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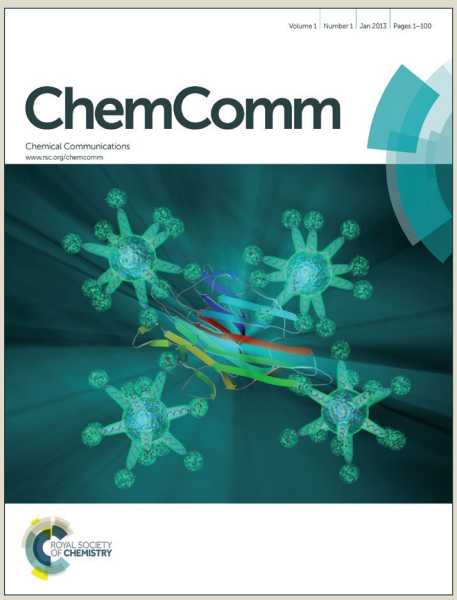

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Imine-functionalised protic NHC complexes of Ir: Direct formation by C-H activation

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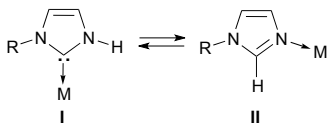
N-arylimine-functionalised protic NHC (pNHC) Ir(I) and Ir(III) complexes are obtained directly from neutral or cationic Ir(I) imidazole complexes using excess $[Ir(cod)(\mu\text{-}Cl)]_2$ or $TlPF_6$, respectively. N-arylimine-functionalised imidazolium salts lead to imidazole or pNHC complexes by competing N-H or C-H bond activation depending on the type of the imidazolium counterion.

The landmark isolation of stable NHCs of the imidazole type made use of bulky N-substituents for the successful kinetic and thermodynamic stabilisation of the reactive carbene species.[1] Since then, bulky alkyl and aryl substituents have been used routinely in the NHC coordination chemistry, exerting also subtle electronic and steric tuning of the C_{NHC}-metal interactions. In contrast, 1H-imidazol-2-ylidene, the simplest parent (R = H) imidazol-type *p*rotic *NHC* (pNHC) has only recently been stabilised by coordination to transition metals (**I**),[2] and the resulting carbene complex may be transformed to its imidazole tautomer (**II**).[3]

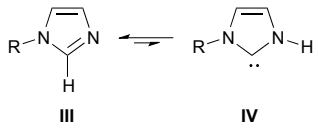


Scheme 1 Tautomerism/metallotropism involving *p*rotic *NHC* (pNHC) and imidazole ligands (M = metal, R = H, alkyl, aryl, functional group).

pNHCs constitute versatile spectator ligands, which, in addition to their strong σ-donor character, provide the option of secondary interactions, (*i.e.* H-bonding), that could be of importance in the design of bifunctional catalysts,[4] substrate recognition[5] and of relevance to biological systems.[6]

The coordination chemistry of pNHCs is a topical area of interest, thanks to the successful development of versatile synthetic methodologies based on building the C-bound heterocycle at the metal coordination sphere,[7] or using suitable N-protecting groups that are removed after coordination,[8] or by facilitating kinetic formation of the M-C_{NHC} bond by C-X bond (X = halide) oxidative-addition of halo-imidazoles.[2a,9] Conceptually simpler is the *direct* pNHC formation.

