Supplementary Information

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

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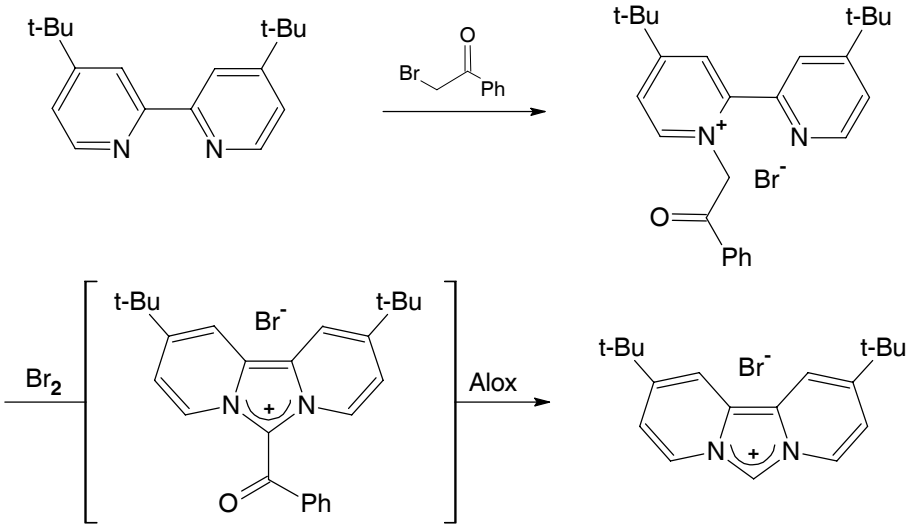
Experimental

General comments: Unless otherwise noted all reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques. Solvents were dried according to standard procedures and saturated with argon prior to use. Chemicals used were obtained from commercial suppliers and used without further purifications. Imidazo[1,5-a]pyridine was prepared according to the literature procedure.[1] Mass spectra were recorded on a Jeol JMS-700 with NBA (nitrobenzylalcohol) or dichloromethane as matrix. Melting points were determined with a Büchi Melting Point B 540 apparatus. NMR spectra were recorded using a Bruker ARX 250, DRX 300 or DRX 500 spectrometer. ^{1}H and ^{13}C{^{1}H}NMR spectra were calibrated to TMS on the basis of the relative chemical shift of the solvent as an internal standard. Elemental analyses were carried out at Mikroanalytisches Laboratorium der Chemischen Institute der Universität Heidelberg.

*Synthesis of 2,10-di-tert-butyl-dipyrido[1,2-c;2',1'-e]imidazoliumbromide (**1•HBr**)*

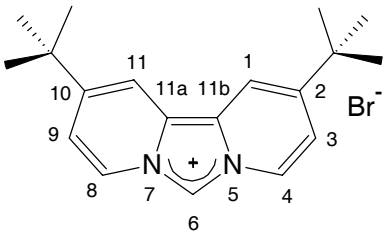


a) Synthesis of 2-(4',4''-di-tert-butyl-2',2''-bipyridiniumbromid)acetophenone

In a 250 ml round bottom flask 50 ml acetonitrile is added to 4.00 g (14.9 mmol) 4,4'-di-*tert*-butyl-2,2'-bipyridin and 2.39 g (12.0 mmol) bromoacetophenone and the reaction mixture is refluxed for 24 h turning into a reddish solution. The solvent is taken off *in vacuo* and the residue purified at silica gel with ethylacetate as eluent. The product is isolated as a yellow powder in 4.44 g (79 %) yield.

δ_H(300 MHz; CD_3CN) 8.86-8.89 (1 H, m, H_{Ar}), 8.17-8.23 (3 H, m, H_{Ar}), 7.85-7.92 (3 H, m H_{Ar}), 7.69-7.75 (1 H, m, H_{Ar}), 7.48-7.56 (3 H, m, H_{Ar}), 6.23 (2 H, s, CH_2), 1.50 (9 H, s, $C(CH_3)_3$), 1.33 (9 H, s, $C(CH_3)_3$); δ_C(125 MHz; CD_3CN) 191.3 (CO), 173.6, 163.8, 153.2, 150.7, 150.1, 148.7, 135.5, 134.7, 130.1, 129.1, 128.1, 125.3, 124.8, 123.9, 64.7 (CH_2), 37.2 ($C(CH_3)_3$), 35.5 ($C(CH_3)_3$), 30.5 ($C(CH_3)_3$), 30.0 ($C(CH_3)_3$).

