

Tuning the electronic properties of an N-heterocyclic carbene by charge and mesomeric effects†‡

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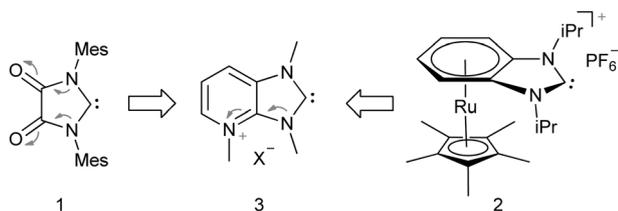
N-Methylation of a pyridoimidazolium salt and subsequent deprotonation afford a cationic NHC ligand. The spectroscopic characteristics of its Rh and Ir metal complexes reveal the reduced donor and enforced π -acceptor behaviour of this ligand system.

The chemistry of N-heterocyclic carbene (NHC) metal complexes dates back to early reports by Wanzlick and Öfele in 1968.¹ The isolation of the first stable NHC by Arduengo² paved the way for thorough and systematic studies on all aspects of NHC chemistry in the past 20 years.³ Especially the modification of their steric and electronic properties enabled NHCs to become a powerful class of ligands for transition metal catalysis⁴ as well as organocatalysis.⁵ Recently, the ability of NHCs to exert a significant degree of π -acceptor character in their transition metal complexes was demonstrated.⁶ Our current interest is focused on the development of electron poor NHCs with increased π -acceptor properties. Two approaches towards this goal are depicted in Scheme 1. In the diamido-NHC **1** the amide resonance shepherds away electron density from the carbene C-atom which as a consequence acquires some electrophilic reactivity.⁷ Alternatively, coordination of a

cationic metal fragment to the aromatic backbone of benzimidazolylidene also leads to an attenuated donor property of NHC **2** with enhanced acceptor character.⁸ In view of this knowledge the question arises whether a mesomeric effect and the action of a cationic charge could be combined within a single molecule. The 1,3-dineopentyl-4-azabenzimidazolylidene (PyINp₂) reported by Heinicke and coworkers⁹ appeared as a suitable system to us in this context if alkylation at the pyridine N-atom to yield the cationic NHC **3** could be accomplished.

In this article we report the synthesis and the properties of the new electron poor NHC **3** whose electron deficiency stems from the combination of mesomeric and charge effects as outlined above.

The dicationic NHC precursors **5a** and **5b** were synthesized in four steps starting from 2,3-diaminopyridine *via* the monocationic derivative **4** described earlier by Heinicke *et al.*⁹ While methylation at the pyridine nitrogen atom failed using Me₃OBF₄ or MeOTf under ordinary conditions, the transformation proceeded smoothly with MeOTf under microwave irradiation affording the dicationic compounds **5** in good yield. Interestingly, when the reaction temperature was confined not to exceed 100 °C, the anticipated *N,N'*-bis(neopentyl) derivative **5b** was the only observed product (74% isolated yield), while running the reaction at 130 °C provided compound **5a** selectively in 91% yield, where the neopentyl group at N3 has been exchanged for a methyl group, as established using NOESY-NMR-spectroscopy (Scheme 2). Both compounds were obtained as white solids that were characterized by NMR spectroscopy and elemental analysis. Their ESI MS spectra feature prominent peaks for the monocations formed from **5a,b** by attachment of an OH⁻ anion.

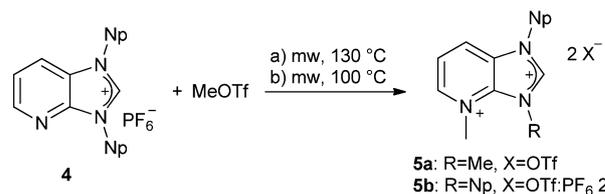


Scheme 1 Combination of mesomeric and charge effects for the design of the new NHC **3**.

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† Dedicated to Prof. Werner Uhl on the occasion of his 60th birthday.

‡ Electronic supplementary information (ESI) available: Experimental and spectroscopic details for **5–12**, computational details and X-ray crystallographic information for **4**, **5a** and **9a**. CCDC 932700–932702. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc42547a



Scheme 2 Synthesis of the NHC precursors **5a** and **5b**.

