Complexation of stable carbenes with alkali metals

Roger W. Alder,* Michael E. Blake, Christel Bortolotti, Simone Bufali, Craig P. Butts, Emma Linehan, Josep M. Oliva, A. Guy Orpen and Michael J. Quayle

School of Chemistry, University of Bristol, Cantock's Close, Bristol, UK BS8 1TS. E-mail: rog.alder@bristol.ac.uk

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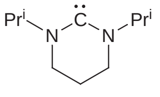
Stable diaminocarbenes, including imidazol-2-ylidenes, undergo complexation with lithium, sodium and potassium species; the crystal structure of a complex of 1,3-diisopropyl-3,4,5,6-tetrahydropyrimid-2-ylidene 1 with $KN(SiMe_3)_2$ is reported.

There is a vast literature concerning carbene complexes of metals. N-Heterocyclic carbenes are reported to complex with 48 elements, but Group 1 metals are notable by their absence.[1] We report ^{13}C NMR shift evidence concerning interaction between stable ylidic diaminocarbenes **1**–**3** and imidazol-2-ylidene **4** with lithium, sodium and potassium species in toluene and THF solutions, and the X-ray structure of $[\mathbf{1}\cdot KN(SiMe_3)_2]_2$. Since carbenes like **1**–**4** are often generated by C-deprotonation of formamidinium and related cations by bases with alkali metal counterions (*e.g.* $KOBu^t$, NaH, and LDA),[2–6] the observation of complexation with these ions is important in understanding of the properties of these carbenes in solution.



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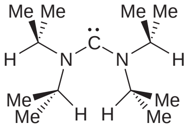

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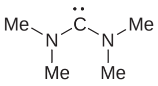

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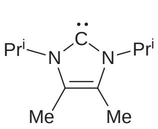

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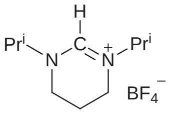

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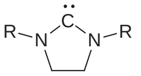

6a R = Pr^i
b R = Me

Carbene **1** can be prepared in 40% yield by deprotonation of **5** with $NaN(SiMe_3)_2$ in THF at −78 °C, exchange of solvent to toluene to permit azeotropic removal of $HN(SiMe_3)_2$, followed by distillation of **1**, which melts close to ambient temperature (all operations involving diaminocarbenes were performed under dry N_2). Precursor **5** is conveniently made by refluxing an equimolar mixture of $Pr^iNH(CH_2)_3NHPr^i$ and NH_4BF_4 in $HC(OEt)_3$ as solvent, with azeotropic removal of EtOH. Diaminocarbene **1** is the first example where the N–C–N group is part of a six-membered ring, and appears to be thermodynamically stable to dimerisation, unlike the five-membered ring analogue **6a**.[7] Thus **1** is stable when generated from **5** using a deficiency of base, but generation of **6a** under these conditions leads to rapid dimerisation, due to catalysis by the dihydroimidazolium precursor.[8]

A solution of free **1** in toluene-d_8 shows resonances at δ_C 236, 58, 36, 22 and 21. The ^{13}C shift of the carbene centre in stable carbenes typically occurs between δ_C 200 and 300,[2–6] but is substantially shielded in known metal complexes, and so provides a sensitive probe for complexation. The chemical shift of the carbene centre in **1** depends on the amount and nature of the alkali metal species present in toluene-d_8 solution (limiting shifts are given in Table 1), but is only affected by the presence of massive amounts (*ca.* 6 equiv.) of $LiN(SiMe_3)_2$ in THF-d_8, presumably because of competition from the solvent for Li. The chemical shifts of **1** and **3**, and of their complexes with Li^+, Na^+ and K^+ ions, have been calculated (Table 1), using the B3LYP/6-31G*/GIAO method.[9] The changes observed on complexation in solution are, not surprisingly, smaller than those calculated for complexation to the bare cations.