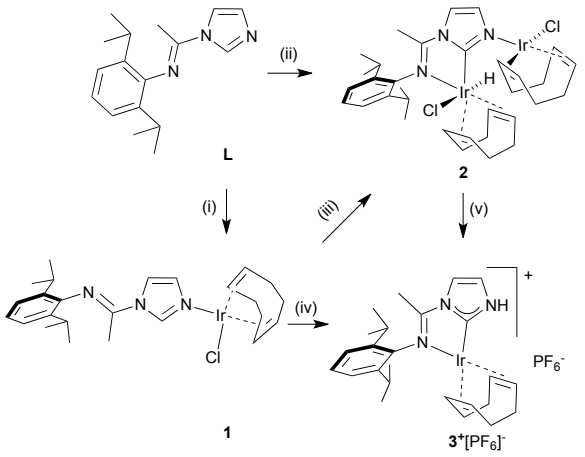
It has been established computationally that 1H-imidazole is more stable than the tautomeric 1H-imidazol-2-ylidene by *ca.* 30 kcal/mol.[3a] However, this energy difference can be suppressed and reversed on metal coordination of the 1H-imidazol-2-ylidene. Analogous comments apply to 1R-imidazole (**III**) and tautomeric pNHCs 1R-imidazol-2-ylidenes (**IV**).



The conversion of coordinated R-imidazole to pNHC (**II** → **I**) was firstly demonstrated experimentally by the acid-catalyzed rearrangement of Ru-imidazol to Ru-pNHC[10] and, more recently, by the deprotonation with an external base of imidazoles coordinated to mononuclear, inert 6-coordinate d^6 Re(I) and Mn(I) carbonyls[11] and $Fe(NO)_2(CO)$,[6a] followed by quenching of the resultant imidazolide with a suitable acid. Conversely, transformation of Ru-coordinated NHC following N-C bond activation to a mixture of coordinated imidazole and pNHC tautomers was studied by experimental and computational means.[3b,3c] Similar rearrangements involving related benzimidazole[12] or pyridine[13] heterocycles have been observed, and associated with catalytic transformations.

From these limited available examples, it appears that the elementary steps involved in C-H and N-H bond cleavage/formation, which may be responsible for tautomerism, may be mechanistically diverse. Furthermore, the presence of functionalities capable of stabilising and directing C *vs.* N metalation has not been thoroughly examined, except in the context of the formation of heteroatom-functionalised NHC spectator ligands.[14]

Herein, we report preliminary studies aiming at the synthesis of N-arylimine-functionalised imidazole and pNHC complexes of iridium (type **I**, R = arylimino, M = Ir), and at gaining insight into the elementary steps that may operate during imidazole to pNHC tautomerism (from **II** to **I** in Scheme 1). The arylimine functional group was selected by virtue of its comparable donor characteristics with the κ^1-N-imidazole ligand and the possible *reversible* formation of chelates.



Scheme 2 Synthesis of complexes **1**, **2** and $\mathbf{3}^{+}[PF_6]^{-}$. Reagents and conditions: (i) 0.5 equiv. of $[Ir(cod)(\mu\text{-}Cl)]_2$, THF, RT, 97% yield; (ii) 1.0 equiv. of $[Ir(cod)(\mu\text{-}Cl)]_2$, THF, RT, 86% yield; (iii) 0.5 equiv. of $[Ir(cod)(\mu\text{-}Cl)]_2$, THF, RT, 86% yield; (iv) 1.0 equiv. of $TlPF_6$, CH_2Cl_2 or MeCN, RT, 85% yield; (v) 1.0 equiv. of $TlPF_6$, -0.5 equiv. $[Ir(cod)(\mu\text{-}Cl)]_2$, CD_2Cl_2, RT.

Reaction of 1-(2,6-di*iso*propylphenylimino)ethylimidazole (**L**)[15] with 0.5 equiv. of $[Ir(cod)(\mu\text{-}Cl)]_2$ in THF led to the isolation of **1** (Scheme 2). Both analytical and spectroscopic (^{1}H- ^{13}C{^{1}H}-NMR and IR) data point to the presence of a N-bound Ir(cod)Cl fragment (see ESI for synthetic details and full characterisation). Particularly diagnostic is a broad peak at δ 8.88 assignable to the C2-*H* (*cf* δ 8.11 in **L**). N-coordination was further corroborated crystallographically (Figure S1 in ESI).‡ Importantly, the arylimino functional group (in *E* configuration in **1**) is dangling.

