X-ray crystal structures of 10π- and 14π-electron pyrido-annelated *N*-heterocyclic carbenes†

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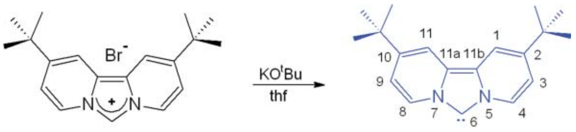
The first X-ray crystal structures of mono- and dipyridoimidazolinylidenes are presented, and the size of the carbene N–C–N angles discussed and correlated with the ^{13}C NMR chemical shifts.

Bipyridocarbene **E** (Fig. 1) belongs to the Arduengo–Wanzlick carbene type[1,2] and was first reported by Weiss *et al.* in 1998.[3] It is a very electron rich *N*-heterocyclic carbene (NHC)[4] due to its 14π-electron system that is in conjugation with the empty carbene p-orbital. This can be demonstrated by the very strong high-field shift of its carbene signal in the ^{13}C NMR spectrum at 196 ppm.[5] This signal is normally found at 235–245 ppm for imidazolidinylidenes[6] **A**, at 235 ppm for benzimidazolinylidenes[7] **B** and between 210 and 220 ppm for imidazolinylidenes **C**.[2]

A position in between **E** and the 6π-electron imidazolinylidenes **C** is taken by 10π-electron monopyridocarbenes **D**, which were also first synthesised in the group of Weiss,[8] and independently reported by Lassaletta *et al.*[9] and Glorius *et al.*[10] The ^{13}C NMR signal of the carbene atom was found between 206 and 210 ppm. Although the electron rich carbenes **D** and **E** are of interest due to their properties as ligands for metal complexes and organocatalysts,[11] no structural data has been reported so far, probably due to the thermolability of these carbenes.

We have now recognised that the introduction of *tert*-butyl groups at the 2- and 10-positions of the bipyrido moiety results in a considerably increased thermal stability. Carbene **1** was generated by deprotonation of the respective imidazolium salt[12] **1**·HBr with KO^{t}Bu (eqn. (1)) and isolated by filtration over Celite® as a thermally stable solid that decomposes above 115 °C.‡



1·HBr **1** (1)

From a concentrated solution of carbene **1** in pentane at −18 °C we were able to obtain crystals that were suitable for X-ray crystal structure analysis.§

The planar bipyrido moiety (Fig. 2) shows alternating single and double bonds in the conjugated π-system that were already found for bipyridocarbenes bound to a (group 6) metalpentacarbonyl moiety,[5,8] resembling the bonding situation in a π-isoelectronic heptafulvalene. In the imidazolinylidene part, the C–C bond length (1.372(4) Å) lies in the range between that found for carbenes of type **C** (1.33–1.35 Å) and **B** (1.395 Å). The N5–C11b (1.411(4) Å) and N7–C11a (1.413(4) Å) bonds are rather long compared to **C** (1.36–1.41 Å) and **B** (1.39–1.40 Å), and the N–C$_{\text{carbene}}$ bonds (1.374(4) and 1.380(4) Å) are of similar length (1.36–1.39 Å). The N–C–N angle of 99.6(2)°, however, is distinctly smaller than in **C** or **B**, and is the smallest ever reported for an imidazoline derived carbene.

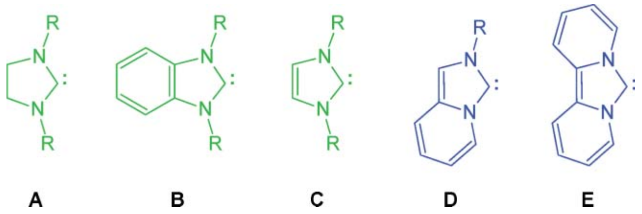


Fig. 1 Overview of imidazoline derived *N*-heterocyclic carbenes (R = alkyl, aryl).

Therefore, we also became interested in the structural properties of the monopyridocarbenes **D**. Though these carbenes were reported to be oils or amorphous solids at room temperature and not stable without further substitution in position 5,[9] we were able to generate and isolate the monopyridocarbene **2** by deprotonating its imidazolium salt **2**·HI at −30 °C with KO^{t}Bu (eqn. (2)) and filtering the solution over Celite®.‡ During the isolation process, handling at room temperature for a few minutes did not lead to noticeable decomposition.