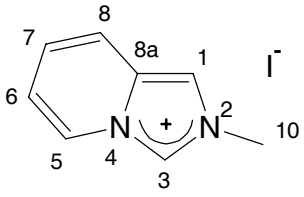
*b) Synthesis of 2,10-di-tert-butyl-dipyrido[1,2-c;2',1'-e]imidazoliumbromide (**1•HBr**)*



To a solution of 4.00 g (8.60 mmol) 2-(4',4"-Di-tert-butyl-2',2"-bipyridiniumbromid)acetophenone (see a)) in 60 ml of pyridine are added dropwise 0.44 ml (8.6 mmol) bromine at 60 °C. After addition, the reaction mixture is stirred for 5 min, cooled down to room temperature and the solvent is taken off *in vacuo*. The dark brown residue is hydrolysed by dissolving it in a 1:1 water-methanol mixture and passing it over a column charged with activated neutral alox (ø = 5 cm, l = 15 cm). The eluent is evaporated *in vacuo* and the residue recrystallised from acetone at -32 °C to yield 1.0 g (33%) of the product as orange-brown crystals.

mp 220 °C (dec.); (Found: C, 63.2; H, 7.0; N, 7.75; Br 22.1. $C_{19}H_{24}N_2Br$ requires C, 63.0; H, 6.9, N, 7.7; Br 22.3%); δ_H(300 MHz, dmso-d_6) 10.13 (1 H, s, 6-H), 8.95 (2 H, dd, J 7.5 and 0.7 4-H and 8-H), 8.62 (2 H, m, 1-H and 11-H), 7.71 (2 H, dd, J 7.5 and 1.9, 3-H and 9-H), 1.39 (18 H, s, $C(CH_3)_3$); δ_C(75 MHz, dmso-d_6) 145.2 (C11a, C11b), 122.9 (C4, C8), 121.6 (C2, C10), 119.8 (C3, C9), 114.5 (C6), 113.1 (C1, C11), 35.2 ($C(CH_3)_3$), 30.0 ($C(CH_3)_3$); m/z (FAB) 281.3 (100%) ($M-Br^-$), 265 (7) ($M-Br^--CH_4$).

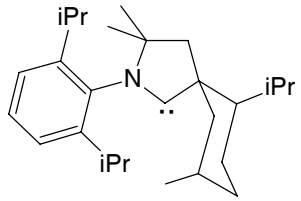
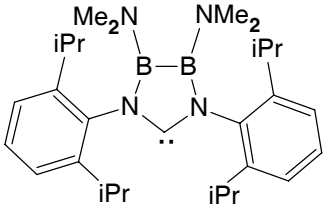
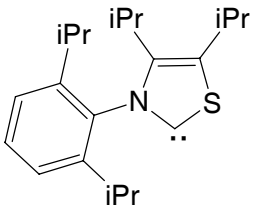
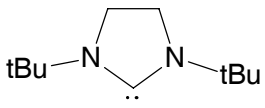
*Synthesis of 2-methyl-pyrido[1,2-c]imidazoliumiodide (**2•HI**)*

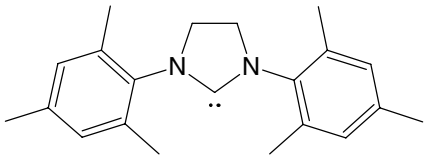
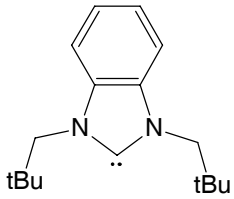
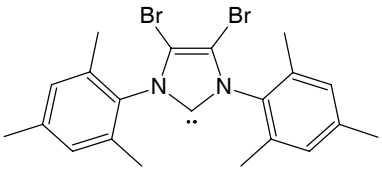
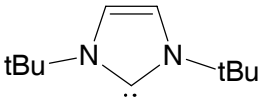
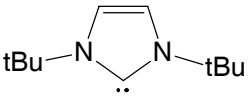
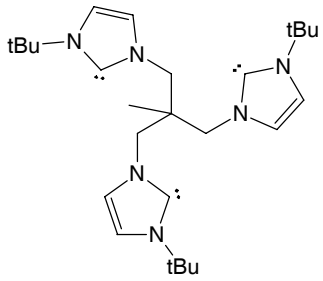
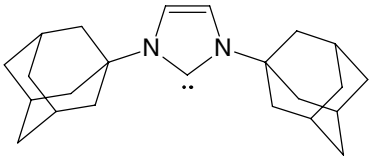
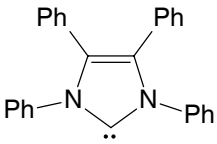