Further reaction of **1** with $[Ir(cod)(\mu\text{-}Cl)]_2$ (0.5 equiv.) or reaction of **L** with 1.0 equiv. of $[Ir(cod)(\mu\text{-}Cl)]_2$ (THF, RT) gave **2** (Scheme 2). Its ^{1}H NMR spectrum (THF-d_8), contains a hydride signal at δ -14.74 and in the ^{13}C NMR spectrum, signals at δ 166.6 and 158.7 are assignable to $C_{(imine)}$ and *C*-$2_{(NHC)}$, respectively. The IR ν(Ir-H) band is observed at 2200 cm^{-1}. The structure of **2** (Fig. 1) revealed a binuclear complex comprising one N-bound Ir(I) centre (*cf.* **1**), and one C2-bound Ir(III) center, formally originating from the second equivalent of $[Ir(cod)(\mu\text{-}Cl)]_2$; crucially, the N-arylimino group is also coordinated to Ir(III) as part of a 5-membered chelate. One can thus consider the N-bound Ir(cod)Cl moiety as a $N_{(imidazole)}$ *'metalla protecting and activating group'*, which in cooperation with the directing effect of the N-arylimine, facilitates C2 metalation. The latter may involve C-H oxidative addition,[16] in line with the observed *cis* Ir-C and Ir-H bond disposition.

With the hope to access a pNHC Ir complex by tautomerism of a more reactive species (*e.g.* $[\mathbf{1}\text{-}Cl^{-}]^{+}$), **1** was treated with the chloride abstracting $TlPF_6$ (in CH_2Cl_2 or MeCN, RT) and, gratifyingly, this led to the isolation of the salt $\mathbf{3}^{+}[PF_6]^{-}$. Its ^{1}H NMR spectrum contains a characteristic new broad singlet at δ 10.36, and the signal of the C2-*H* of the starting material has disappeared, while in the ^{13}C NMR spectrum the N*C*N and *C*=N signals have shifted considerably downfield (from δ 138.3 and 148.9 to 173.6 and 168.0, respectively). The IR absorptions at 3359 and 1613 cm^{-1} are assignable to N-H[8a] and coordinated C=N, respectively.

The structure of $\mathbf{3}^{+}[PF_6]^{-}$ was elucidated crystallographically (see Fig. 2 for the cation and ESI for details).‡ The Ir adopts a distorted square-planar coordination geometry defined by a κ^2(N,C)-bound novel imino-functionalised pNHC and a cod ligand.

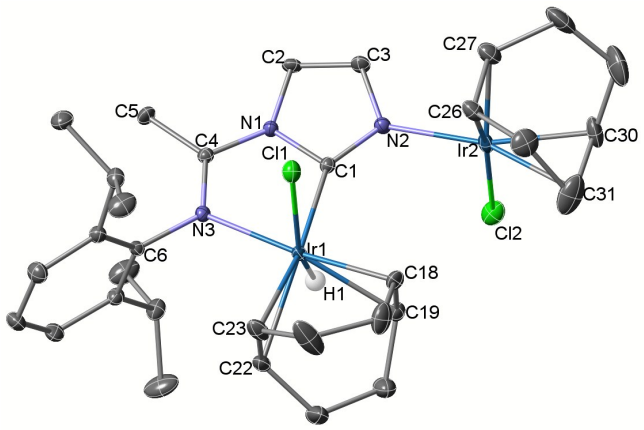


Fig. 1 Molecular structure of **2**. H atoms are omitted for clarity. Thermal ellipsoids are at the 30% level.

The Ir−C_{pNHC} bond distance (1.984(3) Å) is shorter than the average found in other Ir(I)-NHC complexes[17] (2.038 Å, range 1.895 Å−2.194 Å, with shorter bond lengths associated with chelating NHC ligands), probably due to the chelate formation and the small hydrogen substituent at N1 atom. The closest N−H···F(PF_5) distances of 2.37(5) and 2.49(5) Å are consistent with hydrogen bonding interactions.

