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# **Iridium, Ruthenium, and Palladium Complexes Containing a Mesoionic Fused Imidazolylidene Ligand**

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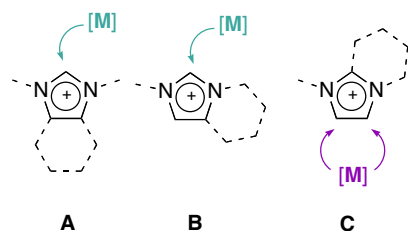
## **Abstract**

Imidazo[1,2-*a*]pyridine consisting of a pyridine fused to an imidazolium salt at the imidazolium N1–C2 bond and hence protected from forming normal imidazole-2-ylidene complexes undergoes selective activation of the C5–H bond with Ag<sub>2</sub>O, *i.e.* at the imidazolium carbon that is proximal to the pyridine nitrogen. While the silver carbene complex is unstable, transmetalation with [IrCp\*Cl<sub>2</sub>]<sub>2</sub>, [RuCl<sub>2</sub>(cym)]<sub>2</sub>, and [PdCl(allyl)]<sub>2</sub> afforded stable mesoionic carbene complexes. Two iridium(III) complexes containing one fused carbene ligand and one palladium(II) complex containing two carbene ligands at the metal center were structurally characterized. The absence of substituents adjacent to the carbene carbon prevents wingtip group activation, and it imparts a reduced stability of the complexes in particular under (mildly) acidic conditions.

## **Introduction**

The discovery and development of N-heterocyclic carbenes (NHCs) as ligands has greatly transformed the organometallic chemistry of transition metals and has demonstrated a marked impact on the application of metals in synthesis, catalysis, materials science, and medicinal chemistry [1–11]. A large variety of NHC ligand structures have been discovered, characterized and applied in metal coordination [12–20]. Ring-fused NHCs are a particular subclass of NHCs that often display distinct characteristics that are different from normal imidazole-derived NHCs [21,22]. The most common ring fusion is of course the annulation of a benzene ring to the C4–C5 bond of the NHC (**A**, Fig. 1), and indeed a plethora of applications have been disclosed based on the benzimidazole ring structure [23–25]. Fused systems that involve one of the imidazole nitrogen atoms (**B**, **C**, Fig. 1) have been less

investigated [26–33], even though a variety of synthetic approaches towards such fused ligand precursor systems are available and allow for the introduction of a variety of coordination motifs [34–40]. Based on our interest in strongly donating carbenes such as mesoionic/abnormal carbenes [41–49], we were particularly interested in fused ligand systems that include the annulation of the imidazole C2 position (C, Fig. 1), since substitution at C2 predisposes the ligand to bind via the imidazole C4 or C5 position and hence to produce abnormal/mesoionic carbenes [13–18].



**Fig. 1** Schematic representation of ring-annulated imidazolium salts and their most probably site of metallation (arrows), green arrows lead to normal carbene complexes, purple arrows to mesoionic/abnormal carbene complexes.

## Results and Discussion

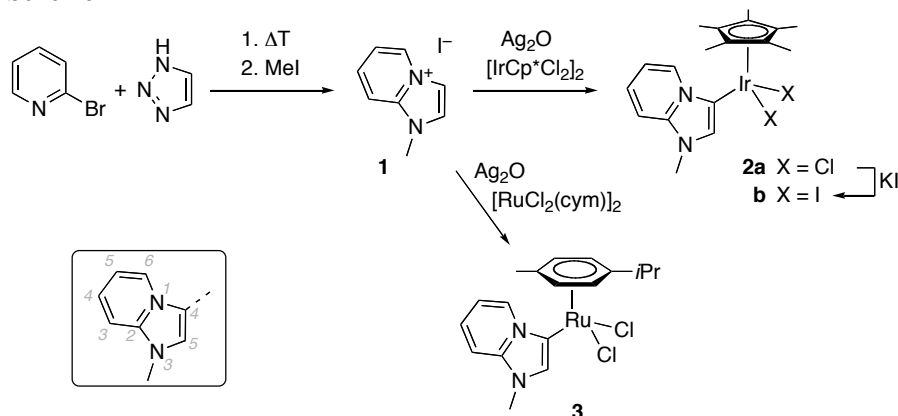
**Ligand synthesis.** The fused imidazo[1,2-*a*]pyridine skeleton was readily available by thermal condensation of 1,2,3-triazole with bromopyridine and subsequent elimination of nitrogen at elevated temperatures according to a procedure described by Hubert and Reimlinger (Scheme 1) [34]. The desired product was obtained as HBr salt in yields significantly higher (75%) than when using chloropyridine as starting material. After neutralization, alkylation with MeI proceeded essentially quantitatively and gave the imidazo[1,2-*a*]pyridinium salt **1** as a pale yellow solid.