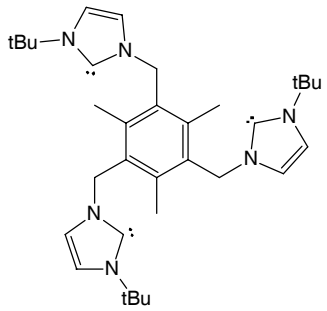
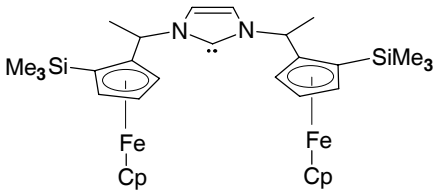
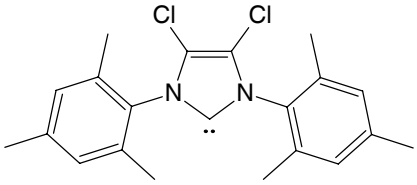
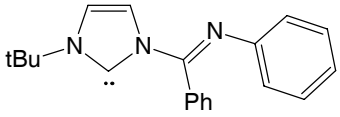
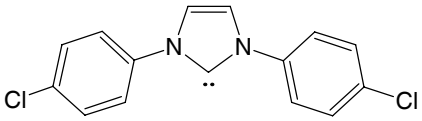
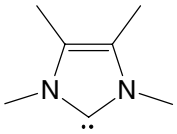
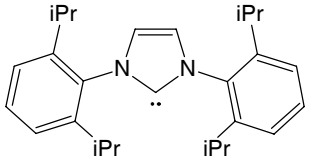
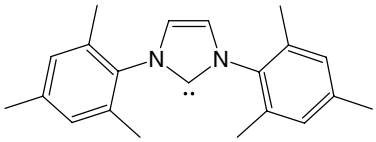
To a solution of 800 mg (6.80 mmol) imidazo[1,5-a]pyridine in 8 ml acetonitrile at 70 °C are added 0.42 ml (6.8 mmol) methyliodide dropwise. After keeping the reaction mixture for 4 h at 70 °C the solvent is distilled off and the residue extracted twice with petrolether. The residue is recrystallised twice from ethanol to yield 1.2 g (67%) of the product as white crystals. mp