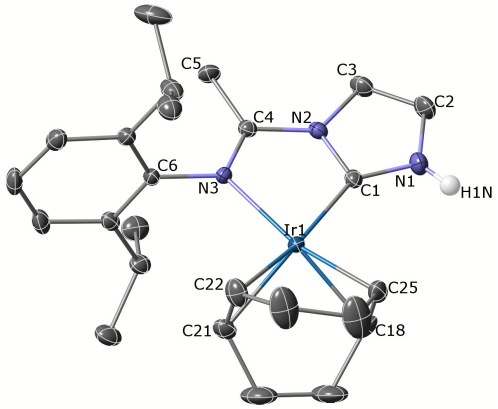
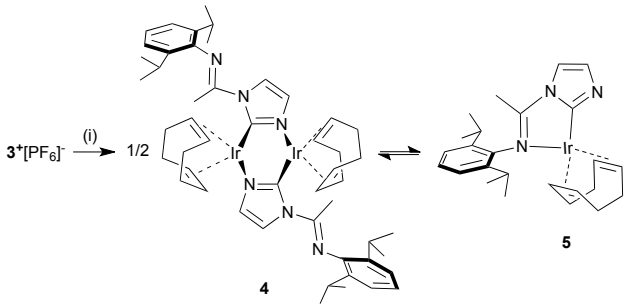


Fig. 2 Molecular structure of the cation in $\mathbf{3}^{+}[PF_6]^{-}$. H atoms are omitted for clarity, except H1(N1). Thermal ellipsoids are at the 30% level.

The tautomerism (**II** → **I** in Scheme 1) of the transient $[\mathbf{1}\text{-}Cl^{-}]^{+}$ to $\mathbf{3}^{+}$, which provides an alternative to the recently reported metalation of 2-chloro-benzimidazole heterocycles and the formation of anionic and pNHC ligands,[9b] may involve concerted, dyotropic-type metalation/H transfer and be driven by the thermodynamic stability of $\mathbf{3}^{+}$ due to Ir-C bond or/and chelate ring formation.[†] It has been reported that the increased electrophilicity (going from Ir(I) to Ir(III) and Ir-Cl to Ir^{+}) favours the formation of the pNHC over imidazole complexes.[3a] Interestingly, abstraction with 1.0 equiv. of $TlPF_6$ of a chloride ligand in **2**, most likely from the Ir(III) centre, also gave $\mathbf{3}^{+}[PF_6]^{-}$, together with $[Ir(cod)(\mu\text{-}Cl)_2]$ which originates from the N-bound Ir(cod)Cl moiety, in quantitative NMR yield (Scheme 2).

In attempts to establish experimentally whether discrete deprotonation/protonation steps may model the reverse reaction, *i.e.* the transformation from pNHC to N-imidazole, the pNHC in $\mathbf{3}^{+}$ was deprotonated with 1.0 equiv. of NaO*t*-Bu (Scheme 3).



Scheme 3 Synthesis of **4** and **5**. Reagents and conditions: (i) 1.0 equiv. of NaO*t*-Bu, CH_2Cl_2, 0 ºC, 70% yield.

A complex with coordinated 'anionic' imidazolide[9b,14a] was not obtained, but rather a mixture of two different iridium species (in a ratio of *ca.* 25:75 by ^{1}H NMR in CD_2Cl_2 at RT). The ^{13}C NMR spectrum of the mixture showed signals due to N*C*N and *C*=N at δ 174.8 and 156.2, δ 179.3 and 166.3, respectively. Attempts to separate the mixture by crystallisation led to the isolation of **4** (the ^{1}H NMR spectrum of which is assignable to the minor component of the mixture) in the form of dark red crystals (Fig. 3). Its structure features a diiridium core with two bridging monoanionic imidazolides in a symmetrical 'boat-like' conformation and no direct Ir-Ir interaction (d(Ir-Ir) = 3.1844(3) Å).‡