In line with the harsh conditions required for the electrophilic methylation of monocation **4**, this species did not show the reactivity typically seen for pyridines due to the greatly reduced basicity. Thus, no complexation occurred to a Cp*Ru⁺-fragment – neither η^1 to the nitrogen atom nor η^6 to the aromatic π -system as reported by Fish *et al.*¹⁰ Furthermore, reactions of **4** with Fe(CO)₅ or CpFe(CO)₂I failed as did the attempt to prepare the corresponding *N*-oxide.

Compared to the monocationic precursor **4** the ¹H NMR signal in DMSO-d₆ for the C2–H is shifted to lower field by 0.3 and 0.2 ppm for the dicationic compounds **5a** and **5b**, respectively, indicating an increased acidity of the C2 proton. Accordingly, while compound **5a** is apparently stable in water, an H–D exchange was observed at the acidic C2 position in D₂O. The ¹⁹F{¹H}-NMR spectrum of compound **5b** revealed that the ratio of hexafluorophosphate to triflate is 1 : 2. Solvent diffusion afforded crystals of compounds **4** and **5a** suitable for X-ray single crystal structure determination.† The geometrical parameters of the two compounds show no significant differences. The pyridine and the imidazole rings are coplanar, thus permitting a π -electron delocalisation throughout the entire system which is necessary to enable the desired resonance structure according to Scheme 1.

The NHC precursors **5a** and **5b** could be deprotonated with potassium *tert*-butoxide (KO^tBu) at low temperature to afford the corresponding free NHC *in situ*. Their intermediate existence was proven by trapping with sulfur. Thus, cooling a mixture of dication **5a**, KO^tBu and elemental sulfur to –80 °C followed by addition of THF resulted in the formation of thione **7** in reasonable yield (41%, Scheme 3) which was characterized using NMR spectroscopy and HRMS-ESI. An analogous selenium derivative could not be obtained.

NHC **6a** also reacted cleanly with [M(COD)Cl]₂ (M = Rh or Ir) to give the cationic NHC metal complexes **8** and **9a**. [(**6b**)Ir(COD)Cl]PF₆ (**9b**) was prepared by the same procedure in the presence of excess KPF₆ to avoid a mixture of triflate and hexafluorophosphate as anions. For complex **8** the ¹³C{¹H}-NMR signal for the carbene C atom is observed at 213.0 ppm, shifted by *ca.* 10 ppm to lower field compared to the analogous complex with a neutral pyridoimidazol-2-ylidene ligand lacking the methyl group at the pyridine moiety.^{9b} The ¹J_{CRh} coupling is not affected by the additional methyl group (53 Hz). The (COD)RhCl complexes of most NHC ligands have their ¹³C NMR signal for the carbene C atom in the range of 180–200 ppm.^{6a,11} For the iridium complexes **9a** and **9b** the respective signals appeared at 205.4 and 209.5 ppm. In addition, crystals of **9b** suitable for X-ray

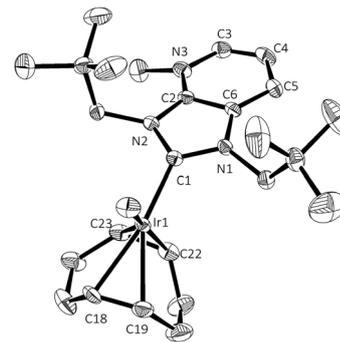
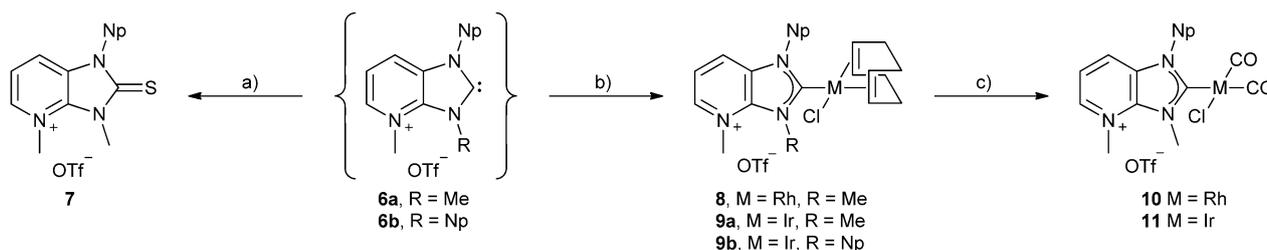


Fig. 1 Molecular structure of complex **9b** (ellipsoids drawn at 30% probability; H atoms and PF₆[–] counterions omitted for clarity).

