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A Stable Four-Membered N-Heterocyclic Carbene

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Since the discovery of the first stable carbenes in the 1980s,[1] significant advances have been realized in organometallic chemistry and catalysis[2] using N-heterocyclic carbene (NHC) ligands due to their unique coordination properties (good σ-donor, poor π-acceptor). However, most of the diaminocarbenes reported in the literature are composed of five-membered rings such as imidazole and triazole. Only two other frameworks have been described: a six-membered ring and an acyclic diaminocarbenes,[3,4] both of which afford increased steric hindrance around the carbene center and electron-donating ability. Thus, slight changes to the NHC architecture have a dramatic effect on the electronic properties. We propose to extend the diaminocarbene family with a more strained system and report here the first synthesis and structural characterization of a four-membered NHC.

The iminium salt **2a** was prepared in 66% yield from the silylamidine **1**[5] as a white powder by addition of (diethylamino)-dichlorophosphine and trimethylsilyl-trifluoromethanesulfonate at room temperature (Scheme 1). The ^{1}H and ^{13}C NMR chemical shifts of the NCHN fragment (δ ^{1}H 9.1 ppm, δ ^{13}C 165 ppm) were in the same range as those observed for imidazolium salts.

By X-ray diffraction,[6] two conformers were revealed in the same single crystal in a 95/5 ratio. They differed by an inversion of the tetrahedral geometry around the phosphorus atom but shared the same position for N1, N2, and the aromatic substituents. Only the major conformer will be described in detail (Figure 1). The structure of **2a** is similar to that of all 1,3-diaza-2-phosphetine cations reported,[7] exhibiting delocalization of the π-electrons along the N1−C1−N2 fragment [N1−C1 1.3306(11) Å, N2−C1 1.3279(11) Å], a small intracyclic N1−P1−N2 angle [70.49(3)°], and longer endocyclic P−N bonds [P1−N1 1.8237(8) Å, P1−N2 1.8136(8) Å] than the exocyclic one [P1−N3 1.6219(8) Å].

Attempts to generate the free carbene under standard conditions led to ring opening by P−N bond cleavage. Even with protection of the phosphino group with bulkier substituents such as diisopropylamino, the addition of potassium *tert*-butoxide to **2b** generated product **3** as a result of nucleophilic attack on the phosphorus. Such reactions demonstrate the electrophilic character of the phosphorus atom in these compounds.

Deprotonation of **2b** can be achieved with more hindered and less nucleophilic bases such as mesityllithium or potassium hexamethyldisilazide in toluene at room temperature. After workup, the carbene dimer **4** was isolated in 45% yield as a yellow powder. The structure of **4** was established by single-crystal X-ray diffraction (Figure 2).[6] The small intracyclic angles [N1A−C1A−N2A 95.30(10)° and N1B−C1B−N2B 95.12(10)°] led to a large C(1A, 1B)−N−$C_{mesityl}$ angle [125−134°], decreasing the steric hindrance around the nitrogen atoms and allowing facile dimerization. In five-membered N-heterocyclic carbenes, the mesityl substituents were sufficient to stabilize the carbene due to a smaller $C_{carbene}$−N−$C_{mesityl}$ angle [122−123°].

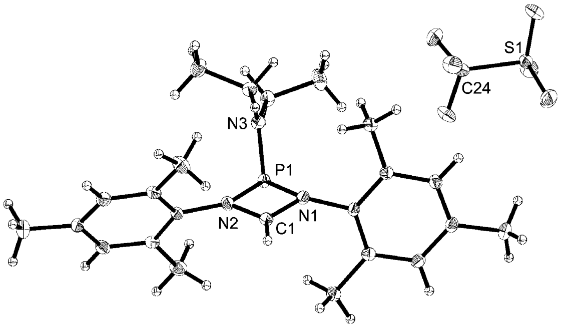
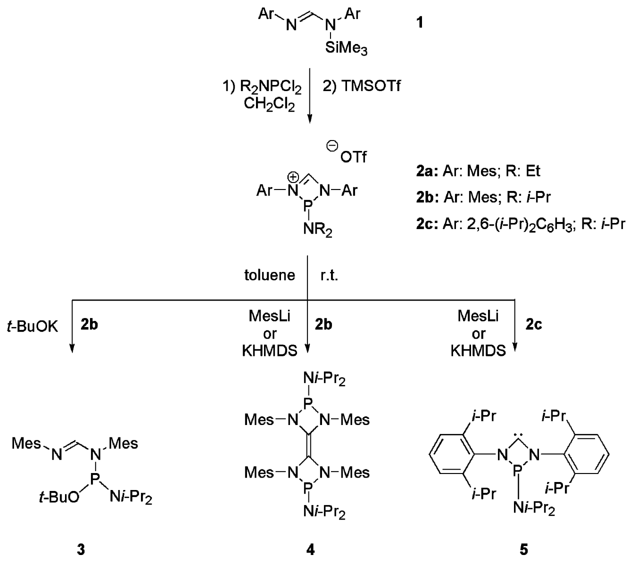


Figure 1. Thermal ellipsoid diagram of **2a** (50% probability). Selected bond distances (Å) and angles (deg): C1−N1 1.3306(11), C1−N2 1.33279(11), P1−N1 1.8237(8), P1−N2 1.8136(8), P1−N3 1.6219(8), N1−C1−N2 104.29(7), N1−P1−N2 70.49(3).

