Supplementary Material for Chemical Communications

Influence of anellation in *N*-heterocyclic carbenes: Detection of novel quinoxaline-anellated NHC by trapping as transition metal complexes

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Experimental details

All preparations were carried out in carefully dried, freshly distilled solvents. Reactions with air- or moisture-sensitive compounds were conducted under an argon atmosphere using Schlenk techniques. NMR spectra were recorded on a multinuclear FT-NMR spectrometer ARX300 (Bruker) at 300.1 (^{1}H) and 75.5 (^{13}C) MHz. Shift reference is tetramethylsilane. Assignment numbers follow nomenclature numbers. Coupling constants refer to J_{HH} unless stated otherwise. Assignments are based on proton-coupled ^{13}C and CH-COSY NMR experiments for selected compounds. A CH-COSY experiment with **3b** optimised for J_{CH} = 5 Hz clearly distinguishes C3a from the more remote C4a by a strong cross-peak for H2 with C3a but not with C4a. Because a cross peak of C3a with only the downfield proton of the benzene ring the latter is assigned to the nearer H5, the more upfield proton of the benzene ring to H6. Melting points (uncorrected) were determined with a Sanyo Gallenkamp melting point apparatus, elemental analysis with a CHNS-932 analyser from LECO using standard conditions.

Starting materials

***N*,*N*'-Dineopentyl-2,3-diaminoquinoxaline (1a).** A stainless-steel autoclave (80 mL), charged with 2,3-dichloroquinoxaline (7.0 g, 35.2 mmol) and neopentylamine (21.3 mL, reactant and solvent), was heated to 120 °C for 3 h. After cooling to room temperature the resulting pale yellow solid was suspended in hexane. The insoluble part (neopentyl amine hydrochloride) was filtered off and washed with hexane. The solvent was evaporated to give 9.2 g (87%) of spectroscopic pure **1a**. Fine purification is achieved by sublimation in high vacuum (10^{-5} Torr, 130°C), mp. 94-96 °C. ^{1}H NMR ($CDCl_3$): δ = 1.06 (s, 18 H, CMe_3), 3.43 (d, ^3J = 5.7 Hz, 4 H, NCH_2), 4.33 (s, 2 H, NH), 7.30 (m, 2 H, H-6,6'), 7.63 (m, 2 H, H-5,5'). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 27.61 (CMe_3), 31.60 (CMe_3), 52.42 (NCH_2), 124.62 (C-5), 125.57 (C-6), 136.96 (C-3a), 145.06 (C-4a). MS (EI, 70 eV): m/z (%) = 301 (11), 300 (61) [M^+], 244 8(17), 243 (100), 214 (11), 192 (32), 173 (20), 129 (20) and lower fragments. Elemental analysis: $C_{18}H_{28}N_4$ (300.45) calcd. C 71.96, H 9.39, N 18.65. Found C 71.81, H 9.87, N 17.98.

***N*,*N*'-Diisopropyl-2,3-diaminoquinoxaline (1b).** An autoclave (80 mL), charged with 2,3-dichloroquinoxaline (2.4 g, 12.1 mmol) and isopropylamine (20 mL, reactant and solvent), was heated to120 °C for 2 h. After cooling to room temperature the resulting raspberry-colour liquid was transferred to a beaker and treated with aqueous NaOH. The compound was extracted several times with ether. The combined organic phases were dried with Na_2SO_4 and filtered. The solvent was evaporated to give 2.8 g (95 %) of spectroscopic pure, pale yellow **1b**, mp. 155-157°C. ^{1}H NMR ($CDCl_3$): δ = 1.32 (d, ^3J = 6.4 Hz, 12 H, CH_3), 4.06 (d, ^3J = 5.8 Hz, 2 H, NH), 4.39 (d sept, ^3J = 6, 6.5 Hz, 2 H, NCH), 7.28 (m, 2 H, H-6,6'), 7.60 (m, 2 H, H-

5,5'). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 22.9 (CH_3), 42.8 (CH), 124.5 (CH-5), 125.7 (CH-6), 137.1 (C_q-3a), 143.8 (C_q-4a). MS (EI, 70 eV, T = 150 °C): m/z (%) = 244 (89) [M^+], 229 (23) [M^+–Me], 201 (100) [M^+–C_3H_7], 187 (51), 160 (17) [M^+–2 C_3H_6], 144 (20). Elemental analysis: $C_{14}H_{20}N_4$ (244.34) calc.: C 68.82, H 8.25, N 22.93: Found: C 68.71, H 8.40, N 22.46.