Addition of 12-crown-4 in portions to solutions of **1** in toluene-d_8 generated from **5** using lithium 2,2,6,6-tetramethylpiperidide (LiTMP) leads to quantitative precipitation of $LiBF_4\cdot$12-crown-4 (no NMR signals for free 12-crown-4 are observed until >1 equiv. has been added), with the ^{13}C NMR shift of the carbene centre moving smoothly from δ_C 218 to 236, indicating that the equilibrium between free **1** and the lithium complex is fast on the NMR timescale. It appears that the $LiBF_4$ formed in the reaction is soluble until the 12-crown-4 is added. On the other hand, portionwise addition of 2 equiv. of $LiN(SiMe_3)_2$ in toluene-d_8 to a solution of free **1** in toluene-d_8, generated using $NaN(SiMe_3)_2$ as described above, leads to the ^{13}C signal moving to δ_C 218, but subsequent addition of 12-crown-4 leads to a limiting shift of δ_C 224, suggesting the formation of a soluble tertiary complex containing 12-crown-4, $LiN(SiMe_3)_2$ and carbene **1**.

Portionwise addition of 2 equiv. of $NaN(SiMe_3)_2$ to free **1** in toluene-d_8 leads to the chemical shift moving smoothly to δ_C 224. When 15-crown-5 is then added in portions, the chemical

Table 1 Limiting observed and calculated ^{13}C NMR chemical shifts for the carbene centre of carbenes **1**, **3** and **4**

		Free	Li complex		Na complex		K complex	
Carbene	Conditions	δ_C	δ_C	[Li]/[carbene]	δ_C	[Na]/[carbene]	δ_C	[K]/[carbene]
1	THF-d_8, $MN(SiMe_3)_2$	237.4	221.2	8.3	—	—	—	—
	Toluene-d_8, $MN(SiMe_3)_2$	236.1	216.8	15.2	221.3	11.1	226.7	17.2
	GIAO calc.[a]	232.7	190.2	—	198.5	—	200.3	—
3	Toluene-d_8, $MN(SiMe_3)_2$	—	238.4	—	—	—	—	—
	THF-d_8, LiTMP	—	244.0	2.6	—	—	—	—
	THF-d_8, LiTMP + LiOTf	—	240.2	5.0	—	—	—	—
	GIAO calc.	246.9	202.9	—	—	—	—	—
4	Toluene-d_8, $MN(SiMe_3)_2$	206.8	195.7	7.0	196.4	7.1	201.1	4.2

[a] For the [carbene–K]$^+$ species, σ is estimated from B3LYP/LANL2DZ calculations, since there is no 6-31G* basis set for K.

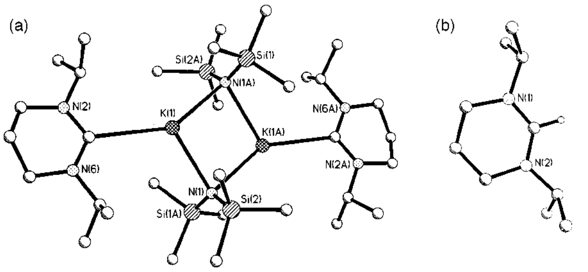

Fig. 1 (a) Molecular structure of [**1**·KN$(SiMe_3)_2]_2$. (b) Molecular structure of the cation of **5**.

Table 2 Structural parameters for **1** and related species

	$C_{carbene}$–N distance/Å	N–$C_{carbene}$–N angle (°)
[**1**·KN$(SiMe_3)_2]_2$	1.345(2)	116.3(2)
DFT structure for **1**	1.353	116.2
5	1.310(2)	125.1(2)
2	1.372(6) (av.)	121.0(5)

shift moves back to δ_C 236 as the free carbene is released. In a similar way, the addition of 2 equiv. of KN$(SiMe_3)_2$ in toluene leads to a chemical shift of δ_C 228. On standing, crystals were obtained from this solution and subjected to X-ray structure determination.† The structure [Fig. 1(a)] shows that dimeric molecules are present with the N$(SiMe_3)_2$ groups acting as bridging ligands. The K···C distance of 3.00 Å is much greater than the M···C distances for non−alkali metal complexes of imidazol-2-ylidenes,[1] which are typically < 2.3 Å. The Cambridge Structural Database[10] yielded no data on potassium complexes with σ-bound sp^2 carbon ligands. However, in the infinite chain structure of $(Me_3Si)_3CK$, the K···C distance is 3.10 Å,[11] while $Me_3Sn(Cl)N{\equiv}CK$ possesses a significantly shorter K···C distance of 2.75 Å,[12] and in KCN itself, the K···C distance is 2.8 Å.[13] Thus the K···C distance in [**1**·KN$(SiMe_3)_2]_2$ appears to be normal, but suggests that the interaction is largely of an electrostatic ion–dipole nature. Mixed complexes of KN$(SiMe_3)_2$ with LiN$(SiMe_3)_2$ and with NaN$(SiMe_3)_2$, displaying a similar dimeric core structure but with two THF ligands co-ordinated to the potassium, show K···O(THF) distances of 2.69 and 2.71 Å respectively.[14] In the light of this structural evidence, it is not surprising that complexation of **1** is more difficult to observe in THF solution.