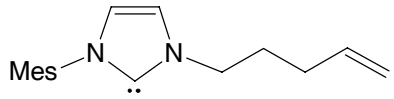
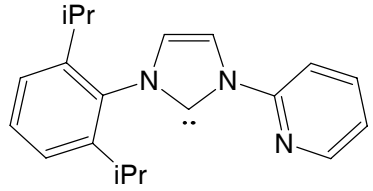
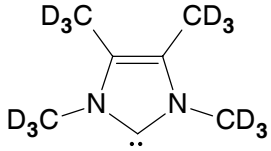
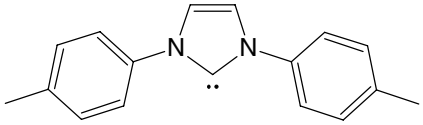
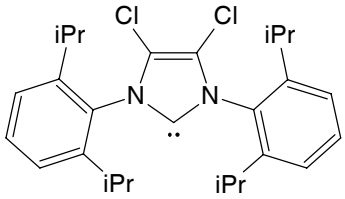
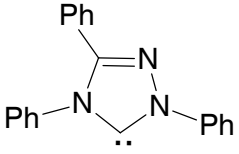
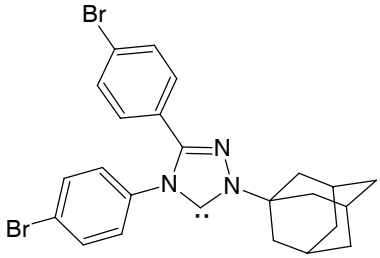
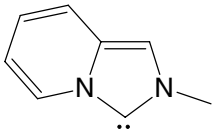
163 °C (from EtOH); (Found, C, 37.25; H, 3.6; N, 10.7; I, 49.1. Calc. for $C_8H_9N_2I$: C, 36.95; H, 3.5; N, 10.8; I, 48.8%); δ_H(250 MHz; CD_3CN) 9.36 (1 H, s, 3-H), 8.45 (1 H, dd, J 7.1 and 0.9, 5-H), 7.85 (1 H, s, 1-H), 7.73 (1 H, d, J 9.4, 8-H), 7.26 (1 H, ddd, J 9.4, 6.8 and 0.9, 7-H), 7.09 (1 H, dd, J 7.1 and 6.8, 6-H), 4.14 (3 H, s, CH_3); δ_C(75 MHz; CD_3CN) 130.9 (C8a), 127.0 (C3), 125.7 (C7), 124.6 (C5), 118.8 (C8), 118.5 (C6), 115.2 (C1), 38.1 (CH_3); m/z (FAB+) 133.1 (100%) (M^+), 393.2 ($2M^+ + I^-$).

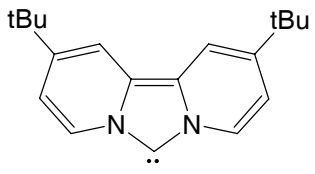
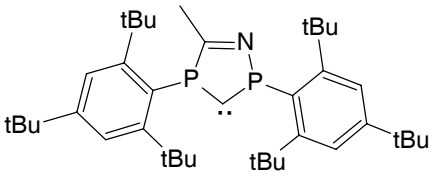
Data to generate Figure 4:

compound	carbene category (Figure 1 + 4)	XCX angle / °	δ_C $C_{carbene}$ (solvent)	literature
	**F**	106.54(18)	319.0 thf-d_8	[2]
	**G**	108.45(8)	303.6 benzene-d_6	[3]
	**H**	104.2(2)	254.3 thf-d_8	[4](X-ray) [5](nmr)
	**A**	106.44(9)	238.25 C_6D_6	[6]

	**A**	104.7(3)	244.5 thf-d_8	7
	**B**	103.5(1) 104.3 (1)	231.5 thf-d_8	8
	**C**	102.4(5)	221.2 benzene-d_6	9
	**C**	102.2(5)	213.2 thf-d_8	10
	**C**	102.19(12)	212.9 benzene-d_6	11
	**C**	102.27(10) 102.15(10) 102.04(10)	214.7 benzene-d_6	12
	**C**	102.2(2)	211.4 benzene-d_6	13
	**C**	102.1(3)	219.6 thf-d_8	14

	**C**	102.25(14) 102.04(15) 101.97(14)	215.2 thf-d_8	15
	**C**	102.0(4)	212.6 toluene-d_8	16
	**C**	101.9(2)	219.9 benzene-d_6	17
	**C**	101.89(17)	223.6 benzene-d_6	18
	**C**	101.7(1)	216.3 thf-d_8	19
	**C**	101.5(1)	213.7 thf-d_8	19
	**C**	101.4	220.6 benzene-d_6	20
	**C**	101.4(2)	219.7 thf-d_8	19

	**C**	101.4(4)	217.1 thf-d_8	21
	**C**	101.3	218.3 benzene-d_6	22
	**C**	101.3(2)	212.47 thf-d_8	23
	**C**	101.2(1)	215.8 thf-d_8	19
	**C**	101.2	220.6 benzene-d_6	20
	**I**	100.6(2)	214.6 benzene-d_6	24
	**I**	100.3(3)	210.1 benzene-d_6	25
 **2**	**D**	100.4(4)	209.7 thf-d_8	this work

 **1**	**E**	99.6(2)	196.3 thf-d_8	this work
	**J**	98.2(3)	184.4 thf-d_8	[26]

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