Influence of anellation in *N*-heterocyclic carbenes: Novel quinoxaline-anellated NHCs trapped as transition metal complexes†

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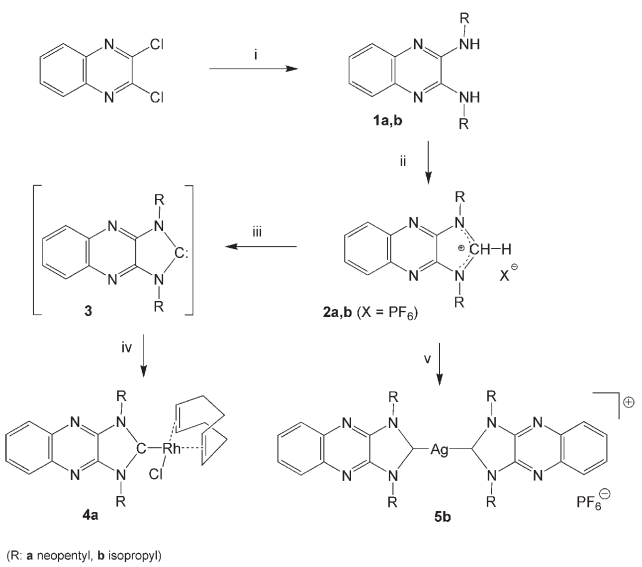
The synthesis, NMR-, and crystal structure data of novel electron-deficient quinoxaline anellated imidazol-2-ylidene precursors and complexes thereof are reported and compared with related less electron-withdrawing or non-anellated *N*-heterocyclic carbenes and complexes to illustrate anellation effects.

N-Heterocyclic carbenes (NHCs), first isolated by Arduengo *et al.*,[1] have strong nucleophilic properties. Thereby they are extremely useful as spectator or active ligands in coordination chemistry and in homogeneous transition metal catalysis.[2–4] In several fields they were found to be superior to phosphine ligands, but the tunability of the electronic properties is (so far) more restricted. While P(III) ligands cover a wide spectrum of compounds with different properties, from highly basic and bulky σ-donor to electron-poor phosphite or low-coordinate phosphorus π-acceptor ligands,[5] the majority of the NHC-ligands are imidazole-2-ylidenes with mainly σ-donor properties. Photoelectron spectroscopy (PES)[6] and quantum chemical investigations[7] show that the amount of π-back-bonding is low, even in $(NHC)_2M$ complexes with electron-rich metals like Pd(0) and Pt(0). Stronger π-acidity and back-bonding may be expected for NHCs which possess lower π-electron density at the two-valent carbon, indicated by strongly downfield shifted $^{13}C^{II}$ NMR signals, *e.g.* in imidazolin-2-ylidenes,[8] benzo-,[9–12] pyrido-, and naphtho-anellated[12] imidazol-2-ylidenes or similar extended anellated naphthopyrimidin-2-ylidenes.[13] An even stronger electron-withdrawal may be expected by anellation with quinoxalines, where the extended π-system is paired with replacement of two CH sites by nitrogen atoms.

