

Synthesis and structural characterisation of stable pyridine- and phosphine-functionalised *N*-heterocyclic carbenes

Andreas A. Danopoulos,^{*a} Scott Winston,^a Thomas Gelbrich,^a Michael B. Hursthouse^a and Robert P. Tooze^b

^a Department of Chemistry, University of Southampton, Highfield, Southampton, UK SO17 1BJ.

E-mail: ad1@soton.ac.uk

^b ICI-Synetix, PO Box 1, Belasis Ave, Billingham, UK TS23 1BL. E-mail: bob_tooze@ici.com

Received (in Cambridge, UK) 21st December 2001, Accepted 25th January 2002

First published as an Advance Article on the web 7th February 2002

Stable, uncoordinated {1-[2-(6-trimethylsilyl)pyridyl]-3-[(2,6-diisopropyl)phenyl]imidazol-2-ylidene}, **I**, and {1-[(diphenylphosphino)ethyl]-3-[(2,6-diisopropyl)phenyl]imidazol-2-ylidene}, **II**, have been synthesised; in the solid state they adopt a conformation with the lone pairs in a mutually *anti* arrangement.

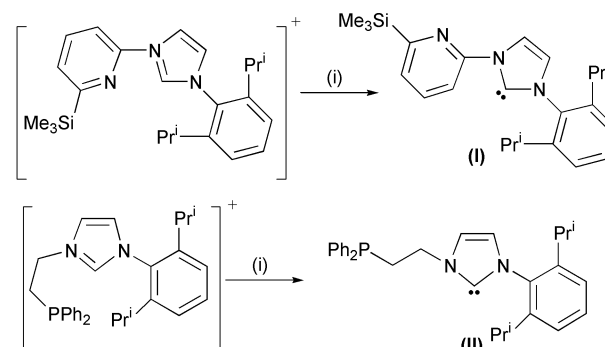
The isolation of free *N*-heterocyclic carbenes (NHC) by Arduengo was a milestone in the development of organic and organometallic chemistry of these remarkable species.^{1,2} The use of bulky alkyl or aryl substituents on the heterocyclic nitrogen atoms was considered as crucial for their stability by providing steric protection of the reactive divalent carbene carbon. NHCs have been intensively explored as spectator ligands on transition metals:² the strong and (usually) inert metal–carbene σ -bond, which has been compared to metal–trialkylphosphine bonding,³ in combination with the numerous opportunities for electronic and steric ligand tuning provide a desirable plateau for transition metal catalyst development. Toward this end ligand designs incorporating the NHC donor connected by suitable linkers to other ‘classical’ heteroatom donors seemed attractive, because they could combine the strong spectator characteristics of the NHCs with functional groups of diverse σ - and π -bonding, softness and size providing control over the coordination environment of the metal and, possibly, its catalytic activity. *N*-heteroatom-functionalised NHC complexes have been synthesised by us⁴ and others⁵ using the following synthetic methods: (i) *in situ* reaction of a liberated functionalised NHC with transition metal precursors; the liberation method involves deprotonation of imidazolium salts with organometallic or inorganic bases in nonprotic solvents; (ii) transmetalation of the functionalised NHC usually from silver(I) and copper(I) complexes; and (iii) reaction of metal precursors with electron rich tetraamino olefins of the Wanzlick-type. All these methods present limitations when complexes with metals in low oxidation state or containing other base-sensitive organometallic co-ligands are targeted.

Herein we wish to communicate preliminary results on the synthesis, isolation and full characterisation of *free* heteroatom-functionalised NHCs. The availability of these species provides exciting opportunities for accessing new families of complexes with a variety of co-ligands by simple substitution chemistry on coordinatively unsaturated metal centres or in complexes with labile ligands.

Deprotonation of the pyridine-substituted imidazolium salt[†] (Scheme 1), by KN(SiMe₃)₂ in THF between –10 and 0 °C followed by crystallisation from petroleum ether gave the functionalised NHC, **I**,[‡] in 75–80% yield as white, air-sensitive but stable at room temperature, crystals. The reaction has been run successfully at up to a 5 g scale.

The structure of **I** was determined by X-ray crystallography and is shown in Fig 1.[§]

The pyridine and carbene rings are coplanar and the pyridine nitrogen and the carbene carbon are mutually ‘*anti*’. This arrangement is probably favoured by the minimisation of electronic repulsions between lone pairs. A similar conformation has been observed in the solid state structure of 2,2’-



Scheme 1 Reagents and conditions: i, KN(SiMe₃)₂/THF, –10 to 0 °C.

bipyridyl.⁶ The dihedral angle between the plane of the bulky [2,6-(diisopropyl)phenyl] substituent and the plane of the carbene ring is 91.7°.