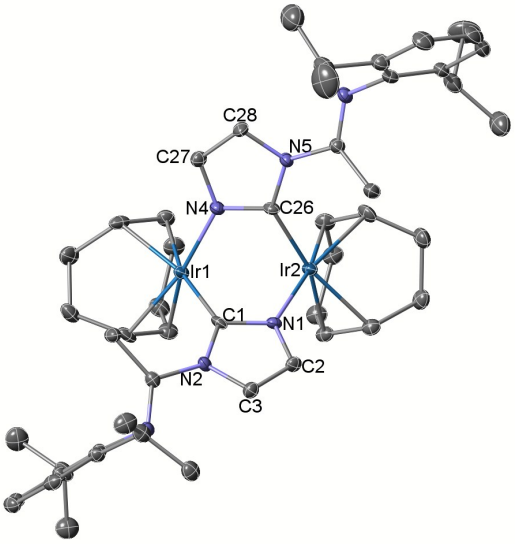
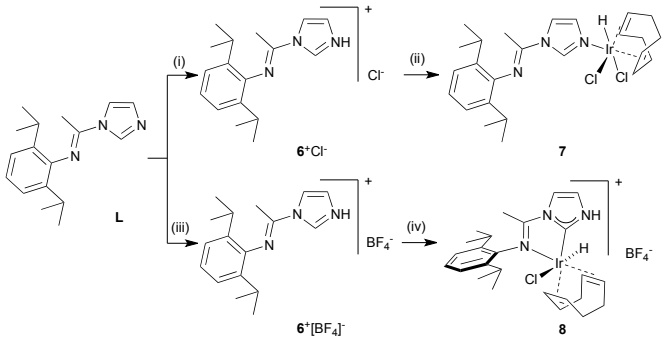


Fig. 3 Molecular structure of **4**. H atoms are omitted for clarity. Thermal ellipsoids are at the 30% level.

Both Ir centres adopt a square planar coordination geometry, defined by the olefinic bonds of the cod ligand, one carbon atom and one nitrogen atom of the imidazolide. Interestingly, the N-arylimine functionality has become dangling. In the supernatant solution after isolation of **4** the same ratio of species was observed (by NMR), and dissolution of crystals of **4** resulted again in the same mixture. This points to the presence of a chemical equilibrium with another (major) partner, the nature of which can be inferred by NMR spectroscopy: on the basis on the general appearance of the spectrum and since the chemical shift of *C*=N of the major partner is similar to the corresponding value for $\mathbf{3}^+$, we suggest that this partner is the neutral, mononuclear complex **5** depicted in Scheme 3.Attempts to protonate the mixture **4** and **5** or deprotonate **1** led to intractable product mixtures.

The role of the '$[Ir(cod)]^+$' fragment in $[\mathbf{1}\text{-}Cl^-]^+$ as 'metalla-protecting and -directing group' for the direct metallation of the C2-H imidazole, raised the question whether non-metal electrophiles, such as a proton, could undertake similar roles. In preliminary experiments, the simple imidazolium salts $\mathbf{L}H^+X^-$ ($\mathbf{6}^+Cl^-$ and $\mathbf{6}^+[BF_4]^-$) (see ESI for synthetic details and full characterisation data) were reacted with $[Ir(cod)(\mu\text{-}Cl)]_2$ (Scheme 4).



Scheme 4 Reactions of $(\mathbf{L}H^+)X^-$ with $[Ir(cod)(\mu\text{-}Cl)]_2$. Reagents and conditions: (i) 1.0 equiv. of HCl (a solution in Et_2O), Et_2O, RT, 85% yield; (ii) 0.5 equiv. of $[Ir(cod)(\mu\text{-}Cl)]_2$, THF, RT, 85% yield; (iii) 1.0 equiv. of $HBF_4{\cdot}Et_2O$, Et_2O, RT, 73% yield; (iv) 0.5 equiv. of $[Ir(cod)(\mu\text{-}Cl)]_2$, THF, RT, 82% yield.