To test the access of quinoxalino-anellated imidazol-2-ylidenes and to compare these with related benzo- and naphtho-anellated NHCs,[9–13] dineopentyl- and diisopropyl-2,3-diaminoquinoxaline **1a** and **1b** were prepared by heating 2,3-dichloroquinoxaline with an excess of the corresponding primary amine, subsequently cyclised and deprotonated. The cyclisation of **1b** by heating $HC(OEt)_3$ in the presence of NH_4PF_6 gave the hexafluorophosphates **2a,b** in good yields (Scheme 1). Attempts to detect the quinoxalino-imidazol-2-ylidene **3a** in the deep violet solution, formed from **2a** and KH in THF at 20 or −50 °C (30 min) by ^{13}C NMR or by complex formation with $[Rh(1,5\text{-}COD)Cl]_2$ in THF did not succeed. However, addition of a suspension of **2a** and $[Rh(1,5\text{-}COD)Cl]_2$ to KH (1 : 0.5 : 1.2) in THF at −78 °C, *i.e.* generation of **3a** in the presence of the trapping reagent, furnished the quinoxaline-anellated NHC–Rh(COD)Cl complex **4a** (Fig. 1), isolated from CH_2Cl_2 as single crystals in reasonable yield. This proves the formation of **3a** as a transient species. The destabilisation of imidazol-2-ylidenes by anellation is known from the easy dimerisation of non-bulky *N*,*N*′-bis-alkylated benzimidazol-2-ylidenes[14] and the monomer–dimer equilibrium for those with isobutyl substituents[15] while the corresponding imidazol-2-ylidenes are monomeric.[2] However, *N*,*N*′-dineopentyl substitution stabilises monomeric benzimidazol-2-ylidenes[9,10,12] and allows to estimate the influence of varying anellation. Comparison with equally *N*,*N*′-disubstituted but distinct anellated imidazol-2-ylidenes shows that the persistence decreases in the order benzimidazol-2-ylidenes (distillable)[10,12] > naphtho[2,3-d]imidazol-2-ylidenes (possible to isolate) > pyrido[2,3-d]imidazol-2-ylidenes (*ca.* 50% of crude product at 20 °C)[12] > **3a** (not detectable at −50 °C) and indicates that the anellation by the electron-deficient quinoxaline considerably destabilises the NHC **3a**. The decreasing stability in the series non-, benzo- and naphtho-anellated imidazol-2-ylidenes is accompanied by an increasing deshielding of the C^{II} nucleus ($\delta^{13}C^{II}$ 217‡),



Scheme 1 Synthesis of quinoxaline-anellated imidazolium salts **2a**,**b** and NHC complexes **4a** and **5b** (synthesis of **4b** and **5a** not tried). *Reagents and conditions*: i. RNH_2, 120 °C, 3 h; ii. $HC(OEt)_3$, NH_4PF_6, 120 °C, 24 or 5 h; iii. KH, THF, –78 °C; ½$[Rh(1,5\text{-}COD)Cl]_2$, 15 h; iv. Ag_2O, mol. sieve, CH_2Cl_2, 20 °C, 24 h.§†

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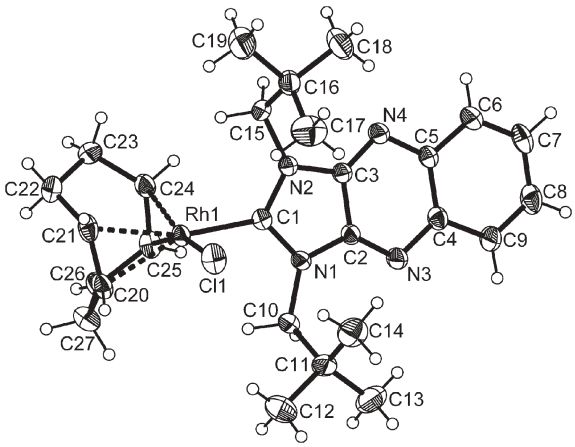


Fig. 1 Molecular structure of **4a** (thermal ellipsoids with 50% probability) and atom labelling scheme. Selected bond lengths (Å) and angles (°): Rh–C1 1.998(3), Rh–C20 2.206(3), Rh–C21 2.253(3), Rh–C24 2.155(3), Rh–C25 2.125(3), C20–C21 1.397(4), C24–C25 1.409(4), C1–N1 1.395(3), C1–N2 1.381(3), N1–C2 1.375(3), N2–C3 1.393(3), C2–N3 1.320(3), C3–N4 1.297(3), N3–C4 1.367(4), N4–C5 1.393(3), C6–C7 1.386(4), C8–C9 1.367(4), C2–C3 1.450(4); C1–Rh–C20 158.4(1), C1–Rh–C21 165.0(1), C1–Rh–C24 92.1(1), C1–Rh–C25 93.0(1), C1–Rh–Cl 91.08(8).