Scheme 1



To avoid this reaction, iminium **2c** was synthesized with ortho isopropyl substituents. Deprotonation of **2c** with mesityllithium or potassium hexamethyldisilazide at room temperature generated the carbene **5**. The ^{13}C NMR signal for the carbene center appeared at 285 ppm as a doublet ($^2J_{CP} = 13$ Hz). To our knowledge, this chemical shift is the most downfield reported for a diaminocarbene.[8] Single crystals[6] were obtained from a saturated pentane solution at −50 °C (Figure 3). Surprisingly, the structure shows that **5** does not possess C_2 symmetry; the mesityl groups are nonsymmetric [C1−N1−C2 126.21(13)°, C1−N2−C14 121.87(13)°]. As expected, the N1−C1−N2 angle [96.72(13)°] is significantly smaller than the analogous angles observed in isolated diaminocarbenes [100−121°]. The N−C1 bonds [C1−N1 1.373(2) Å, C1−N2

10.1021/ja047892d CCC: $27.50 © 2004 American Chemical Society

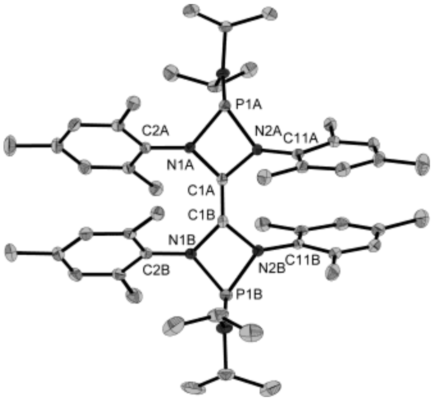


Figure 2. Thermal ellipsoid diagram of **4** (50% probability), (H atoms are omitted). Selected bond distances (Å) and angles (deg): C1A−C1B 1.3335(17), N1A−C1A−N2A 95.30(10), N1B−C1B−N2B 95.12(10), C2A−N1A−C1A 134.14(10), C11A−N2A−C1A 127.79(10), C2B−N1B−C1B 132.99(11), C11B−N2B−C1B 125.49(10).

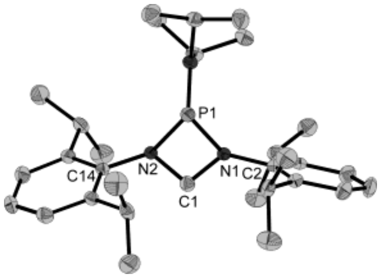


Figure 3. Thermal ellipsoid diagram of **5** (50% probability), (H atoms are omitted). Selected bond distances (Å) and angles (deg): C1−N1 1.373(2), C1−N2 1.387(2), N1−C1−N2 96.72(13), C1−N1−C2 126.21(13), C1−N2−C14 121.87(13).

1.387(2) Å] are short, suggesting interaction of the nitrogen with the carbene center, but the geometry around the nitrogen atoms is not strictly planar [sum of the bond angles = 355.1° and 348.2°], presumably due to the ring strain.

This report demonstrates the preparation of the first stable four-membered ring diaminocarbene. Studies of its coordination properties with transition metals are currently in progress.

Acknowledgment. We thank Lawrence M. Henling and Michael W. Day for X-ray crystallography studies. E.D.-A. is grateful to the Ministère des Affaires Etrangères (France) for a Lavoisier postdoctoral fellowship. This work was supported by the National Science Foundation.

Supporting Information Available: Full experimental details and spectroscopic data for **2**−**6**. X-ray crystallographic data (CIF) for **2**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Igau, A.; Grützmacher, H.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **1988**, *110*, 6463−6466. (b) Igau, A.; Baceiredo, A.; Trinquier, G.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 621−622. (c) Arduengo, A. J., III, Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361−363.

(2) (a) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39−92. (b) Jafarpour, L.; Nolan, S. P. *Adv. Organomet. Chem.* **2001**, *46*, 181−222. (c) Enders, D.; Gielen, H. *J. Organomet. Chem.* **2001**, 617−618. (d) Hillier, A. C.; Grasa, G. A.; Viciu, M. S.; Lee, H. M.; Yang, C.; Nolan, S. P. *J. Organomet. Chem.* **2002**, *653*, 69−82. (e) Perry, M. C.; Burgess, K. *Tetrahedron: Asymmetry* **2003**, *14*, 951−961. (f) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290−1309.