1,3-Dineopentyl-quinoxalino[2,3-d]imidazolium hexafluorophosphate (2a). **1a** (1.5 g, 5.00 mmol), NH_4PF_6 (815 mg, 5.00 mmol) and triethyl orthoformate (15 mL) were heated to 120 ºC for 5h in a rectification apparatus to separate ethanol from the reaction mixture. After cooling to room temperature a solid was precipitated and washed with hexane (3 x 10 mL). Then the product was extracted with CH_3CN to give 1.19 g (52%) colourless crystals of **2a**, mp. >300° C. ^1H (CH-COSY) NMR (D_6-DMSO): δ = 1.11 (s, 18 H, CH_3); 4.49 (s, 4 H, NCH_2), 8.09 (m, 2 H, 6-H), 8.38 (m, 2 H, 5-H), 10.50 [in CD_2Cl_2 9.66] (s, 1 H, 2-H). ^{13}C (FIDRES 0.332; CH-COSY) NMR (D_6-DMSO): δ = 27.06 (quart, ^1J = 126 Hz, C*Me*$_3$), 32.95 (s, *Cq*Me$_3$), 56.44 (t br, ^1J = 144 Hz, NCH_2), 128.87 ($^1J \approx$ 167 Hz, CH-5), 131.20 ($^1J \approx$ 170 Hz, CH-6), 138.23 (dd, $^3J_{C\text{-}H2}$ = 6.6, $^3J_{C\text{-}H(neop)}$ = 3.7 Hz, C_q-3a), 140.35 (m, C_q-4a), 153.16 (dm, ^1J = 221, ^3J = 5 Hz, {^1H}: s and t, $^1J_{CD}$ = 84.7 Hz, C_q-2; t). Elemental analysis: $C_{19}H_{27}F_6N_4P$ (456.41). Calculated: C 50.00, H 5.96, N 12.28. Found: C 49.86 H 6.00, N 12.15.

1,3-Diisopropyl-quinoxalino[2,3-d]imidazolium hexafluorophosphate (2b). **1b** (2.0 g, 8.19 mmol), NH_4PF_6 (1.3 g, 8.0 mmol) and triethyl orthoformate (15 mL) were heated to 120 ºC for 24 h in a rectification apparatus with separation of ethanol from the reaction mixture. After cooling to room temperature the solvent was removed in vacuum, and the residue was washed with hexane (3 x 10 mL). Then the product was extracted with CH_3CN to give 2.5 g (76%) colourless crystals of **2b**. ^1H (CH-COSY) NMR (CD_3CN): 1.81 (d, ^3J = 6.8 Hz, 12 H, Me), 5.21(sept, ^3J = 6.8 Hz ,2 H, NCH), 8.04 (m, 2 H, H-6,6'), 8.32 (m, 2 H, H-5,5'), 9.59 (s, 1 H, H-2). ^{13}C NMR (FIDRES 0.116; CH-COSY) (CD_3CN): δ = 21.59 (quart, quint, ^1J = 128.9, $^2J \approx {}^3J$ = 4.4 Hz, CH_3), 53.27 (dd sept, ^1J = 146.1, ^3J = 1.3, ^2J = 4.4 Hz, NCH), 130.09 (dm, $^1J \approx$ 160 Hz, CH-5), 132.47 (dm, $^1J \approx$ 167 Hz, CH-6), 138.61 (dd, $^3J_{C\text{-}H2}$ = 6.8, $^3J_{C\text{-}H(i\text{Pr})}$ = 3.3 Hz, C_q-3a), 142.00 (m, C_q-4a), 148.12 (dt, ^1J = 218.8, ^3J = 5 Hz, CH-2). Elemental analysis: $C_{15}H_{19}F_6N_4P$ (400.31). Calculated: C 45.01, H 4.78, N 14.00. Found: C 45.72 H 4.78, N 13.98.