**Iridium and ruthenium complexation.** Metallation of **1** via C–H bond activation using  $[\text{IrCp}^*\text{Cl}_2]_2$  in refluxing toluene did not produce any carbene complex and just returned starting materials. As a consequence, the silver carbene formation and subsequent transmetallation was considered [49,50], even though abnormal silver carbene complexes were noted to be very unstable and often have too short lifetimes to be useful for transmetallation [51–53]. Upon reaction of **1** with  $\text{Ag}_2\text{O}$ , indeed, a silver carbene complex formed as inferred from the disappearance of the resonance of one imidazolium proton at  $\delta_{\text{H}}$  8.2 ppm in the  $^1\text{H}$  NMR spectrum and an associated minor shifts of the residual signals due to the different substitution pattern upon metallation. Attempts to isolate and fully characterize the putative complex were unsuccessful due to its limited stability. For example, gradual decomposition was observed in  $\text{CDCl}_3$  solution within a few hours, yielding

predominantly the protonated ligand precursor together with some other unidentified compounds.

Due to the restricted stability of the silver carbene complex, a one-pot procedure was applied which involved a mixture of ligand precursor **1**, Ag<sub>2</sub>O, and the transmetallating agent in order to trap any formed silver carbene. According to this procedure, several metal carbene complexes were successfully prepared from **1**. Complex **2a** was obtained from **1** at room temperature upon transmetallation of the in-situ generated silver carbene intermediate with [IrCp\*Cl<sub>2</sub>]<sub>2</sub>, or cleaner, when starting from the imidazolium tetrafluoroborate salt. The iodide analogue **2b** was prepared either in situ or in a stepwise manner from **2a** and an iodide source such as KI in acetone. Likewise, the ruthenium(II) complex **3** was isolated when using [RuCl<sub>2</sub>(cym)]<sub>2</sub> for transmetallation. Both complexes formed in high spectroscopic yield (>90% according to <sup>1</sup>H NMR spectroscopic analysis of crude reaction mixtures). Complexes **2a** and **3** were readily purified by recrystallisation or by column chromatography on silica, albeit with substantially lower yields. In contrast, purification of complex **2b** by column chromatography was unsuccessful. Both complexes **2** and **3** are stable for weeks in the solid state even when stored in air.

**Scheme 1**

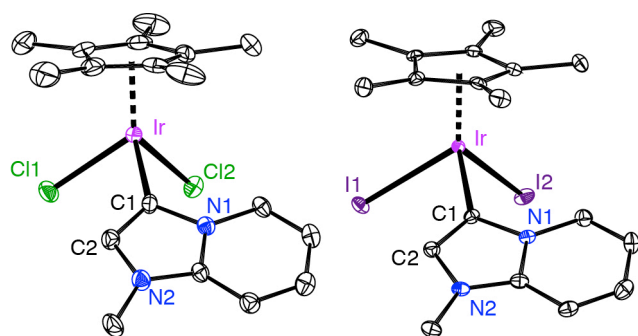


Complex **2a** and **2b** have very similar analytical features. Complex **2a** was characterized by <sup>1</sup>H NMR spectroscopy and showed a singlet for the CH<sub>imid</sub> at δ<sub>H</sub> 6.96 ppm, which is substantially upfield compared to the imidazolium precursor (δ<sub>H</sub> 8 ppm). Also the pyridinic protons shift to slightly higher field upon metallation (Δδ ca. 0.5 ppm) apart from the C6-bound proton, which is deshielded to almost 9 ppm. The iridium-bound carbon resonates at 128.4 ppm, a value significantly low when compared to shifts in similar fused iridium(III) carbene complexes [30], yet in good agreement with other abnormal imidazolylidene