231.8,[9,10,12] and 239.9[12] ppm), caused mainly by the decreasing π-charge density at C^{II} which thus is the main reason for the destabilisation. The lower persistence of the pyrido[2,3-d]- as compared to the naphtho[2,3-*d*]imidazol-2-ylidene is probably due to lower barriers for consecutive reactions by lack of symmetry as shown for the homologous *N*-heterocyclic silylene[16] while the instability of **3a** with two N atoms symmetrically placed in an anellated ring is attributed to the low π-density and growing electrophilicity at C^{II}. In a bis(quinoxaline)-anellated *N*-heterocyclic germylene this led to coordination of LiCl with chloride bound at Ge^{II} and Li^+ at two N-atoms of the anellated rings.[17]

In contrast to **3a**, the rhodium complex **4a** is quite stable. It can be handled even in air and purified by column chromatography on silica gel. Due to the high stability of such NHC complexes and the high CH acidity of the quinoxalino-imidazolium salts, indicated by low field H(2) NMR signals (**2a,b** δ 9.66, 9.59 ppm in CD_2Cl_2, CD_3CN), the generation of NHC complexes from **2** is possible also without deprotonation agents. An example is the reaction of **2b** with silver oxide which gives the cationic bis(quinoxalino-imidazol-2-yliden) silver complex **5b** (Fig. 2) in high yield. Since NHC–silver complexes are capable of transmetallation,[18] this points the way to further quinoxaline-anellated NHC transition metal complexes.

For comparison of **3** and **5** with analogous non-anellated NHC species, *N*,*N*′-dineopentyl-imidazol-2-ylidene **6a** and its silver complex of the type L_2Ag^+ BF_4^- **7a** were also prepared (Scheme 2) from the respective imidazolium salts, obtained *via* the diimine chloromethyl pivalate condensation, recently published for cyclic diimines.[19]

The structures of the quinoxaline-anellated NHC precursors and complexes in solution were elucidated by conclusive NMR data.§ Crystal structures of **4a** and **5b** were determined from single crystals grown from CH_2Cl_2 solution. Characteristic features in the

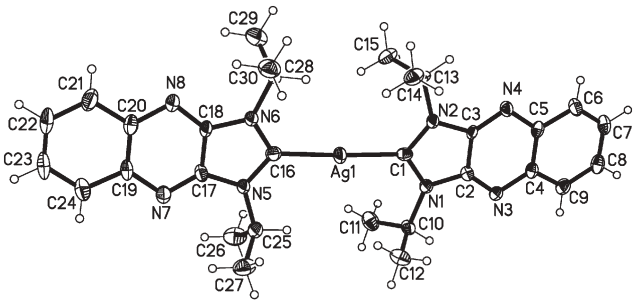
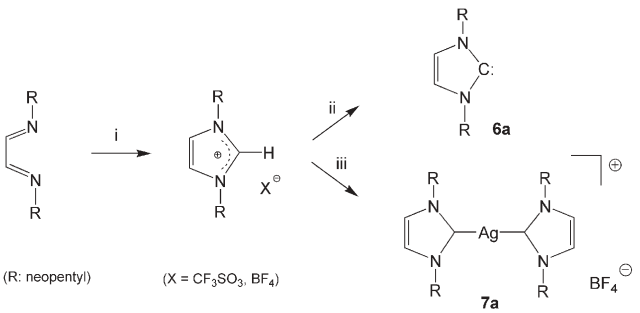


Fig. 2 Molecular structure of **5b** (thermal ellipsoids with 50% probability) and atom labelling scheme; PF_6^- and 3 CH_2Cl_2 omitted for clarity. Selected bond lengths (Å) and angles (°): Ag–C1 2.088(4), Ag–C16 2.090(5), C1–N1 1.370(5), C1–N2 1.351(5), C16–N5 1.364(5), C16–N6 1.352(6); C1–Ag–C16 177.67(19), N1–C1–N2 107.1(4), N5–C16–N6 107.2(4).