Deprotonation attempts with KH of ***quinoxalino[2,3-d]imidazolium salts.*** A suspension of **2a** (384 mg, 0.841 mmol) in d_8-THF was added at –78 ºC to a suspension of 30% KH in mineral oil (130 mg, 0.97 mmol), washed before with THF. The mixture was stirred at –50 to –60 °C overnight. After rapid filtration, the ^1H and ^{13}C NMR spectra were measured at –50 °C, showing a mixture, but no signal with δ >160 (C^{II} signal expected for **3a** at δ >240).

Transition metal complexes

(1,3-Dineopentyl-quinoxalino[2,3-d]imidazole-2-ylidene)rhodium(cyclooctadiene-1,5) chloride (4a). The suspension of **2a** (279.4 mg, 0.612 mmol) and [Rh(1,5-COD)Cl]$_2$ (151.0 mg, 0.306 mmol) in THF was added at –78 °C to a suspension of 30% KH in mineral oil (98.1 mg, 0.73 mmol). The mixture was allowed to come to room temperature and stirred overnight. The solvent was removed in vacuum, and the residue was subjected to chromatography on silica gel/hexane. After elution of ([Rh(1,5-COD)Cl]$_2$) with CH_2Cl_2, pure **4a** was eluted with CH_2Cl_2/1%MeOH. Crystallisation from saturated solution in CH_2Cl_2 provided 139 mg (41%) of yellow crystals. ^1H NMR ($CDCl_3$): δ 1.31 (s, 18 H, Me), 2.05 (m, 4 H, CH_2), 2.50 (m, 4 H, CH_2), 3.15 (br q, 2 H, =CH), 4.86 (d, $^4J(^{103}Rh^1H)$ = 13.6 Hz, 2 H, CH_2), 5.25 (d, $^4J(^{103}Rh^1H)$ = 13.5 Hz, 2 H, CH_2), 5.37 (br m, 2 H, =CH), 7.74 (m, 2 H, H-6,6'), 8.11 (m, 2 H, H-5,5'). $^{13}C\{^1H\}$ NMR (150.90 MHz; DEPT 75.47 MHz) ($CDCl_3$): δ = 28.93 (CH_2), 30.17 (C*Me*$_3$),

32.98 (CH_2), 33.58 (CMe_3), 60.08 (NCH_2), 70.72 (d, $J(^{103}Rh^{13}C)$ = 14.6 Hz, CH=), 102.52 (d, $J(^{103}Rh^{13}C)$ = 6.5 Hz, CH=), 128.86, 128.91 (CH-5, CH-6), 138.50 (C_q-3a), 141.18 (C_q-4a), 219.46 (d, $^1J(^{103}Rh^{13}C)$ = 52 Hz, C_q-2). Elemental analysis: Anal. Found: C, 55.96 (incomplete combustion); H, 6.73; N, 10.19. Calc. for $C_{27}H_{38}ClN_4Rh$ (557.03): C, 58.22; H, 6.88; N, 10.06.