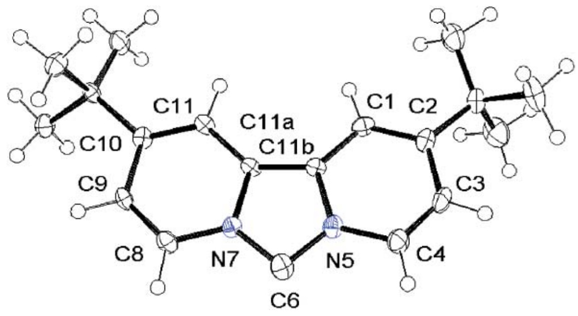


Fig. 2 ORTEP diagram of **1**. Selected bond lengths (Å) and angles (°): N7–C8 1.386(4), C8–C9 1.333(4), C9–C10 1.443(4), C10–C11 1.364(4), C11–C11a 1.410(4), C11a–N7 1.413(4), C11a–C11b 1.372(4), N7–C6 1.374(4), C6–N5 1.380(4), N5–C11b 1.411(4), C11b–C1 1.411(4), C1–C2 1.356(4), C2–C3 1.436(4), C3–C4 1.343(4) and C4–N5 1.379(4); N7–C6–N5 99.6(2), C6–N7–C11a 115.2(3) and N7–C11a–C11b 105.0(2).

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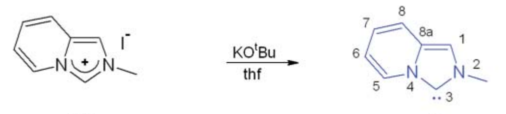
† Electronic Supplementary Information (ESI) available: Experimental details and spectroscopic data of **1**·HBr and **2**·HI, and the data to generate Fig 4. See DOI: 10.1039/b517816a



2·HI **2** (2)

From a concentrated solution of monopyridocarbene **2** in pentane at −30 °C we managed to obtain colourless crystals suitable for X-ray structure analysis.§ There are four independent molecules of **2** in the asymmetric unit, of which one molecule is disordered over two different positions. The values reported here are therefore the arithmetic mean of the three ordered molecules. As in the bipyridocarbene **1**, the pyrido moiety of carbene **2** shows alternating single and double bonds (Fig. 3). Because of the unsymmetrical *N*-substitution pattern, the N4–C3 bond adjacent to the pyridine ring is longer (1.389(6) Å) than the N2–C3 bond (1.355(6) Å). Also, N4–C8a is longer (1.405(5) Å) than C1–N2 (1.373(6) Å). The C8a–C1 bond length (1.355(6) Å) is similar to that found in imidazolinylidenes **C**. Remarkable again is the very small N–C–N angle of 100.4(4)°.

Taking a closer look at the N–C–N angles of different 5-membered ring carbene types reveals that the angle is biggest in the two saturated carbenes of type **A** (104.7(3) and 106.44(9)°). The structure of benzimidazolinylidene **B** shows an angle of 103.9(1)°, whereas the imidazolinylidenes **C** show angles between 101.2(1)–102.4(5)°. Including the data of the structures presented here (N–C–N 100.4(4)° (**2**) and 99.6(2)° (**1**)), a consistent trend between the N–C–N angle and the ^{13}C NMR chemical shift of the carbene signal can be recognised.

To visualise this trend (Fig. 4) we have plotted the ^{13}C NMR chemical shifts of the carbene signals of 24 carbenes (**A–C**, **1** and **2**) against their N–C–N angles, available from the literature.[13,14] Other structural parameters, such as the $C_{carbene}$–N or C–C bond lengths, however, do not follow such a trend.[15]

This correlation is not only limited to imidazoline derived carbenes—the data of other 5-membered ring carbenes like pyrrolidine carbene **F**,[16] carbene **G**[17] with a diboron backbone, the thiazol and triazol carbenes **H**,[18] **Ia**[19] and **Ib**,[20] or even the *P*-heterocyclic carbene **J**[21] fit quite well into this scheme (Fig. 5).

In conclusion, we have presented the first X-ray crystal structures of a mono- and a dipyridocarbene. The N–C–N angles of these two carbenes are the smallest reported so far for NHCs.