Scheme 2 Synthesis of imidazol-2-ylidene **6a** and NHC complex **7a**. *Reagents and conditions*: i. Ag_2O, $ClCH_2OC(O)CMe_3$, 50 °C, 24 h, CH_2Cl_2; ii. KH, THF, –78 °C; iii. Ag_2O, CH_2Cl_2, 20 °C, 24 h.§†

NMR spectra of **2a–b**, **4a** and **5b** are the strong downfield shifts of the NCH proton signals. They are attributable to the ring current effect and in **4a** and **5b** even stronger than in the anellated imidazolium salts **2a–b**. The anisotropic influence of the 1,5-COD ligand in **4a** shifts the second NCH_2 signal further downfield. Another feature are the much stronger downfield shifts of $^{13}C(2)$ in **4a** and **5a** as compared to those in **2a–b**. This is attributed to the interplay of delocalisation of π density within the aromatic system and repulsion by σ-electrons of the polar C(2)-metal bond and core electrons of the transition metal. As compared to $\delta^{13}C(2)$ and the extreme π-repulsion by the C^{II} lone electron pair of the free NHC ligands, however, the downfield shift is much lower. The shielding of C^{II} by complexation of the NHC is increasing with the anellation as shown by comparison of **6a** and **7a** ($\Delta\delta^{13}C^{II}$ −35 ppm) with the analogous benzo- and naphtho-anellated compounds ($\Delta\delta^{13}C^{II}$ −38.6, −42.4 ppm)[12] and suggests an even larger difference for quinoxaline-anellation. For the Rh complexes the trend is the same. For a given metal, π-back-bonding should increase with decreasing electron density at C(2) of the ligand, what in turn should cause increasing π-electron repulsion and thus diminish or even level the influence of back bonding on the complexation shifts $\Delta\delta$. As a clear effect is observed, it is more likely that π-back-bonding is small in Ag and Rh complexes, also with electron-poor anellated NHCs. This is supported by the small differences in the metal-C^{II} bond lengths of non- and benzo-, naphtho- or quinoxaline-anellated imidazol-2-ylidene-Rh(COD)Cl (2.021–2.036;[12,18] 1.998–2.026 Å[12,20]) or silver complexes (2.056–2.78;[21] 2.059–2.090 Å[12,22]) and similar Rh–C and short

C=C distances of the COD double bond in *trans*-position of the carbene ligands. The N–C^{II} bond lengths in isostructural bis(dimesityl-imidazol-2-ylidene) I^+, Ag^+ and Ni(0) complexes (1.346, 1.358, 1.375 Å) were used to classify these into not capable, capable and very capable of π-back bonding, respectively,[23] but the values observed in **5b** (1.351–1.370 Å) vary nearly over the whole range, suggesting that this method only allows for a rough estimation. The average value in **5b** (1.359 Å) corresponds to a bond capable of π-back bonding in the above classification.

In conclusion, it was shown that increasing extension of the π-system and electron withdrawal causes increasing destabilisation of NHC. While dineopentylbenzimidazol-2-ylidene is even distillable and the naphthoimidazol-2-ylidene isolable, **3a** is instable. In contrast, the complexes are quite stable. Comparison of the ^{13}C NMR data suggests a very strong σ-, π-electron repulsion and deshielding at C^{II} in the NHC ligands, explaining also the decreasing stability, while the effect in the NHC complexes is much lower due to the rather covalent bond to the transitions metals (Rh^I, Ag^I). The structural data available so far suggest that in complexes of electron-deficient anellated NHC, even with electron-rich transition metals, the σ-donor properties are dominant. A more sophisticated picture of the various contributions to the bonding in these systems, including the extent of π-back donation, is currently the subject of a detailed quantum chemical study.