Bis(1,3-Diisopropyl-quinoxalino[2,3-d]imidazole-2-ylidene)silver hexafluorophosphate (5b). Ag_2O (289.4 mg, 1.25 mmol), freshly dried molecular sieve (3A, 1 g) and **2b** (500 mg, 1.25 mmol) was added to a Schlenk tube. CH_2Cl_2 (15 mL) was added (after replacement of air by argon). The resulting suspension was stirred for 24 h at ambient temperature and filtered. The solvent of the filtrate was partly removed in vacuum (to 5 mL), and hexane (10 mL) was added. The white precipitate was filtered and recrystallised from CH_2Cl_2 to give 850 mg (89%) colourless crystals of mp. >300°C. ^{1}H NMR (CD_2Cl_2): 1.99 (d, ^3J = 6.8 Hz, 12 H), 5.41 (sept, ^3J = 6.8 Hz, 2 H), 7.93 (m, 2 H, H-6,6'), 8.29 (m, 2 H, H-5,5'). $^{13}C\{^1H\}$ (DEPT) NMR (CD_2Cl_2): δ = 22.63 (CH_3), 54.92 (NCH), 129.44, 130.36 (CH-6, CH-5), 139.57 (d, $^3J(^{107/109}Ag^{13}C)$ = 6.5 Hz, C_q-3a), 140.18 (C_q-4a), 197.39 (dd, $^1J(^{107/109}Ag^{13}C)$ = 185.8, 214.9 Hz, C_q-2). MS (EI, 70 eV, T = 345 ° C): m/z (%) = 270 (6) [**2b**-H+O$^+$], 256 (4), 255 (6) [**2b**$^+$], 228 (7), 221 (15), 218 (14), 41 (100). Anal. Found: C, 47.76; H, 4.66; N, 14.68. Calcd. for $C_{30}H_{36}AgF_6N_8P$ (761.50): C, 47.32; H, 4.77; N, 14.71.

1,3-Dineopentyl-imidazol-2-ylidene (6a).
a) Glyoxal bis(neopentylimine) (1.10 g, 5.60 mmol), $AgCF_3SO_3$ (1.73 g ,6.73 mmol) and then chloromethyl pivalate (1.13 mL, 7.84 mmol) were added to CH_2Cl_2 (10 mL). The tube was sealed and stirred in the dark at 50 °C for 24 h. After the solution was cooled to room temperature the mixture was filtered, the solvent was evaporated in vacuum, and the resulting oil was washed several times with ether to give 1.45 g (72%) of the ionic liquid 1,3-dineopentyl- imidazolium triflate. ^{1}H NMR ($CDCl_3$): δ = 0.98 (s, 18 H, CMe_3), 4.02 (s, 4 H, NCH_2), 7.32 (br s, 2 H, H-4, H-5), 8.87 (br S, 1 H, H-2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 26.79 (CMe_3), 32.31 (CMe_3), 61.02 (NCH_2), 123.28 (CH-4, CH-5), 137.23 (CH-2).
b) A suspension of 1,3-dineopentyl- imidazolium triflate (175 mg, 0.488 mmol) in THF was added at –78 ºC to a suspension of 30% KH (105 mg, 0.79 mmol) in mineral oil, washed before use with THF**.** The mixture was allowed to come to room temperature and stirred overnight. After filtration the solvent was removed in vacuum. The residue was extracted with diethyl ether and the ether evaporated to give 56 mg (55%) NMR spectroscopic pure oily **6a**. ^{1}H NMR (C_6D_6): δ = 0.90 (s, 18 H, CMe_3), 3.72 (s, 4 H, NCH_2), 6.48 (s, 2 H, H-4, H-5). $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 28.62 (CMe_3), 33.37 (CMe_3), 63.06 (NCH_2), 120.48 (CH-4, CH-5), 217 (br, C_q-2).