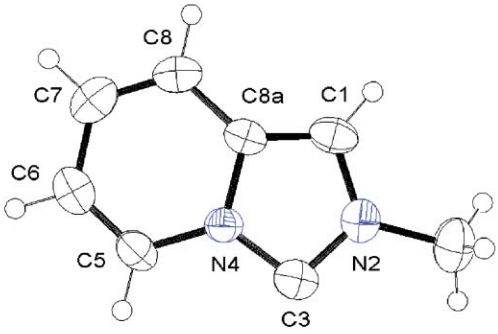


Fig. 3 ORTEP diagram of **2**. Selected bond lengths (Å) and angles (°): N4–C5 1.382(5), C5–C6 1.342(7), C6–C7 1.427(7), C7–C8 1.344(7), C8–C8a 1.417(6), C8a–N4 1.405(5), N4–C3 1.389(6), C3–N2 1.355(6), N2–C1 1.373(6) and C1–C8a 1.355(6); N4–C3–N2 100.4(4), C3–N4–C8a 113.1(3) and N4–C8a–C1 104.9(4). Values reported are the arithmetic mean of the three ordered molecules.

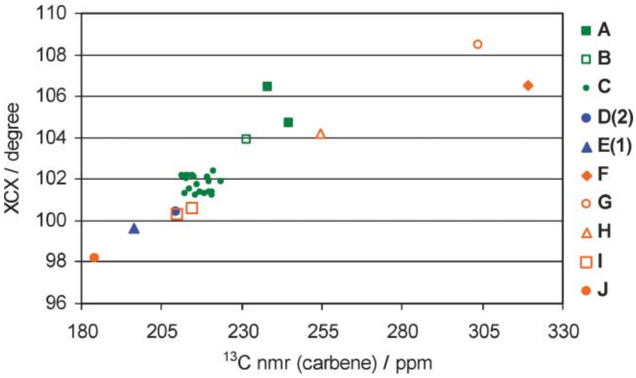


Fig. 4 Plot of the X–$C_{carbene}$–X angles of 5-membered ring carbenes against the chemical shift of the carbene ^{13}C NMR signal (X = C, N, P, S).

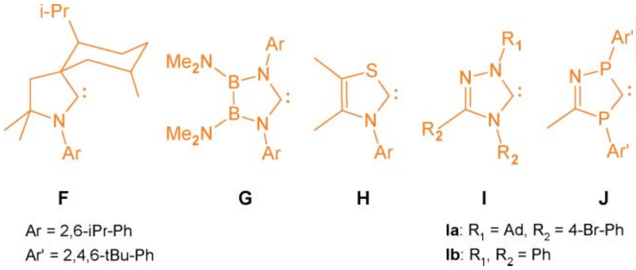


Fig. 5 Structurally characterised 5-membered heterocyclic carbenes that are not imidazoline derived.

The decrease of this angle is congruent with the high-field shift of the carbene signal in ^{13}C NMR spectra. To prove this observation further and to elucidate a possible causal relationship, the preparation and investigation of other types of 5-membered ring carbenes is a current goal within our group.

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Notes and references

‡ Synthesis of **1**: 350 mg (970 μmol) of the imidazolium salt **1**·HBr and 169 mg (1.46 mmol) KO^{t}Bu were stirred at room temperature in 10 ml of THF for 1 h. The reaction mixture was then filtered over Celite® and the solvent removed *in vacuo*. The yellow residue was extracted with 10 ml of pentane, filtered, and the solvent evaporated *in vacuo* to yield 151 mg (55%) of the free carbene as a yellow powder. Crystals that were suitable for X-ray crystal structure analysis were obtained from a concentrated solution of **1** in pentane at −32 °C. mp 115 °C (dec.). δ_H(500 MHz; THF-d_8, −30 °C) 8.44 (2 H, dd, J = 7.6 and 1.0 Hz, 4-H, 8-H), 7.82 (2 H, m, 1-H, 11-H), 6.94 (2 H, dd, J = 7.6 and 2.0 Hz, 3-H, 9-H) and 1.35 (18 H, s, C(CH_3)$_3$); δ_C(125 MHz; THF-d_8, −30 °C) 196.3 (C6), 141.4 (C2, C10), 129.8 (C4, C8), 122.9 (C11a, C11b), 115.0 (C3, C9), 112.6 (C1, C11), 35.6 (C(CH$_3$)$_3$) and 30.8 (C(CH$_3$)$_3$); m/z (EI) 280.1929 (M$^+$, $C_{19}H_{24}N_2$ requires 280.1939) and 265.1704 (M$^+$ − CH$_3$, $C_{18}H_{21}N_2$ requires 265.1705).