complexes [42,54]. Both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra revealed only one set of signals, which strongly indicates chemoselective metallation either at the imidazolium C4 or C5 position (*cf* Scheme 1 for atom labeling). The significant deshielding of the pyridinic C6-bound proton points to an interaction of this site with the  $\text{IrCp}^*\text{Cl}_2$  fragment and hence metallation at the imidazole C5 position. Moreover, the singlet at  $\delta_{\text{H}}$  3.80 ppm attributed to the  $\text{NCH}_3$  group shows a nuclear Overhauser effect (nOe) with the singlet of the imidazole heterocycle at  $\delta_{\text{H}}$  6.96 ppm as well as with the doublet due to the pyridinic C3-bound proton at  $\delta_{\text{H}}$  7.35 ppm, providing evidence that the site *ortho* to the  $\text{NCH}_3$  group is not metallated. These two mutually independent probes strongly suggest selective activation of the C5–H bond during silver carbene complex formation. Chemoselective C5–H bond activation seems to be governed by electronic factors, in particular imparted by the electron-withdrawing impact of the fused pyridine system, which activates the  $\alpha$ -position as typical in classical *N*-ylide chemistry [55–58]. Steric factors seem much less relevant, due partly to the linear coordination geometry assumed for the silver carbene intermediate [59], and also due to the small size of the methyl substituents at nitrogen. Related low-valent iridium(I) carbene complexes derived from imidazo[1,2-*a*]pyridine systems were reported previously, though in those cases, substituents at the imidazole C4 or C5 position were introduced to direct the metallation exclusively to the imidazole C5 or C4 site, respectively [30].

Complex **2b** shows essentially identical NMR spectroscopic characteristics as the chloride analogue **2a**. Most notable differences are the stronger deshielding of the pyridinic C6–H resonance ( $\delta_{\text{H}}$  9.07 ppm; *cf* 8.96 ppm in **2a**) and the  $\text{N–CH}_3$  signal ( $\delta_{\text{H}}$  4.02 ppm; *cf* 3.80 ppm in **2a**) and the carbenic resonance in the  $^{13}\text{C}$  NMR spectrum, which appeared ca. 10 ppm higher field than in **2a** ( $\delta_{\text{C}}$  118.9 ppm).

The structures of complexes **2a** and **2b** were confirmed by X-ray diffraction studies. The molecular structures unambiguously confirm the chemoselectivity of metallation as deduced from spectroscopic analyses in solution (Fig. 2). The Ir–C bond length is identical within esd's in both complexes, 2.034(5) Å and 2.036(2) Å, respectively (Table 1). This distance is similar to related iridium NHC complexes [30,60–64]. The piano-stool geometry is slightly flatter in the iodide complex **2b**, as indicated by the consistently wider angles between the three “legs”, while most of the angles involving the  $\text{Cp}^*$  centroid are more acute than in the chloride analogue **2a**.

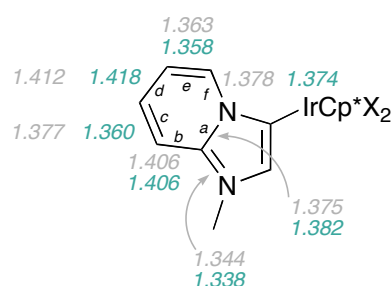


**Fig. 2** ORTEP presentation of the molecular structures of **2a** (a) and **2b** (b; 50% probability, H atoms omitted for clarity).

**Table 1.** Selected bond lengths (Å) and angles (deg) for complexes **2a** and **2b**.

	<b>2a</b> (X = Cl)	<b>2b</b> (X = I)
Ir–C1	2.034(5)	2.036(2)
Ir–X1	2.4117(11)	2.71165(16)
Ir–X2	2.4307(11)	2.72149(16)
Ir–Cp <sub>centroid</sub>	1.798(2)	1.8258(9)
C1–C2	1.372(6)	1.368(3)
C1–Ir–X1	85.82(12)	87.16(6)
C1–Ir–X2	88.09(13)	93.07(6)
X1–Ir–X2	88.50(4)	90.173(5)
C1–Ir–Cp <sub>centroid</sub>	129.47(15)	125.91(6)
X1–Ir–Cp <sub>centroid</sub>	123.42(8)	124.17(3)
X2–Ir–Cp <sub>centroid</sub>	128.01(8)	125.26(3)

In both complexes, bond length analysis suggests a pronounced localization of the double bonds in the annelated pyridine ring and formation of a 2-pyridylidene-type ground structure [65–68]. Specifically, the pyridine *c* and *e* bonds are significantly shorter than average conjugated C–C bonds and indicate partially localized C=C double bonds, while the *b* and *d* bonds are elongated (Fig. 3). Similarly, the imidazole 2,3-bond, which does not form part of the pyridyl framework is substantially shorter than the pyridyl *a* bond, pointing to a localized 2-pyridylidene unit.



