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Bis(diethylamino)carbene and the mechanism of dimerisation for simple diaminocarbenes

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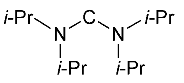
Bis(diethylamino)carbene is kinetically stable to dimerization in THF at ambient temperature; dimer formed during carbene generation arises from reaction of the carbene with the precursor formamidinium ion; this is probably the commonest route to tetraaminoethene dimers, and in a related case the intermediate protonated tetraaminoethene can be observed by NMR.

Most studies of diaminocarbenes have been concerned with five-membered ring species (imidazol-2-ylidenes and imidazolin-2-ylidenes),[1,2] although it is increasingly clear that six-membered and acyclic diaminocarbenes may be stronger bases and better σ-donor ligands.[3–5] We reported the preparation of the first stable acyclic diaminocarbene bis(diisopropylamino)carbene **1** in 1996.[6] We also reported that solutions containing dipiperidinylcarbene and bis(dimethylamino)carbene **2** could be easily generated at ambient temperatures in THF,[7] although it subsequently emerged that these are complexed to lithium derived from the bases used in their generation.[8] Bertrand[9] has recently reported the preparation of metal-free **2** at −80 °C from the reaction of 2-chloro-1,1,3,3-tetramethylformamidinium chloride with $Hg(SiMe_3)_2$. On warming to 0 °C, **2** disappeared without forming any of the well-known dimer **3**. We now report the generation of bis(diethylamino)carbene **4** (Scheme 1) and experiments which reveal how the known dimer **5**[10] is formed.



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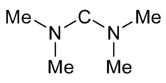

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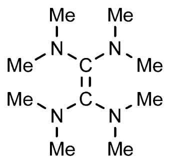

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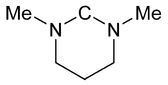

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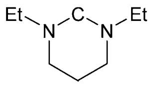

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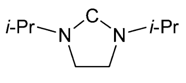

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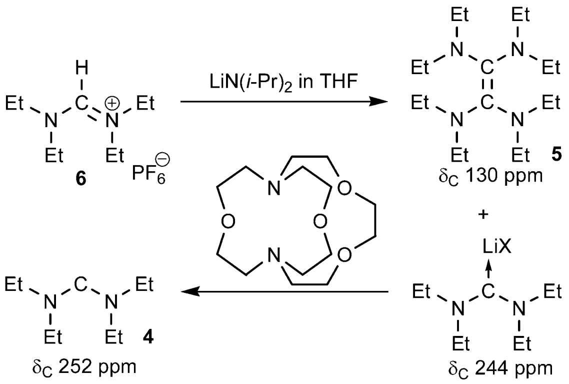


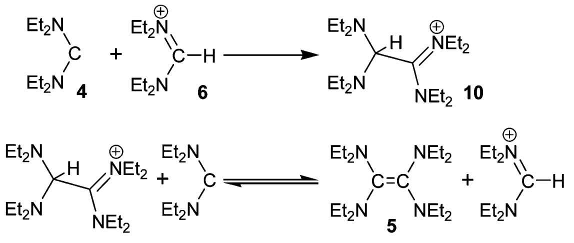
Scheme 1

Carbene **4** was generated by adding LDA (1 equiv.) in THF to a THF solution of tetraethylformamidinium hexafluorophosphate **6** (Scheme 1).[11] The THF was removed by evaporation and the residue taken up in hexane and filtered to remove inorganic salts (all operations were carried out under an atmosphere of dry nitrogen). The filtrate was evaporated, and the residue taken up in THF-d_8 for NMR.[12] As shown in Scheme 1, this results in mixtures of carbene and dimer, each recognised by their distinctive ^{13}C NMR shifts; the ratio of carbene to dimer is typically *ca.* 70 : 30. Addition of 1 equivalent of [2.1.1] cryptand results in the ^{13}C resonance for the carbene centre shifting from 244 ppm to 252 ppm. Addition of more cryptand does not lead to any further shift in the ^{13}C resonance, so free carbene is clearly now present (we have reported[8] that crown ethers are inadequate for removing lithium complexation). Once formed, the free bis(diethylamino)carbene **4** remains essentially unchanged in THF solution at ambient temperature for at least a week. A small amount of general decomposition is observed, but no dimer beyond that already present is formed.

It is clear that **4** is kinetically stable even though equilibrium surely favours the dimer. Bertrand[9] has reported that diaminocarbene **7** generated by reaction of 2-chloro-1,4,5,6-tetrahydro-1,3-dimethylpyrimidinium chloride with $Hg(SiMe_3)_2$ is indefinitely stable and can be sublimed at 40 °C. We have observed that **7**, **8** and **9**,[13] generated by deprotonation, do not dimerise over periods of days at room temperature in THF-d_8, so that carbene **4** is far from unique in this respect. On the contrary, we know of no authentic example of direct dimerisation of a diaminocarbene.