Synthesis of **2**: 600 mg (2.30 mmol) of 2-methylpyrido[1,2-*c*]imidazolium iodide (**2**·HI) and 280 mg (2.50 mmol) KO^{t}Bu were suspended at −18 °C in 20 ml of pre-cooled THF and stirred for 30 min. The suspension was then quickly filtered through Celite® and the solvent of the yellow filtrate evaporated at −18 °C *in vacuo*. The reddish oily residue was extracted at room temperature with 10 ml of pentane, the volume of the extract then reduced to 7 ml at −18 °C and cooled down to −32 °C. The product was formed as colourless crystals that were isolated by decantation and dried *in vacuo* to yield 420 mg (71%) of the carbene **2**. The free carbene is extremely air sensitive and shows only limited stability at room temperature.

δ_H(250 MHz; THF-d_8) 8.12 (1 H, ddd, J = 7.2, 2.2 and 1.1 Hz, 5-H), 7.21 (1 H, ddd, J = 9.3, 2.2 and 1.1 Hz, 8-H), 7.20 (1 H, s, 1-H), 6.63 (1 H, ddd, J = 9.3, 6.4 and 1.1 Hz, 7-H), 6.30 (1 H, ddd, J = 7.2, 6.4 and 1.1 Hz, 6-H) and 3.94 (3 H, s, CH_3); δ_C(75 MHz; THF-d_8) 209.7 (C3), 132.1 (C8a), 131.8 (C5), 122.0 (C7), 117.8 (C8), 110.9 (C6), 110.8 (C1) and 39.1 (CH_3); m/z (FAB$^+$) 132.0688 (100%) (M$^+$, $C_8H_8N_2$ requires 132.0687), 131 (31), 117 (11), 104 (14), 93 (67) and 79 (23).

§ Crystal data for compound **1**: yellow-orange crystal (irregular), dimensions 0.44 × 0.06 × 0.04 mm, crystal system monoclinic, space group $P2_1/c$, $Z = 4$, a = 12.052(7), b = 11.180(6), c = 11.965(7) Å, β = 97.78(1)°, V = 1597.2(15) Å^3, ρ = 1.166 g cm^{-3}, T = 100(2) K, $\Theta_{\max}$ = 20.87°, radiation Mo-K$_\alpha$, λ = 0.71073 Å, 0.3° ω-scans with CCD area detector, covering a whole sphere in reciprocal space, 7473 reflections measured, 1681 unique (R_{int} = 0.0796), 1227 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS[22] based on the Laue symmetry of the reciprocal space, μ = 0.07 mm^{-1}, $T_{\min}$ = 0.97, $T_{\max}$ = 1.00, structure solved by direct methods and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXTL[23] software package, 196 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit = 1.03 for observed reflections, final residual values $R1(F)$ = 0.053, $wR(F^2)$ = 0.095 for observed reflections, residual electron density = −0.15 to 0.18 e Å^{-3}. CCDC 292418.

Crystal data for compound **2**: colourless crystal (polyhedron), dimensions 0.50 × 0.40 × 0.10 mm, crystal system monoclinic, space group $P2_1$, $Z = 8$, a = 10.0322(3), b = 13.6913(3), c = 10.4751(3) Å, β = 92.964(2)°, V = 1436.87(7) Å^3, ρ = 1.222 g cm^{-3}, T = 200(2) K, $\Theta_{\max}$ = 24.11°, radiation Mo-K$_\alpha$, λ = 0.71073 Å, 0.3° ω-scans with CCD area detector, covering a whole sphere in reciprocal space, 11357 reflections measured, 2390 unique (R_{int} = 0.0576), 1893 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS[22] based on the Laue symmetry of the reciprocal space, μ = 0.08 mm^{-1}, $T_{\min}$ = 0.96, $T_{\max}$ = 0.99, structure solved by direct methods and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXTL[23] software package, 427 parameters refined, hydrogen atoms were treated using appropriate riding models except of the hydrogen atoms H1 of C1, which were refined isotropically, Flack absolute structure parameter 0(4), goodness of fit = 1.11 for observed reflections, final residual values $R1(F)$ = 0.052, $wR(F^2)$ = 0.118 for observed reflections, residual electron density = −0.18 to 0.21 e Å^{-3}. CCDC 292419. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b517816a

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14 Data were taken from the Cambridge Structural Database and the literature reported therein, see supplementary information for more details†.

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