diffraction were obtained by solvent diffusion (Fig. 1). The C1–Ir1 distance of 200.7(4) pm is close to the shorter end of the range usually observed for other (NHC)Ir(COD)Cl complexes (201–210 pm).¹² The distances between the Ir1 and the COD C atoms *trans* to the NHC are significantly elongated (220.0(4) and 222.5(4) pm). In (NHC)Ir(COD)Cl complexes where the NHC is derived from imidazole or imidazolidine, distances between 216 and 218 pm are usually observed.¹² Conclusively, the geometrical data suggest a significant degree of π -backbonding from the Ir to the carbene C at the expense of the back-donation to the *trans* olefinic C=C bond in accord with the situation for other π -acidic NHCs.^{6a,7} The C1–N2 distance of 139.3(5) pm is 2 pm longer compared to the neutral complex (PyINp₂)Rh(COD)Cl.^{9b}

The Tolman electronic parameter (TEP) is a frequently employed measure for the donor properties of NHC ligands and it can be easily obtained from the IR spectroscopic analysis of NHC metal carbonyl complexes. Therefore, the dicarbonyl complexes **10** and **11** were prepared by bubbling a slow CO stream through a solution of the corresponding COD complexes **8** and **9a** in CH₂Cl₂ for 20 minutes. For comparison, (PyINp₂)Rh(CO)₂Cl (**12**) with the related neutral pyridoimidazol-2-ylidene ligand was also prepared according to the same protocol. All three complexes were examined using IR spectroscopy and the CO stretching vibrations and TEP values – calculated according to a relationship established by Plenio and Nolan¹³ – are given in Table 1. As can be seen, the methylation at the pyridine N atom has a drastic effect with the TEP value being shifted by 12 wavenumbers to 2067 cm^{–1} for the cationic NHC **6a**. This shift is more pronounced than that due to the coordination of a cationic Cp*Ru fragment to a benzimidazol-2-ylidene.⁸ According to its TEP value, the new cationic carbene derivative **6** is among the



Scheme 3 Synthesis of compounds **6–11**. Reagents employed: (a) 1/8 S₈ in THF, over night at –80 °C to rt; (b) [M(COD)Cl]₂ in THF, over night at –80 °C to rt, M = Rh, Ir; (c) CO in CH₂Cl₂, 30 min, rt.

Table 1 $\bar{\nu}_{\text{CO}}$ and TEP values of 10–12

Complex	NHC	$\bar{\nu}_{\text{CO}}^a$ (cm ⁻¹)	TEP (cm ⁻¹)
10	6a	2022, 2095	2067
11	6a	2003, 2082	2067
12	pyINp ₂	2003, 2084	2055

^a IR data were collected in CH₂Cl₂.

least electron donating NHCs, comparable to dicyano- and diamido-substituted imidazol-2-ylidenes.^{6a,7}

DFT calculations were carried out in order to get more information about the electronic properties of the new carbene **6a** compared to its neutral, unmethylated relative PyINpMe (**13**). In both derivatives, the carbene lone pair at C2 constitutes the σ -type HOMO while the π -type LUMO shows a significant contribution from the p-orbital on the carbene C atom which is necessary for a π -back bonding from the metal. The HOMO–LUMO gap decreases significantly from the neutral carbene **13** (4.93 eV) to the cationic NHC **6** (3.73 eV). In addition, the LUMO is energetically much more stabilized by the introduction of the cationic charge than the HOMO. Thus, the low lying LUMO (–6.26 eV) should enable carbene **6** to exert significant acceptor character.

A similar pattern arises when the singlet–triplet (S–T) gaps are calculated for both species. The S–T gap also provides an estimate of the reactivity of a carbene species.^{14,15} Whereas the S–T gap of 72.5 kcal mol⁻¹ for the neutral NHC **13** is within the range reported for other imidazole based NHCs (which are approximately 83 kcal mol⁻¹), the S–T gap of the cationic carbene **6** is significantly reduced and amounts to only 53.2 kcal mol⁻¹. This value approaches the value of the Alder-type carbene C(N⁺Pr)₂ (~41 kcal mol⁻¹) or the cyclic amino(alkyl) carbenes (~47 kcal mol⁻¹).¹⁶ Interestingly, while a small S–T gap correlates frequently with carbene dimerisation, no such reaction was observed in the case of carbene **6** which decomposed to unidentified products in the absence of a trapping reagent. Further investigations into the reactivity of carbenes **6** are currently in progress.

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