Notes and references

‡ **Selected substance and ^{13}C NMR data**: (75.5 MHz). For **2a**: yield 1.19 g (52%), C-2 (D_6-DMSO) δ 153.2; **2b**: yield 2.5 g (76%), C-2 (CD_3CN) δ 148.1; **4a**: yield 139 mg (41%), C-2 ($CDCl_3$) δ 219.5 (d, $^1J_{RhC}$ = 52 Hz); **5b**: yield 850 mg (89%), C-2 (CD_2Cl_2) δ 197.4 (dd, $^1J_{AgC}$ = 185.8, 214.9 Hz); **6a**: yield 56 mg (55%), C-2 (C_6D_6) δ 217; **7a**: yield 224 mg (63%), C-2 (CD_2Cl_2) δ 181.9 ppm (dd, $^1J_{AgC}$ = 185.8, 213.8 Hz).

§ Selected single crystals of **4a**, and **5b**, respectively, were mounted inside thin-wall glass capillaries. Data were collected on a Bruker/Nonius Apex-X8 diffractometer, using Mo Kα-radiation (λ = 0.71073 Å). Crystal data for **4a**: $C_{27}H_{37}ClN_4Rh$ (Mr = 555.97 g mol^{-1}), triclinic, space group $P\bar{1}$, a = 8.273(2), b = 12.672(3), c = 13.085(3) Å, α = 83.42(3)°, β = 83.12(3)°, γ = 82.76(3)°, U = 1344.2(5) $Å^3$, Z = 2, D_c = 1.374 g cm^{-3}, μ(Mo Kα) = 0.756 mm^{-1}, F(000) = 578, specimen 0.52 × 0.25 × 0.12 mm, T = 293(2) K, 46726 reflections collected for 3.09 ⩽ θ ⩽ 33.50°, index ranges −12 ⩽ h ⩽ 12, −17 ⩽ k ⩽ 18, −20 ⩽ l ⩽ 20, independent reflections 9086 [R(int) = 0.0569], multiscan absorption correction (SADABS), refinement by full-matrix least-squares on F^2, data/restraints/parameters 9086/0/298, goodness-of-fit on F^2 1.086, final R indices [$I > 2\sigma(I)$] R^1 = 0.0454, wR^2 = 0.1148, R indices (all data) R^1 = 0.0696, wR^2 = 0.1271, largest diff. peak and hole 1.260 and −1.165 e $Å^{-3}$; **5b**·$3CH_2Cl_2$: $C_{33}H_{42}AgCl_6F_6N_8P$ (1016.29), triclinic, space group $P\bar{1}$, a = 9.550(1), b = 14.096(2), c = 16.484(2) Å, α = 89.293(5)°, β = 78.318(4)°, γ = 88.874(4)°, U = 2172.6(4) $Å^3$, Z = 2, D_c = 1.554 g cm^{-3}, μ(Mo Kα) = 0.931 mm^{-1}, F(000) = 1028, specimen 0.21 × 0.16 × 0.14 mm, T = 293(2) K, 36199 reflections collected for 2.98 ⩽ θ ⩽ 26.10°, index ranges −10 ⩽ h ⩽ 11, −17 ⩽ k ⩽ 17, −20 ⩽ l ⩽ 20, independent reflections 8129 [R(int) = 0.0730], multiscan absorption correction (SADABS), refinement by full-matrix least-squares on F^2, data/restraints/parameters 8129/0/496, goodness-of-fit on F^2 1.015, final R indices [$I > 2\sigma(I)$] R^1 = 0.0504, wR^2 = 0.0986, R indices (all data) R^1 = 0.1157, wR^2 = 0.1199, largest diff. peak and hole 1.014 and −0.905 e $Å^{-3}$. CCDC 289615–289616. For crystallographic data in CIF format see DOI: 10.1039/b512884f

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