DALTON COMMUNICATION

C–H activation with *N*-heterocyclic carbene complexes of iridium and rhodium

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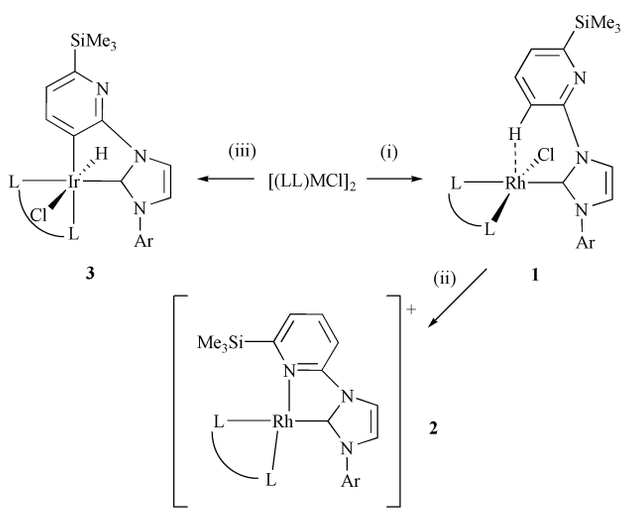
The first example of intramolecular, room temperature activation of a C–H bond in *N*-pyridine functionalised heterocyclic carbene complexes of iridium is reported.

The current research effort in the area of *N*-heterocyclic carbene (NHC) complexes of platinum group metals has originated from the desire to develop high activity phosphine free catalysts.[1] In comparison to the electronically similar phosphine systems,[2] NHC based catalysts are considered to be robust and not susceptible to deactivation by cyclometallation or P–C cleavage reactions even at high temperatures.[1] However, the mechanism and the detailed nature of the catalytic species have been relatively unexplored even for the most common palladium catalysed Heck couplings. In more recent developments, the attachment of other functional groups to NHCs has given rise to versatile ligand designs, featuring hemilability, electronic asymmetry of the active sites, *etc*.[3,4] We have recently described the isolation and full characterisation of *N*-functionalised bidentate chelate or tridentate 'pincer' NHCs and their use in the synthesis of platinum group metal complexes under mild conditions.[5] In this communication we describe the functionalisation of these ligands by activation of the C–H bonds of the pyridine ring at room temperature.

Interaction of $[M(\eta^4\text{-}1,5\text{-cyclooctadiene})Cl]_2$, M = Rh or Ir, with one equivalent of 1-[(2-(6-trimethylsilyl)pyridyl]-3-[(2,6-di-*iso*-propyl)phenyl]imidazol-2-ylidene[5a] (py-NHC), resulted in the isolation of the air stable crystalline products **1** and **3** in quantitative yields (Scheme 1), which were characterised by spectroscopic and analytical methods.



Scheme 1 Reagents and conditions: (i) 1eq. py-NHC in thf, −78 °C to room temperature; (ii) $Na\{B[3,5\text{-}C_6H_3(CF_3)_2]_4\}$ in ether; (iii) 1eq. py-NHC in thf, −78 °C to room temperature. L–L = η^4-1,5-cyclooctadiene.

The ^{1}H-NMR spectrum of **1**† showed peaks assignable to the coordinated cyclooctadiene and the NHC ligand framework. However, the peak due to the H5 of the pyridine ring was dramatically deshielded by *ca.* 2 ppm, relative to the free ligand, indicating strong interaction of this hydrogen with the metal centre. The spectrum remained unchanged up to 70 °C. Since $^1J_{C\text{–}H3}$ (167 Hz) was not significantly different from a typical aromatic C–H coupling constant, we reasoned that the observed shift originated from an intramolecular hydrogen bond rather than an agostic interaction. This interaction is persistent at 100 °C for at least 48 h (by NMR).

A further insight into the structure of **1** was obtained from a single crystal X-ray diffraction study (Fig. 1).‡

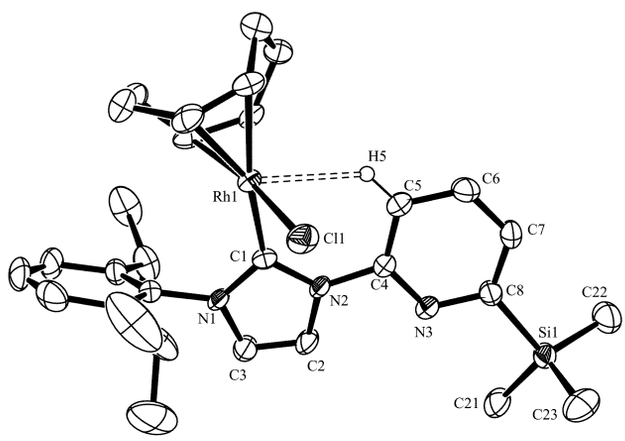


Fig. 1 Molecular structure of **1**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids shown at 50% probability. Selected bond lengths (Å) and angles (°): Rh1–C1 2.029(4), Rh1–Cl1 2.372(1); C1–Rh1–Cl1 89.89(11).

