C*C*H$_3$), 56.07 (s, *C*CH$_3$), 115.76 (4–*C*Si), 116.05 (s, N*C*H), 121.62 (s, 1,2–*C*Si), 127.94 (s, 3,5–*C*H), 190.65 (N*C*N); ^{7}Li NMR (C_6D_6) δ –7.78; ^{29}Si NMR (C_6D_6) δ –12.42 (s, 1 Si), –12.09 (s, 2 Si); Anal. Calcd for $C_{25}H_{49}LiN_2Si_3$: C, 64.04; H, 10.53; N, 5.97%. Found: C, 63.92; H, 10.44; N, 5.70%.

Preparation of **2b**. At 23 °C, a solution of [$(Me_3Si)_3C_5H_2$]Li (257 mg, 0.9 mmol) in 20 ml of benzene was treated with a solution of carbene **1b** (300 mg, 0.9 mmol) in 20 ml of benzene. After stirring for 2.5 h the solvent was removed in vacuo to give a white solid. Analysis by NMR spectroscopy revealed only the adduct **2b**. Recrystallization from hexane at –26 °C gave 230 mg (41%) of a microcrystalline powder. mp 224–230 °C; ^{1}H NMR (C_6D_6) δ 0.45 (s, SiC*H*$_3$, 9 H), 0.57 (s, SiC*H*$_3$, 18 H), 1.60 (m, $Ad_{4,6,10}$, 12 H), 1.82 (s br, $Ad_{2,8,9}$, 12 H), 2.10 (s br, $Ad_{3,5,7}$, 6 H), 6.54 (s, NC*H*, 2 H), 7.03 (s, C*H*, 2 H); ^{13}C NMR (C_6D_6) δ 1.60 (s, Si*C*H$_3$), 2.98 (s, Si*C*H$_3$), 29.84 (s, $Ad_{3,5,7}$), 36.06 (s, $Ad_{4,6,10}$), 44.69 (s, $Ad_{2,8,9}$), 56.74 (s, Ad_1), 114.72 (4–*C*Si), 116.10 (s, N*C*H), 121.97 (s, 1,2–*C*Si), (not observed, possibly under solvent), (s, 3,5–*C*H), 188.72 (N*C*N); ^{7}Li NMR δ (C_6D_6) δ –7.63; ^{29}Si NMR (C_6D_6) δ –12.48 (s, 1 Si), –12.29 (s, 2 Si); Anal. Calcd for $C_{37}H_{61}LiN_2Si_3$: C, 71.09; H, 9.84; N, 4.48%. Found: C, 69.32; H, 8.96; N, 4.20%.

Preparation of **2c**. At 23 °C, a solution of [$(Me_3Si)_3C_5H_2$]Li (289 mg, 1 mmol) in 20 ml of benzene was treated with a solution of carbene **1c** (304 mg, 1 mmol) in 30 ml of benzene. After stirring for 2 h the solvent was removed in vacuo to give a white solid. Analysis by NMR spectroscopy revealed only the adduct **2c**. Recrystallization from hexane at –26 °C gave 455 mg (77%) as cream colored needles. mp 210–212 °C, ^{1}H NMR (C_6D_6) δ 0.27 (s, SiC*H*$_3$, 9 H), 0.29 (s, SiC*H*$_3$, 18 H), 1.90 (s, 2,6–C*H*$_3$, 12 H), 2.19 (s, 4–C*H*$_3$, 6 H), 6.00 (s, C*H*, 2 H), 6.57 (s, NC*H*, 2 H), 6.81 (s, Ar*H*, 4 H); ^{13}C NMR (C_6D_6) δ 1.77 (s, Si*C*H$_3$), 2.84 (s, Si*C*H$_3$), 18.40 (s, 2,6–*C*H$_3$), 21.36 (s, 4–*C*H$_3$), 116.76 (4–*C*Si), 121.74 (1,2–*C*Si), 122.03 (s, N*C*H), 125.70 (s, 3,5–*C*H), 130.02 (s, Mes *C*–3.5), 135.01 (s, Mes *C*–2,6), 137.22 (s, *C*–1), 139.21 (s, *C*–4), 198.13 (s, N*C*N); ^{7}Li NMR (C_6D_6) δ –9.01; ^{29}Si NMR (C_6D_6) δ –12.66 (s, 1 Si), –12.34 (s, 2 Si); Anal. Calcd for $C_{35}H_{53}LiN_2Si_3$: C, 70.89; H, 9.01; N, 4.72%. Found: C, 71.65; H, 8.13; N, 6.34%.

7 Crystal data for **2a** at –80 °C with Mo Kα radiation: a = 988.5 (1), b = 1636.5 (1), c = 973.3 (1) pm, α = 96.326 (5)°, β = 97.183 (5)°, γ = 84.541 (5)°, triclinic, $P\bar{1}$, Z = 2, μ(Mo) = 1.62 cm^{-1}, 3365 unique reflections with $I > 3\sigma(I)$. Dc = 1.006 g/cc. The structure was solved by direct methods (MULTAN) and refined by full–matrix least–squares on F. Silicon, carbon and nitrogen were refined with anisotropic thermal parameters. Hydrogens were refined with isotropic thermal parameters. The data to parameter ratio was 7.03. The largest residual electron density in the final difference Fourier map was 0.25 e/Å^3 near C112. The error of fit was 1.37 and the maximum shift in the last least–squares cycle was 0.06. The final R factors were R = 0.040 and R_W = 0.042. Further details of the crystal structure have been deposited with the Cambridge Crystallographic Data Centre.

8 This drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL of E. Keller (Kristallographisches Institut der Universität Freiburg, Germany), which was modified by A. J. Arduengo, III to produce the back and shadowed planes. The planes bear a 50–pm grid and the lighting source is at infinity so that shadow size is meaningful.

9 A. J. Arduengo, III, H. Bock, H. Chen, D. A. Dixon, J. C. Green, W. A. Herrmann, N. L. Jones, M. Wagner, and R. West, *J. Am. Chem. Soc. 116*, 6641 (1994).

10 P. Jutzi, E. Schlüter, S. Pohl, and W. Saak, *Chem. Ber.*, **118**, 1959 (1985).

11 B. Schiemenz and P. P. Power, *Angew. Chem., Int. Ed. Engl.*, **35**, 2150 (1996).

12 K. Ruhlandt–Senge, J. J. Ellison, R. J. Wehmschulte, F. Pauer, and P. P. Power, *J. Am. Chem. Soc.*, **115**, 11353. (1993).

13 G. Boche, C. Hilf, K. Harms, M. Marsch, and J. C. W. Lohrenz, *Angew. Chem., Int. Ed. Engl.*, **34**, 487 (1995).

14 R. H. Cox and H. W. Terry, *J. Magn. Reson.*, **14**, 317 (1974).