In an analogous way deprotonation of the 1-[(diphenylphosphino)ethyl]-3-[(2,6-diisopropyl)phenyl]imidazolium[†] bromide by KN(SiMe₃)₂ in THF gave the diphenylphosphine-functionalised NHC **II** in 60–70% yield as colourless, air-sensitive crystals (Scheme 1). The structure of **II** has been determined by X-ray diffraction and is shown in Fig. 2.[§] In this case too the molecule adopts a conformation in which the lone pairs on the phosphorus and the carbene carbon are mutually ‘*anti*’. A similar conformation has been observed in the solid state structure of 1,2-bis-(diphenylphosphino)ethane.⁷ The dihedral angle between the plane of the bulky [2,6-(diisopropyl)phenyl] substituent and the plane of the carbene ring is 83.2°.

It is interesting to notice that for the isolation of **I** and **II** the presence of bulky groups on both nitrogen atoms of the heterocyclic ring is not necessary. It has recently been proposed that the stability of imidazol-2-ylidenes is dependent on both electronic and steric factors.⁸ Furthermore, the isolation of **II** shows that, in contrast to the known reactivity of phosphines

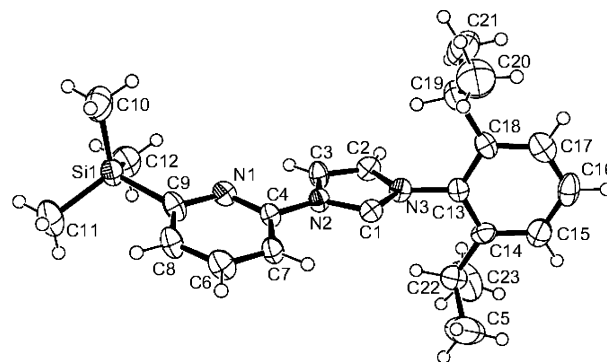


Fig. 1 Molecular structure of **I**. Thermal ellipsoids shown at 50% probability. There are two independent molecules in the asymmetric unit. Selected bond lengths (Å) and angles (°): C1–N2 1.366(7), C1–N3 1.360(7), C2–C3 1.311(7), C2–N3 1.387(7), C3–N2 1.392(7); dihedral angle C1–N2–C4–N1 169.0, C14–C13–N3–C1 91.7.

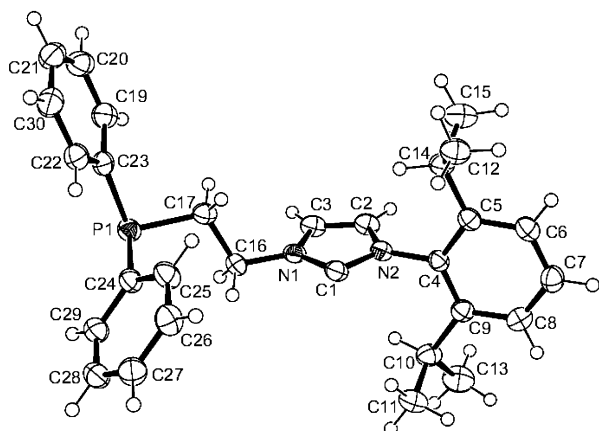


Fig. 2 Molecular structure of **II**. Selected bond lengths (Å) and angles (°): C1–N1 1.367(4), C1–N2 1.378(4), C2–C3 1.337(4), C2–N2 1.386(4), C3–N1 1.386(4), C16–N1 1.459(4), C16–C17 1.513(4), C17–P1 1.843(3); dihedral angle C9–C4–N2–C1 83.2, N1–C16–C17–P1 167.2.

with classical carbenes which give rise to phosphoranes, the phosphine ligands are inert to NHC.⁹

Preliminary results indicate that **I** and **II** show rich reactivity with metal precursors from across the transition series. This area, as well as the synthesis of a range of functionalised NHCs, are currently under investigation and results will be reported in due course.

Notes and references

† The pyridine-substituted imidazolium bromide was prepared from 1-(2,6-diisopropylphenyl)imidazole and 2-bromo-6-trimethylsilyl pyridine, following an analogous procedure to the one described in the literature.^{4b}

1-[β-(Diphenylphosphino)ethyl]-3-[(2,6-diisopropyl)phenyl]imidazolium bromide was prepared by reduction of the phosphinoyl in 85–90% yield by modification of literature methods.^{3f} 1-[β-(Diphenylphosphino)ethyl]-3-mesityl]imidazolium bromide can be made similarly in comparable yields.

1-[γ-(Diphenylphosphino)propyl]-3-[(2,6-diisopropyl)phenyl]imidazolium bromide was also prepared by radical coupling of PPh₂H and {1-(allyl)-3-[(2,6-diisopropyl)phenyl]imidazolium bromide} or the phosphinoyl reduction method mentioned above. It can also be deprotonated under similar conditions.

‡ *Spectroscopic data*: for **I**: ¹H NMR (C₆D₆) δ 8.3–7.0 (multiplet, 8H, aromatic), 2.5 (septet, 2H) (CH₃)₂CH, 1.1–1.3 (d of d, 12H) (CH₃)₂CH, 0.4 (s, 9H) SiMe₃.