Where did the dimer formed in the reaction used to prepare **4** come from? A reasonable hypothesis is that it results from reaction of **4**, a powerful nucleophile, with **6** (Scheme 2).[14] Fortunately **6** is relative soluble in THF, and so it is possible to add a solution of this slowly by syringe pump to LDA in THF. The result of this reverse addition procedure is the formation of nearly pure carbene **4** with <5% dimer **5**. Further confirmation of the source of **5** comes from an experiment in which 0.5 equivalent of LDA in THF is added to a THF solution of **6**. This reaction cleanly produces 0.5 equivalent of dimer **5** with 0.5 equivalent of **6** remaining unchanged; no carbene **4** is observed. Clearly carbene **4** is a sufficiently powerful base that it rapidly deprotonates the intermediate **10**.

There appears to be no report on the protonation of tetraaminoethenes, although they may be expected to be strongly basic. However Chen and Jordan[15] demonstrated by elegant labeling experiments that dimer formation during thiazolium ion-catalysed



Scheme 2

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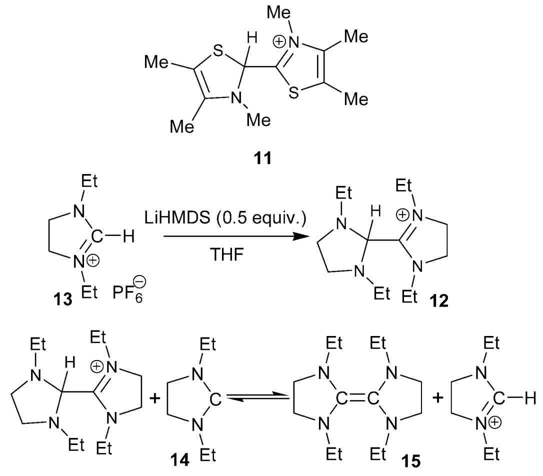

Scheme 3

benzoin condensation occurred *via* intermediate **11** (Scheme 3), which was observed by ^{13}C NMR. We have found by NMR[16] that **12** is cleanly formed when 0.5 equivalent of LiHMDS in THF is added to a THF solution of **13** (Scheme 3). The ^{1}H and ^{13}C NMR chemical shifts for **12** closely resemble those for **11**; in particular we note the non-equivalence of the ethyl and ring methylene groups in the aminal ring of **12**. Presumably the proton transfer equilibrium now lies to the left because **14** is unable to deprotonate **12**. B3LYP/6-31G* calculation[17] of the proton affinities of **4** (1171), **5** (1054), **14** (1125) and **15** (1130 kJ mol^{-1}) provide some support for this explanation of the difference between the two cases.

In summary, we report that rather simple diaminocarbenes like **4**, **7**, **8**, and **9** can have long lifetimes in THF solution even when dimerization is thermodynamically favourable, but we also find that dimerization occurs rapidly in the presence of proton sources which generate formamidinium ions. Ion **12** represents the first observation of a C-protonated tetraaminoethene.

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12 ^{1}H NMR for metal-free **4** (in THF-d$_8$): 1.14 (t, 12H); 3.31 (q, 8H); ^{13}C NMR (in THF-d$_8$): 16.0; 49.1; 252.2 ppm.

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14 This mechanism is essentially the reverse of that proposed by Lemal to explain the formation of products derived from diaminocarbenes during electrophilic attack on tetraaminoethenes: D. M. Lemal, R. A. Lovald and K. I. Kawano, *J. Am. Chem. Soc*, 1964, **86**, 2518.

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16 ^{1}H NMR for **12** (in CD$_2$Cl$_2$): 1.02 (t, 6H); 1.20 (t, 6H); 2.40 (m, 2H); 2.53 (m, 2H); 2.60 (m, 2H); 3.29 (m. 2H); 3.70 (q, 4H); 3.86 (s, 4H); 3,91 (s, 1H); ^{13}C NMR (in CD$_2$Cl$_2$): 12.0; 12.9; 41.8; 46.7; 46.9; 49.7; 78.76 (*C*H); 165.0 (amidinium carbon) ppm.

17 Calculations were performed with the Jaguar program package (Jaguar 4.2 edn.; Schrodinger, Inc., Portland, OR, USA, 1991–2002) using Becke's three-parameter exchange functional (A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648) with the correlation functional of Lee, Yang and Parr (B3LYP) (C. T. Lee, W. T. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785); full details will be reported elsewhere.