**Fig. 3.** Bond length alteration in iridium complexes **2a** and **2b**; values for **2a** in grey (esds  $\leq 0.007$  Å for all bonds) and for **2b** in green (esds 0.003 Å for all bonds).

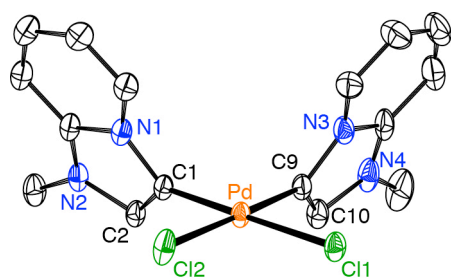
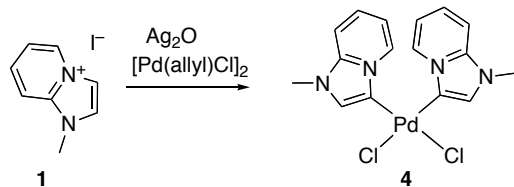
**Palladium complexation.** Transmetallation according to similar procedures as described for complexes **2** and **3** involving the palladium precursor  $[\text{PdCl}(\text{allyl})]_2$  afforded the biscarbene complex **4** together with minor other species (Scheme 2). Attempts to use a similar transmetallation procedure with  $[\text{PdCl}_2(\text{NCMe})_2]$  were not successful and the imidazolium ligand precursor was recovered. Despite extensive efforts to purify complex **4**, we did not succeed in obtaining microanalytically pure material. Purification was thwarted by the formation of palladium black during this process, which may point towards a limited stability of complex **4** or the anticipated transient (allyl)(carbene)palladium complex intermediate [69]. Of note,  $^1\text{H}$  NMR analysis of the soluble fractions does not indicate formation of any products by reductive elimination and neither a 4-(allyl)-imidazolium derivative nor a 4-chloroimidazolium salt was detected. [70,71]. In contrast, mass spectrometric analysis of crude product mixtures suggests formation of an allylimidazolium salt (signal at 173.1320 amu). Additionally, mass peaks at 279.0435 and 411.0803 indicate the presence of  $[\text{Pd}(\text{allyl})\text{carbene}]^+$  and  $[\text{Pd}(\text{allyl})(\text{carbene})_2]^+$ , respectively, as potential intermediates during the generation of **4**.

Complex **4** is stable for days in  $\text{CDCl}_3$  solution. Decomposition was observed after several weeks, however, by the formation of a black residue. This process is accelerated at higher temperatures, which regenerates the imidazolium precursor **1** as evidenced by the appearance of two doublets at 8.95 and 8.17 ppm corresponding to the imidazolium protons bound to C4 and C5. Similarly, addition of  $\text{NH}_4(\text{BF}_4)$  induces rapid demetallation and formation of the imidazolium salt **1.BF<sub>4</sub>** according to  $^1\text{H}$  NMR spectroscopy.

The coordination mode of carbenes to the  $\text{PdX}_2$  unit is variable and both dimeric  $[\text{Pd}(\text{carbene})\text{X}_2]$  as well as monomeric biscarbene systems of type  $[\text{PdX}_2(\text{carbene})_2]$  have precedents [72–76]. Coordination of two carbene ligands to the palladium centre has been surmised from HR-MS data, which show a molecular ion at 439.9788 amu in good agreement with the expected 439.9787 amu for the molecular ion  $[\mathbf{4}]^+$ . Moreover, an X-ray structure analysis unambiguously confirmed the formation of complex **4**. The molecular structure (Fig. 4) features a palladium center in a distorted square-planar geometry and the two carbene ligands in mutual *cis* position. The two asymmetric carbene ligands are in mutual *syn* arrangement, with both pyridyl fragments located on the same side of the palladium coordination plane. The two carbene ligands are almost perpendicular to the metal

coordination plane, torsion angles are  $70.86^\circ$  and  $73.60^\circ$  for C2–C1–Pd–C9 and C10–C9–Pd–C1, respectively. The two heterocycles are in a disrotatory arrangement and form a V-shaped ligand sphere.