(3) (a) Alder, R. W.; Blake, M. E.; Bortolotti, C.; Bufali, S.; Butts, C. P.; Linehan, E.; Oliva, J. M.; Orpen, A. G.; Quayle, M. J. *Chem. Commun.* **1999**, 241−242. (b) Bazinet, P.; Yap, G. P. A.; Richeson, D. S. *J. Am. Chem. Soc.* **2003**, *125*, 13314−13315. (c) Otto, M.; Conejero, S.; Canac, Y.; Romanenko, V. D.; Rudzevitch, V.; Bertrand, G. *J. Am. Chem. Soc.* **2004**, *126*, 1016−1017.

(4) Alder, R. W.; Allen, P. R.; Murray, M.; Orpen, A. G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1121−1123.

(5) Silylamidines **1** were prepared from the *N,N′*-diarylformamidine.[9] *n*-Butyllithium solution in hexanes (7.1 mmol) was added slowly to a THF (30 mL) solution of formamidine (7.1 mmol) at room temperature followed by trimethylsilyl chloride (0.77 g, 0.71 mmol) after 30 min. Evaporation and extraction with ether gave the desired product.

(6) Crystal data for **2a**: $C_{24}H_{33}F_3N_3O_3PS$, $M = 531.56$, triclinic, space group $P\bar{1}$, $a = 10.5668(3)$ Å, $b = 11.8758(4)$ Å, $c = 12.7952(4)$ Å, $\alpha = 67.7490(10)°$, $\beta = 65.7880(10)°$, $\gamma = 67.4890(10)°$, $V = 1305.19(7)$ Å^3, $Z = 2$, μ(Mo Kα) = 0.71073 Å, crystal size = 0.37 × 0.26 × 0.25 mm^3, 50465 reflections collected (15049 independent, $R_{\mathrm{int}} = 0.0566$), 348 parameters, R1 [$I > 2\sigma(I)$] = 0.0450, wR2 [all data] = 0.0850. For **4**: $C_{50}H_{72}N_6P_2$, $M = 819.08$, monoclinic, space group $P2_1/c$, $a = 13.7626(6)$ Å, $b = 16.2123(8)$ Å, $c = 21.7085(10)$ Å, $\beta = 101.3420(10)°$, $V = 4749.1(4)$ Å^3, $Z = 4$, μ(Mo Kα) = 0.71073 Å, crystal size = 0.33 × 0.31 × 0.21 mm^3, 76278 reflections collected (14587 independent, $R_{\mathrm{int}} = 0.0787$), 811 parameters, R1 [$I > 2\sigma(I)$] = 0.0500, wR2 [all data] = 0.0770. For **5**: $C_{31}H_{48}N_3P$, $M = 493.69$, monoclinic, space group $P2_1/n$, $a = 8.9994(10)$ Å, $b = 26.366(3)$ Å, $c = 12.6593(14)$ Å, $\beta = 94.240(2)°$, $V = 2995.5(6)$ Å^3, $Z = 4$, μ(Mo Kα) = 0.71073 Å, crystal size = 0.41 × 0.22 × 0.07 mm^3, 26662 reflections collected (6905 independent, $R_{\mathrm{int}} = 0.0643$), 508 parameters, R1 [$I > 2\sigma(I)$] = 0.0525, wR2 [all data] = 0.0846. Data were collected at 98(2) K for **2a**, 100(2) K for **4** and 100(2) K for **5** on Bruker SMART 1000 diffractometer. The structures were solved by direct methods (SHELXS-97),[10] and refined using the least-squares method on F^2.[11] Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 228866 (**2a**), 231890 (**4**), 234638 (**5**).

(7) Roques, C.; Mazières, M.-R.; Majoral, J.-P.; Sanchez, M.; Jaud, J. *Inorg. Chem.* **1989**, *28*, 3931−3933.

(8) Range for $\delta^{13}C_{\mathrm{carbene}}$ in diaminocarbenes: five-membered ring 205−245 ppm, six-membered ring 236−242 ppm, acyclic 236−256 ppm. In the case of monoaminocarbenes, more downfield chemical shifts have been reported: (a) Solé, S.; Gornitzka, H.; Schoeller, W. W.; Bourissou, D.; Bertrand, G. *Science* **2001**, *292*, 1901−1903. (b) Merceron-Saffon, N.; Baceiredo, A.; Gornitzka, H.; Bertrand, G. *Science* **2003**, *301*, 1223−1225.

(9) Taylor, E. C.; Ehrhart, W. A. *J. Org. Chem.* **1963**, *28*, 1108−1112.

(10) Sheldrick, G. M. *Acta Crytallogr.* **1990**, *A46*, 467.

(11) Sheldrick, G. M. *SHELXL-97*. Program for Crystal Structure Refinement, University of Göttingen, 1997.

JA047892D