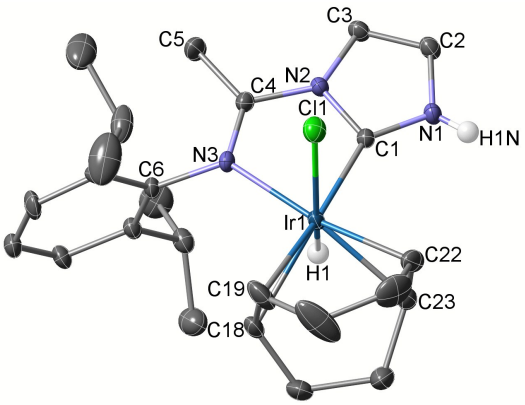


Fig. 4 Molecular structure of $\mathbf{8}^+$ in $\mathbf{8}^+[BF_4]^-$. H atoms are omitted for clarity, except H1(N1). Thermal ellipsoids are at the 30% level.

Unexpectedly, the selectivity of the reactions is dependent on the nature of X^-. The reaction of $\mathbf{6}^+Cl^-$ with 0.5 equiv. of $[Ir(cod)(\mu\text{-}Cl)]_2$ in THF at room temperature gave the Ir hydride complex **7**, formally a product from the oxidative addition of the N-H bond to Ir(cod)Cl (Ir-*H* at δ -12.10 in CD_2Cl_2, ν(Ir-H) at 2206 cm^{-1}). In contrast, the reaction of $\mathbf{6}^+[BF_4]^-$ with 0.5 equiv. of $[Ir(cod)(\mu\text{-}Cl)]_2$ under the same conditions, yielded the Ir hydride complex salt $\mathbf{8}^+[BF_4]^-$ (Ir-*H* at δ -14.50 in CD_2Cl_2, ν(Ir-H) at 2211 cm^{-1}, ν(N-H) at 3241 cm^{-1}). The cation $\mathbf{8}^+$ (Fig. 4)‡ formally arises from the oxidative-addition of the C2-H bond to Ir(I). Similarly to the Ir(III) centre in **2**, the Ir in $\mathbf{8}^+$ is in a distorted octahedral coordination geometry defined by a κ^2(C,N) pNHC–imino chelate, one cod ligand and *trans* hydride and chloride ligands. The presence of a N−H···F(BF_3) hydrogen bond can also be deduced from the metrical data (N−H···F distance 2.721(3) Å). The underlying reason behind the anion-dependent selectivity is under investigation but it is clear that the presence of a coordinating anion (Cl^- *vs.* BF_4^-) favors a monodentate behaviour of ligand **L**.

In conclusion, we have isolated and characterised novel Ir(I) and Ir(III) intermediates involved in the formation of N-arylimine-

functionalised pNHC complexes of Ir by the direct C-H activation of the corresponding imidazoles and imidazolium salts. These results highlight the importance of the imidazole pre-coordination or the use of the imidazolium salts for successful pNHC isolation. In the former case, binuclear or cationic Ir species are implicated in the C2-H metalation, in the latter, counterion effects influence the selectivity for N-H *vs.* C-H activation. The insight provided may be useful in understanding subtle mechanistic details and developing simpler synthetic methodologies relevant to pNHC complex formation. These targets are being further pursued in our laboratory.

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Notes and references

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†The role of chelate ring formation in addition to the difference or Ir-N *vs.* Ir-C bond energies may be important in rationalising the relative thermodynamic stability of the complexes studied. To estimate these key factors, we initiated the study of the N to C rearrangement in Ir(I) complexes with 1,4-di(arylimino)imidazoles; preliminary experimental results support that Ir-C bond strength is an important factor contributing to the thermodynamic stability.

‡ Electronic Supplementary Information (ESI) available: Experimental and X-ray crystallographic data. CCDC 1039710-1039714. See DOI: 10.1039/c000000x/

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