**Scheme 2**



**Fig. 4** ORTEP presentation of the molecular structure of **4** (30% probability, H atoms and cocrystallized  $\text{CHCl}_3$  and  $\text{H}_2\text{O}$  molecules omitted for clarity). Selected bond distances ( $\text{\AA}$ ) and angles (deg): Pd–C1 1.981(4); Pd–C9 1.990(4); Pd–Cl1 2.3877(10); Pd–Cl2 2.3752(10); C1–Pd–C9 88.12(15); C1–Pd–Cl1 178.68(10); C1–Pd–Cl2 90.01(10); C9–Pd–Cl1 90.56(12); C9–Pd–Cl2 178.13(12); Cl2–Pd–Cl1 91.30(4).

In the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrum, a single set of sharp resonances was observed, which indicates either a rigid arrangement with  $C_s$  symmetry, or a rotation about the Pd–C bonds that is fast on the NMR time scale. Variable temperature experiments down to  $-20^\circ\text{C}$  did not reveal any signal broadening that would support restricted Pd–C bond rotation at this temperature. Similar *cis* coordination of the two carbene ligands in related  $[\text{Pd}(\text{carbene})_2\text{X}_2]$  complexes has been reported, often in a mixture with the corresponding *trans* isomer. In the case of **4**, the absence of any sterically hindering *ortho* substituents at the carbene may facilitate the thermodynamically more favored *cis* coordination of the two high *trans*-influencing carbene ligands. Similarly, the absence of steric bulk in *ortho* position may facilitate rotational flexibility.

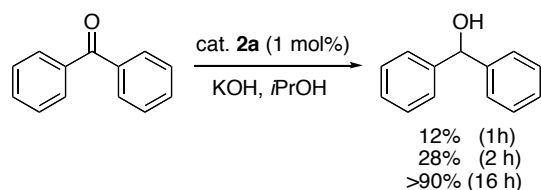
The absence of substituents in positions adjacent to the carbene bond may have beneficial implications in suppressing bond activation processes as observed in related NHC complexes with *ortho* substituents [77,78]. The absence also directly affects the stability of the complexes. For example, complex **2a** is unstable under acidic conditions, which is in significant contrast to the stability of related iridium(III) carbene complexes [79]. The

complex readily decomposes when exposed to dilute HCl in CH<sub>2</sub>Cl<sub>2</sub> (ca. 30 mM) solution and within minutes, the ligand precursor **1** and [IrCp\*Cl<sub>2</sub>]<sub>2</sub> were observed as the major products by <sup>1</sup>H NMR spectroscopy.

**Other metals.** While the transmetallation route is typically rather general, all our attempts to synthesise a rhodium(I) or an iridium(I) complex from the fused imidazolium salt **1** and [MCl(cod)]<sub>2</sub> in the presence of Ag<sub>2</sub>O have failed thus far (cod = 1,5-cyclooctadiene). Inefficient transmetallation was noted previously when using an imidazo[1,5-a]pyridinium system [30], and failure to isolate any desired complex may be a direct consequence of the weak carbene–metal bond. Likewise, the preparation of a copper(I) compound via transmetallation from silver with CuCl was unsuccessful, presumably again due to a low stability of the copper complex when bound to the abnormal and sterically unprotected imidazolylidene ligand [80].

**Preliminary Catalytic applications.** Based on the established track record of iridium carbene complexes in hydrogen transfer catalysis [81–87], the catalytic activity of complex **2a** was investigated in transfer hydrogenation using *i*PrOH as sacrificial hydrogen donor. In a representative reaction, benzophenone was used as model substrate (Scheme 3). The reaction requires the addition of KOH as a base (substrate/base/catalyst 100:10:1) and proceeds at moderate rates, leading to essentially full conversion within 16 h. This activity is substantially lower than that reported for related carbene iridium(III) complexes and may be a direct consequence of the limited stability of the iridium–carbene bond in **2a** as a consequence of the low steric protection.