The structural parameters of the carbene ligand itself are similar to those obtained from B3LYP/6-31G* DFT calculations for free **1**, and to those observed for **2** (Table 2). In the complex, the isopropyl groups are oriented away from the bulky N$(SiMe_3)_2$ groups, as might be expected. However, the same conformation is observed‡ for **5** [Fig. 1(b)], and is also calculated to be preferred by free **1**. The decrease in the N–$C_{carbene}$–N angle on deprotonation of **5** is striking, but some decrease has been observed in every other comparable case.[2,3,5] The increase in the $C_{carbene}$–N distance on deprotonation of **5** is also in line with previous examples, and suggests some decrease in π-bonding in **1** compared with **5**.

Complexation with alkali metal species also occurs with imidazol-2-ylidene **4**, although the upfield shifts are somewhat less than for **1** (Table 1). Bis(diisopropylamino)carbene **2** is much more hindered that **1** due to the buttressing effect of the isopropyl groups,[4] and we see little evidence for complexation in this case. Conversely, the least hindered carbenes[15] like **3** should be better ligands and their behaviour may be affected by the presence of metal species even in THF. This carbene has been generated using LDA or LiTMP bases and all attempts so far to remove the lithium species have resulted in precipitates which could not be separated without destroying the carbene. The question of alkali metal co-ordination to **3** and bis(*N*-piperidyl) carbene is particularly important with regard to the rates and mechanism of dimerisation of these carbenes. Metal ions might act as Lewis acid catalysts for dimerisation, as is observed for protons,[8,15] but strong complexation should eventually suppress dimerisation. Preliminary results suggest the latter effect is dominant, thus reaction of $HC(NMe_2)_2{\cdot}Cl$ with LiTMP in toluene-d_8 leads to a solution of **3** in which its half-life is extended to many days as compared to a few hours in THF. Addition of 2.4 equiv. of LiOTf to THF solutions of **3** generated using 2.6 equiv. of LiTMP leads to an upfield shift (Table 1) and halves the rate of dimerisation. The half-life of **3** in the absence of lithium may therefore be quite short, although Denk *et al.*[7] have reported that **6b**, which is surely less hindered than **3**, can be observed at ambient temperatures when prepared by reaction of the corresponding thione with potassium metal. The dimerisation of **3**, and the influence of metal species on this process, are the subject of continuing studies.

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Notes and references

† *Crystal data* for [**1**·KN$(SiMe_3)_2]_2$: $C_{32}H_{76}K_2N_6Si_4$, *M* = 735.55, colourless block, 0.52 × 0.46 × 0.42 mm, triclinic, $P\bar{1}$ (no. 2), a = 9.413(1), b = 10.937(3), c = 12.306(2) Å, α = 73.97(2), β = 73.132(12), γ = 69.426(10)°, V = 1113.5(3) Å^3, T = 173 K, Z = 1, μ = 0.348 mm^{-1}, 11499 reflections measured, 5034 independent, 4058 observed, 202 parameters. The structure was solved by direct methods and refined on F^2. R_1 = 0.0266 for observed data and 0.0343 for all data.

‡ *Crystal data* for **5**: $C_{10}H_{21}BF_4N_2$, *M* = 256.10, colourless block, 0.4 × 0.4 × 0.2 mm, orthorhombic, $P2_12_12_1$ (no. 19), a = 8.434(1), b = 10.467(3), c = 15.389(4) Å, V = 1358.57(5) Å, T = 173 K, Z = 4, μ = 0.112 mm^{-1}, 8599 reflections measured, 3095 independent, 2184 observed, 199 parameters, 94 restraints. The structure was solved by direct methods and refined on F^2. R_1 = 0.0394 for observed data and 0.0664 for all data. The BF_4 counterion was disordered over two sites and restrained in geometry. CCDC 182/1119. The crystallographic data is available in CIF format from the RSC web site, see: http://www.rsc.org/suppdata/cc/1999/241/

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