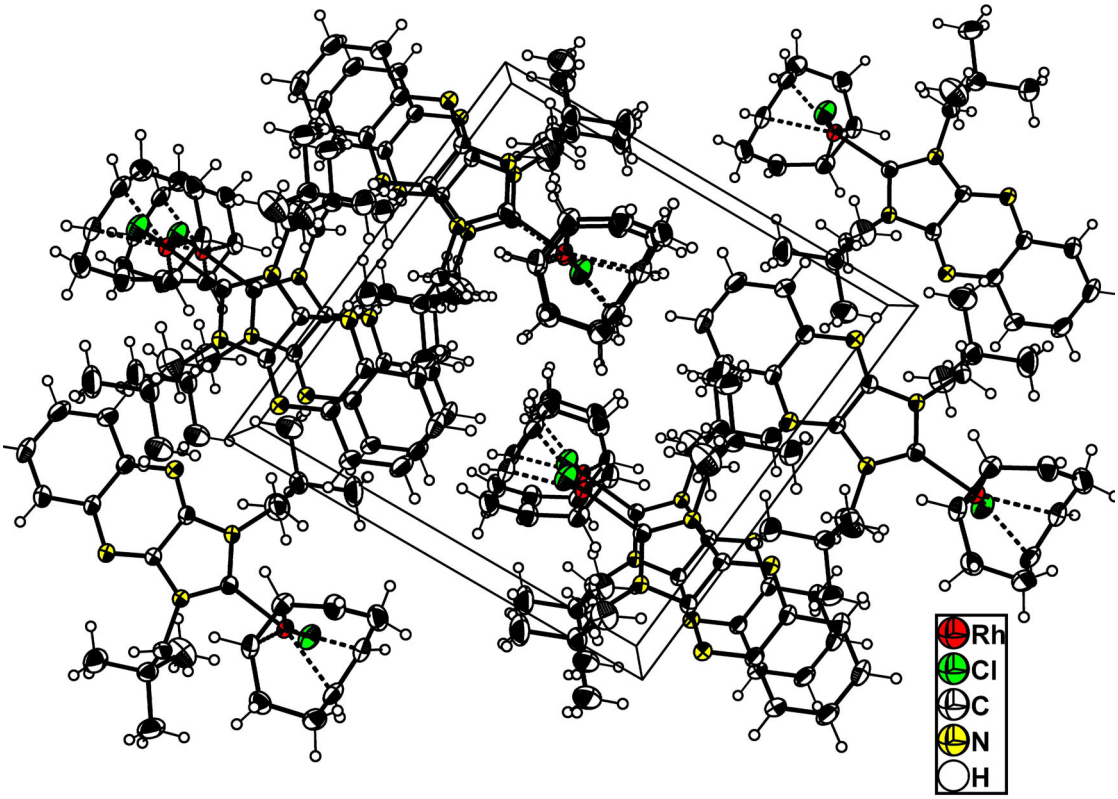
Bis(1,3-dineopentyl-imidazol-2-ylidene) silver tetrafluoroborate (7a).
a) Glyoxal bis(neopentylimine) (435 mg, 2.22 mmol), $AgBF_4$ (519 mg, 2.67 mmol) and then chloromethyl pivalate (0.45 mL, 3.12 mmol) were added to CH_2Cl_2 (10 mL) , treated and worked up as described above affording 464 mg (71%) of the ionic liquid 1,3-dineopentyl-imidazolium tetrafluroborate. ^{1}H NMR ($CDCl_3$): δ = 0.98 (s, 18 H, CMe_3), 4.03 (s, 4 H, NCH_2), 7.38 (br s, 2 H, H-4, H-5), 8.69 (br s, 1 H, H-2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 26.69 (CMe_3), 32.19 (CMe_3), 60.69 (NCH_2), 123.35 (CH-4, CH-5), 136.78 (CH-2).
b) Ag_2O (133 mg, 0.574 mmol) was added to a solution of 1,3-dineopentyl-imidazolium tetrafluroborate (170 mg, 0.574 mmol) in 10 mL of CH_2Cl_2.The suspension was stirred for 24 h at ambient temperature, filtered and washed with CH_2Cl_2. The solvent of the filtrate was partly removed in vacuum (residual solution ca. 2 mL), hexane (4 mL) was added, and the resulting white precipitate was separated and recrystallised from CH_2Cl_2 yielding 224 mg (63%) single crystals. ^{1}H NMR (CD_2Cl_2): δ = 1.02 (s, 18 H, CMe_3), 3.94 (s, 4 H, NCH_2), 7.09

(d br, $^{4}J(^{107/109}Ag^{1}H)$ = 1.8 Hz, 2 H, H-4, H-5). $^{13}C\{^{1}H\}$ (DEPT) NMR (CD_2Cl_2): δ = 28.10 (CMe_3), 32.97 (CMe_3), 63.71 (NCH_2), 122.99 (d, $^{3}J(^{107/109}Ag^{1}H)$ = 5.9 Hz, CH-4, CH-5), 181.93 (dd, $^{1}J(^{13}C\text{-}^{107/109}Ag)$ = 185.8, 213.8 Hz, C_q-2).

Crystal structures of 4a and 5b

CIF files for 4a and 5b

Packing of **4a** in the crystal



Packing of **5b** in the crystal