For **II**: ¹H NMR (C₆D₆) δ 8.0–7.2 (multiplet, 15H, aromatic), 4.8 (d of t, 2H) and 2.9 (t, 2H) ethylene linker protons, 2.2 (septet, 2H) (CH₃)₂CH, 1.1–1.3 (d of d, 12H) (CH₃)₂CH. ³¹P{¹H} NMR (C₆D₆) δ –23.2.

§ *Crystal data*: for **I**: C₂₃H₃₁N₃Si, *M* = 377.2, colourless, crystal dimensions 0.15 × 0.15 × 0.03 mm, monoclinic, space group *P2₁/n* (no. 14), *a* = 22.1736(5), *b* = 10.6162(2), *c* = 22.1766(6) Å, β = 99.1950(10)°, *V* = 5153.3(2) Å³, *T* = 150 K, *Z* = 8, *D_c* = 0.973 Mg m^{–3}, μ(Mo–Kα) = 0.101 mm^{–1}, λ = 0.71073 Å, 44 430 reflections measured, 9033 unique (*R_{int}* = 0.1776) which were used in all calculations. The final *wR*(*F*²) was 0.2662 (all data) and *R* = 0.1042 [*F* > 2σ(*F*)].

For **II**: C₂₉H₃₃N₂P, *M* = 440.54, colourless, crystal dimensions 0.04 × 0.03 × 0.01 mm, monoclinic, space group *P2₁/c* (no. 14), *a* = 16.1180(13), *b* = 11.4876(8), *c* = 14.2506(8) Å, β = 108.920(2)°, *V* = 2496.0(3) Å³, *T* = 150 K, *Z* = 4, *D_c* = 1.172 Mg m^{–3}, μ(Mo–Kα) = 0.129 mm^{–1}, λ = 0.71073 Å, 8197 reflections measured, 4505 unique (*R_{int}* = 0.0669) which were used in all calculations. The final *wR*(*F*²) was 0.1183 (all data) and *R* = 0.0567 [*F* > 2σ(*F*)].

CCDC reference numbers 176893 and 176894.

See <http://www.rsc.org/suppdata/cc/b1/b11659b/> for crystallographic data in CIF or other electronic format.

- 1 A. J. Arduengo III, *Acc. Chem. Res.*, 1999, **32**, 913.
- 2 For recent reviews, see: D. Bourisou, O. Guerret, F. P. Gabai and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39; W. A. Herrmann and C. Köcher, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2162.
- 3 J. C. Green, R. G. Scurr, P. L. Arnold and F. G. N. Cloke, *Chem. Commun.*, 1997, 1963.
- 4 (a) A. A. D. Tulloch, A. A. Danopoulos, R. P. Tooze, S. M. Cafferkey, S. Kleinhenz and M. B. Hursthouse, *Chem. Commun.*, 2000, 1247; (b) A. A. D. Tulloch, A. A. Danopoulos, S. Winston, S. Kleinhenz and G. Eastham, *J. Chem. Soc., Dalton Trans.*, 2000, 4499; (c) A. A. D. Tulloch, A. A. Danopoulos, G. J. Tizzard, S. J. Coles, M. B. Hursthouse, R. S. Hay-Motherwell and W. B. Motherwell, *Chem. Commun.*, 2001, 1270.
- 5 (a) M. F. Lappert, *J. Organomet. Chem.*, 1993, **451**, 389; (b) J. C. C. Chen and I. J. B. Lin, *Organometallics*, 2000, **19**, 5113; (c) D. S. McGuinness and K. S. Cavell, *Organometallics*, 2000, 741; (d) E. Peris, J. A. Loch, J. Mata and R. H. Crabtree, *Chem. Commun.*, 2001, 201; (e) P. L. Arnold, A. C. Scarisbrick, A. J. Blake and C. Wilson, *Chem. Commun.*, 2001, 2340; (f) W. A. Herrmann, C. Kocher, L. J. Goossen and G. R. J. Artus, *Chem. Eur. J.*, 1996, **2**, 1627; (g) A. Fürstner, H. Krause, L. Ackermann and C. W. Lehmann, *Chem. Commun.*, 2001, 2240; (h) C. Yang, H. M. Lee and S. P. Nolan, *Org. Lett.*, 2001, **3**, 1511.
- 6 M. H. Chisholm, J. C. Huffman, I. P. Rothwell, P. G. Bradley, N. Kress and W. H. Woodruff, *J. Am. Chem. Soc.*, 1981, **103**, 4945.
- 7 C. Pelizzi and G. Pelizzi, *Acta Crystallogr., Sect. B*, 1979, **35**, 1785.
- 8 V. P. W. Böhm and W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2000, **39**, 4036; F. E. Hahn, L. Wittenbecher, D. Le Van and R. Fröhlich, *Angew. Chem., Int. Ed.*, 2000, **39**, 541; Y. Liu, P. E. Lindner and D. M. Lemal, *J. Am. Chem. Soc.*, 1999, **121**, 10 626.
- 9 D. E. C. Corbridge *Phosphorus: An Outline of its Chemistry, Biochemistry and Technology*, Elsevier, Amsterdam, 4th edn., 1990, p. 314.