The coordination sphere of the square planar metal (16e$^-$) centre comprises the carbene carbon, the cyclooctadiene and the chloride; the pyridine nitrogen remains uncoordinated, pointing away from the metal. In addition there is a close contact between the rhodium and the H on C5 (Rh1–H5 = 2.532 Å, H was experimentally located) of the pyridine ring, indicating that the structure observed in solution is maintained in the solid state. The possibility that the pyridine nitrogen remains uncoordinated due to the steric constraints imposed by the trimethylsilyl group was explored by the reaction of **1** with $Na\{B[3,5\text{-}C_6H_3(CF_3)_2]_4\}$ in ether. The reaction instantaneously formed the air stable salt **2** (Fig. 2)‡ in quantitative yield, in which the pyridyl function is coordinated to the metal. It is therefore plausible to assume that pre-dissociation of the chloride is necessary before the coordination of pyridine takes place.

Light green **3** was isolated in quantitative yield from the reaction of py-NHC with $[Ir(\eta^4\text{-}1,5\text{-cyclooctadiene})Cl_2]_2$ under the same conditions as **1**. The ^{1}H-NMR spectrum of **3**† shows a characteristic hydride peak at −15.5 ppm [IR 2202 cm^{-1} (υIr–H)] and the absence of the doublet assigned to the H3 of the pyridine ring, implying that metallation has taken place. This was confirmed by a single crystal X-ray diffraction study (Fig. 3).‡

In this case the coordination sphere of the iridium(III) centre comprises the carbene carbon, the carbon of the metallated

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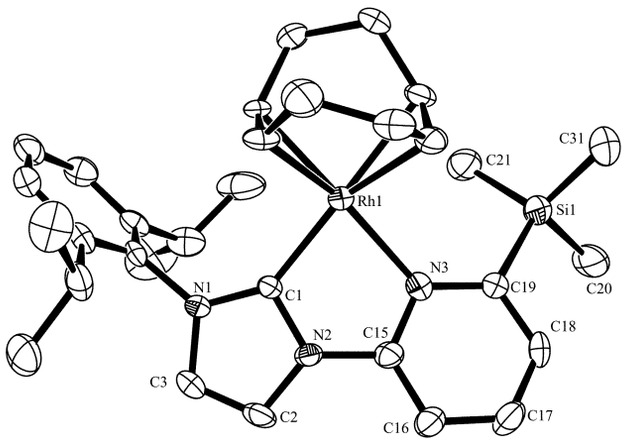

Fig. 2 Molecular structure of the cation in **2**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids shown at 50% probability. In addition to the borate anion, the unit also contains one molecule of toluene. Selected bond lengths (Å) and angles (°): Rh1–C1 2.028(6), Rh1–N3 2.156(5); C1–Rh1–N3 78.4(2), Rh1–C1–N2 110.2(4), C1–N2–C15 119.9(5), N2–C15–N3 113.6(5), C15–N3–Rh1 108.1(4).

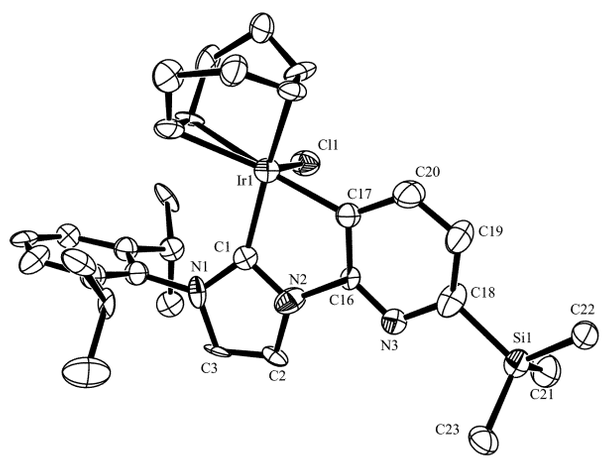

Fig. 3 Molecular structure of **3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids shown at 50% probability. Selected bond lengths (Å) and angles (°): Ir1–C1 2.018(19), Ir1–Cl1 2.501(4), Ir1–C17 2.022(15); C17–Ir1–Cl1 86.1(5), C1–Ir1–C17 78.8(7), Cl1–Ir1–C1 85.3(5).

pyridine ring, the cyclooctadiene and the chloride; the hydride could not be located experimentally.

Although oxidative addition of imidazolium and alkyl or aryl substituent C–H bonds of NHC rhodium and iridium complexes have been reported,[7] this is the first example involving functionalised NHC ligands. It is remarkable that this reaction takes place under mild conditions.§ The formation of **1** and **3** is possibly kinetically controlled.

The preliminary observations described here are expected to have important implications on the use of NHC ligands in catalysis, the design of new ligands supporting desired catalytic transformations and the understanding of the mode of catalytic action of known *N*-functionalised NHCs. These issues are now under investigation in our group.

