Bis(*N*-piperidyl)carbene and its slow dimerisation to tetrakis(*N*-piperidyl)ethene

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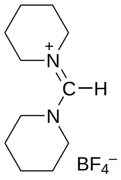
An unhindered bis(*sec*-amino)carbene can be generated by deprotonation of an amidinium ion with lithium diisopropylamide, and undergoes remarkably slow dimerisation to the corresponding tetraaminoethene.

When amidinium salt **1** is treated with lithium diisopropylamide in THF at −80 °C, allowed to warm to room temperature, the THF removed and the residue dissolved in [$^2H_8$]toluene (all operations conducted under dry nitrogen), signals for two species are seen in the ^{13}C NMR spectrum. One of these is readily identified as the known[1] tetrakis(*N*-piperidyl)ethene **2** (δ 25.7, 27.4, 51.6 and 134.6). The other species has lines at δ 24.8, 27.2, 53.1 and 236.8, and we assign this to bis(*N*-piperidyl)carbene **3**, on the basis of the chemical shift for the unique carbon [the central carbon in **4** absorbs at δ 255,[2] and other known[3] ylidic bis(*sec*-amino)carbene derivatives all absorb in the range δ 210–270]. All likely alternatives absorb at much lower chemical shifts (the central carbon of **1** occurs at δ 154, the carbonyl carbon in the urea absorbs at δ 171, and triaminomethane derivatives typically absorb at about δ 100). The subsequent behaviour of **2** and **3** is conveniently monitored by following the CH_2–N absorptions in the ^1H NMR spectrum, which come at δ 2.90 for **2** and δ 3.15 for **3**. Careful purification of all reagents and rigorous exclusion of air and water leads to solutions where the signals for **2** increase proportionally as those for **3** disappear (integration with respect to the residual protons in the solvent);† however, even under these conditions the reaction rate is only first order with respect to the carbene **3**. Signals for **3** persist for >24 h in [$^2H_8$]toluene, but conversion to **2** occurs within 3 h in [$^2H_8$]THF.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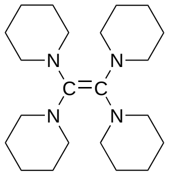
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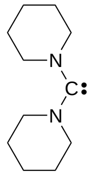
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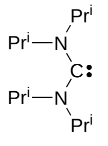
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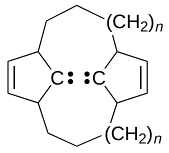
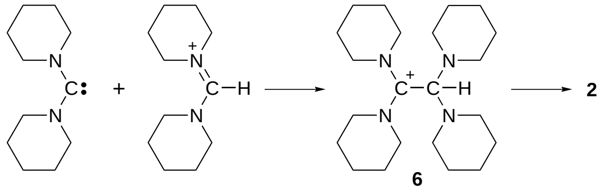

5a *n* = 1
b *n* = 2

Why is some dimer generated in the initial reaction with base, and why is dimerisation first order in carbene? We suggest that, during the initial reaction, carbene **3** attacks precursor **1** to generate substituted amidinium ion **6**, which is then deprotonated to give **2** (see Scheme 1). This is the reverse of the mechanism proposed by Lemal[4] to account for reactions of the tetraaminoethene derivatives studied by Wanzlick which give products apparently derived from bis(*sec*-amino)carbenes. Wanzlick[5] had proposed that there was reversible dissociation of the tetraaminoethenes, but Lemal showed that this was not the case through a crossover experiment. The subsequent slow conversion of **3** to **2** may occur by rate-limiting regeneration of low concentrations of **1** from **3** (*e.g.* by reaction with residual diisopropylamine), followed by the steps in Scheme 1. Clearly uncatalysed dimerisation of **3** is too slow to be competitive; we estimate that $\Delta G^\ddagger \geqslant 100$ kJ mol^{-1} for this process in [$^2H_8$]toluene. Arduengo *et al.*[6] have recently reported the generation of a stable thiazol-2-ylidene and its dimer; they find that the carbene only dimerises in the presence of the thiazolium ion precursor, further supporting Scheme 1.

Why is dimerisation of **3** so sluggish? Both thermodynamic and kinetic factors must be considered. Recent calculations[7,8] and experimental results[9] with imidazol-2-ylidenes show that dimerisation of these carbenes can actually be thermodynamically unfavourable. In particular, Taton and Chen[9] have shown that intramolecular double bond formation is favourable for **5a**, but that equilibrium favours the bis-carbene for **5b**. These remarkable observations are partially due to loss of aromaticity in the tetraazafulvalene dimers and calculations predict a dissociation energy of about 200 kJ mol^{-1} for the parent tetraaminoethene,[8] still much lower than for ethene itself (710 kJ mol^{-1}). Steric effects will reduce the dissociation energy in **2** somewhat, but the conversion of **3** to **2** is clearly favourable, and so there must be a high intrinsic barrier to the dimerisation. Hoffmann *et al.*[10] pointed out that dimerisation of singlet methylene to ethene is forbidden along the least motion pathway. They proposed a non-least motion pathway in which the sp^2 lone pair of one methylene approached the empty p orbital of the other. In their extended Hückel calculations, this approach led to ground state ethene without activation energy. More sophisticated theoretical calculations[11] suggest a barrier of about 170 kJ mol^{-1} for this non-least motion process and moreover that it leads to an excited state of ethene. There are therefore good theoretical grounds for expecting a very significant electronic barrier in this sort of process. In addition, there could be significant steric interactions between the piperidyl rings of **3** in the non-least motion approach. We note that both rate-limiting proton transfer (as suggested above) and the uncatalysed non-least motion process are likely to involve considerable charge separation in the transition state, and so will occur faster in more polar solvents.

The persistence of the diaminocarbene **3** is very striking and it now seems that almost any bis(*sec*-amino)carbene should be observable‡ at ambient temperatures under conditions which take account of the strong basicity[12] and nucleophilicity of these species. In fact, $(Me_2N)_2C$ (δ_C 244.4) has now been generated



Scheme 1

using similar procedures and a study of its behaviour is currently in progress.

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Footnotes and References

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† Carbene **3** is extremely sensitive to reaction with impurities. In early experiments, even with the usual precautions, signals for **3** disappeared over 1–3 h without a concomitant increase in the absorptions due to **2**.

‡ Unhindered 1,3-dialkyl-4,5-dihydroimidazol-2-ylidenes with isopropyl and methyl substituents have been generated and observed to dimerise slowly: M. K. Denk, A. Thadani, K. Hatano and A. Lough, *Angew. Chem.*, in the press.

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