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Notes and references

† Spectroscopic data for **1**: NMR (C_6D_6), ^{1}H, δ 10.85 (1H, d, pyridine H5), 8.0 (1H, s, imidazolylidene), 7.4 (t, 1H, pyridine H4), 7.3 (d of t, 2H, $C_6H_3Pr^i_2$), 7.2 (1H, d, pyridyl H3), 6.9 (1H, d, $C_6H_3Pr^i_2$), 6.2 (1H, s, imidazolylidene), 5.3 and 4.3 (two d of m, 1H each, olefinic protons of cyclooctadiene), 1.8 and 2.2 (m, 8H, aliphatic protons of cyclooctadiene), 4.2 and 2.3 [septet, 2H, $C_6H_3CH(CH_3)_2$], 1.6, 1.1, 1.0 and 0.8 [four d, 12H, $C_6H_3CH(CH_3)_2$], 0.2 [s, 9H, $Si(CH_3)_3$].

For **2**: NMR (CD_2Cl_2), ^{1}H, δ, 8.0, 7.8, 7.4, 7.3, 7.2 and 6.9 (m, 16H, aromatic), 4.8 and 3.6 (two m, 2H each, olefinic protons of cyclooctadiene), 2.2 and 1.7 (m, 8H, aliphatic protons of cyclooctadiene), 2.5 [septet, 2H, $C_6H_3CH(CH_3)_2$], 1.1 and 1.4 [two d, 12H, $C_6H_3CH(CH_3)_2$], 0.2 [s, 9H, $Si(CH_3)_3$].

For **3**: NMR (C_6D_6), ^{1}H, δ 7.6, 7.4, 7.3, 7.0 and 6.2 (m, 8H, aromatic), 4.5 and 3.0 (two m, 4H, olefinic protons of cyclooctadiene), 1.8 and 2.2 (m, 8H, aliphatic protons of cyclooctadiene), 3.8 and 2.4 [septet, 2H, $C_6H_3CH(CH_3)_2$], 1.6, 1.2, 1.0 and 0.9 [four d, 12H, $C_6H_3CH(CH_3)_2$], 0.2 [s, 9H, $Si(CH_3)_3$], −15.5 (s, 1H, hydride). IR (cm^{-1}) 2202 (υIr–H).

‡ Crystal data for **1**: $C_{31}H_{41}Cl_1N_3Rh_1Si_1$, M = 624.13 g mol^{-1}, yellow crystal, 0.1 × 0.08 × 0.03 mm^3, monoclinic, $P2(1)/n$ (no. 14), a = 10.3072(4), b = 21.6566(8), c = 14.1863(6) Å, β = 98.883(1)°, V = 3128.7(2) Å^3, T = 150 K, Z = 4, ρ = 1.325 mg m^{-3} μ(Mo-Kα) = 0.693 mm^{-1}, λ = 0.71073 Å, 16713 reflections measured, 5658 unique (R_{int} = 0.1071) which were used in all calculations. The final $wR(F^2)$ was 0.1066 (all data) and R = 0.0503 [$F > 2\sigma(F)$]. Pyridine hydrogens were located experimentally, all others were fixed.

For **2**: $C_{70}H_{63}B_1F_{24}N_3Rh_1Si_1$, M = 1544.04 g mol^{-1}, orange crystal, 0.1 × 0.1 × 0.1 mm^3, triclinic, $P\bar{1}$ (no. 2), a = 13.1410(4), b = 16.6819(4), c = 18.5852(7) Å, α = 72.274(1), β = 69.556(1), γ = 69.840(2)°, V = 3504.33(19) Å^3, T = 150 K, Z = 2, ρ = 1.463 mg m^{-3}, μ(Mo-Kα) = 0.368 mm^{-1}, λ = 0.71073 Å, 37869 reflections measured, 13990 unique (R_{int} = 0.1951) which were used in all calculations. The final $wR(F^2)$ was 0.2194 (all data) and R = 0.0827 [$F > 2\sigma(F)$].

For **3**: $C_{31}H_{42}Cl_1Ir_1N_3Si_1$, M = 712.42 g mol^{-1}, green needle, 0.03 × 0.01 × 0.01 mm^3, monoclinic, $P2(1)/n$ (no. 14), a = 8.1132(16), b = 14.308(3), c = 25.784(6) Å, β = 93.99(1)°, V = 2985.7(11) Å^3, T = 150 K, Z = 4, ρ = 1.585 mg m^{-3}, μ(Mo-Kα) = 4.626 mm^{-1}, λ = 0.71073 Å, 10106 reflections measured, 4213 unique (R_{int} = 0.1444) which were used in all calculations. The final $wR(F^2)$ was 0.1711 (all data) and R = 0.0781 [$F > 2\sigma(F)$]. All structures were collected on a KappaCCD area detector diffractometer with an FR591 rotating anode employing an Oxford Cryostreams low temperature device. All solutions and refinements were performed using the WinGX package[6] and all software packages within. All non-hydrogen atoms were refined using anisotropic thermal parameters and hydrogens were added using a riding model. CCDC reference numbers 183891–183893. See http://www.rsc.org/suppdata/dt/b2/b205617h/ for crystallographic data in CIF or other electronic format.

§ We have now observed C–H activation with rhodium functionalised NHC complexes that will be reported in a full paper.

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