**Scheme 3**



## Conclusion

Unsubstituted imidazo[1,2-a]pyridine-derived carbenes constitute an attractive novel ligand system. The precursors are easily synthesized and allow for introducing further functionality, for example through flexible *N*-alkylation. Procedures for the metallation of these ligands with iridium(III), ruthenium(II), and palladium(II) have been successfully developed. The

ligand imparts features that are absent in classical imidazole-derived carbenes, in particular because of the absence of protecting bulky substituents at the positions adjacent to the carbene site. A current limitation pertains to the stability of the complexes, *e.g.* towards acids and acidic materials including silica. The introduction of chelating substituents may substantially increase the stability, with obvious implications for catalysis and other applications in materials science and biochemical areas.

## Experimental Section

**General.** Solvents were purified using an alumina/catalyst column system (Thermovac Co.). All other reagents were commercially available and were used as received. Unless specified otherwise, NMR spectra were recorded at 25 °C on Varian Innova spectrometers operating at 300, 400 or 500 MHz (<sup>1</sup>H NMR) and 75, 100 or 125 MHz (<sup>13</sup>C{<sup>1</sup>H} NMR), respectively. Chemical shifts (δ in ppm, coupling constants *J* in Hz) were referenced to residual solvent resonances. Assignments are based on homo- and heteronuclear shift correlation spectroscopy. Microanalyses were performed by the Microanalytical Laboratory at University College Dublin, Ireland; residual solvents were also identified by <sup>1</sup>H NMR spectroscopy. HR-MS was performed on a Waters 2795-LCT Mass Spectrometer using ESI-TOF ionization.

***N*-methyl-imidazo[1,2-*a*]pyridinium iodide 1.** In the absence of any solvent, 1*H*-triazole (1.0 mL, 17 mmol) and 2-bromopyridine (2.0 mL, 20 mmol) were mixed in a pressure vessel and stirred at 160 °C for 14 h. The resulting solid was cooled to room temperature, dissolved in hot MeCN (100 mL) and filtered and washed with MeCN (3 × 100 mL). The filtrate was concentrated to ca. 30 mL and layered with Et<sub>2</sub>O (200 mL). A white precipitate formed, which was isolated by filtration and dried. The solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and washed with KOH (1M, 100 mL). The organic phase was separated, dried over MgSO<sub>4</sub>, filtered, and the volatiles were removed under reduced pressure. The resulting solid was dissolved in MeCN (15 mL) and MeI (1.5 mL, 24 mmol) and heated in a microwave reactor (3 h, 100 °C). The mixture was layered with Et<sub>2</sub>O (50 mL), which induced the formation of a pale yellow precipitate. This solid was filtered off, washed with copious amounts of Et<sub>2</sub>O and dried under vacuum to afford compound **1** in overall 47% yield (2.07 g, 8.0 mmol). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN) δ 8.73 (d, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, 1H, H<sub>py</sub>), 8.17 (d, <sup>3</sup>J<sub>HH</sub> = 2.2 Hz, 1H, H<sub>imid</sub>), 7.98–7.91 (m, 2H, H<sub>py</sub>), 7.90 (d, <sup>3</sup>J<sub>HH</sub> = 2.2 Hz, 1H, H<sub>imid</sub>), 7.47 (ddd, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, <sup>3</sup>J<sub>HH</sub> =

6.0 Hz,  $^4J_{\text{HH}} = 1.0$  Hz, 1H,  $H_{\text{py}}$ ), 4.03 (s, 3H,  $\text{NCH}_3$ ).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  140.2 ( $\text{C}_{\text{py}}$ ), 133.9 ( $\text{CH}_{\text{py}}$ ), 129.7 ( $\text{CH}_{\text{py}}$ ), 126.5 ( $\text{CH}_{\text{imid}}$ ), 117.4 ( $\text{CH}_{\text{py}}$ ), 115.1 ( $\text{CH}_{\text{imid}}$ ), 111.3 ( $\text{CH}_{\text{py}}$ ), 34.2 ( $\text{NCH}_3$ ). Anal. calcd. for  $\text{C}_8\text{H}_9\text{N}_2\text{I}$ : C, 36.95; H, 3.49; N, 10.77. Found: C, 36.16; H, 3.19; N, 10.40. HR-MS found 133.0766; calcd for  $\text{C}_8\text{H}_9\text{N}_2$   $[\text{M}-\text{I}]^+$ : 133.0760.

The corresponding  $\text{BF}_4$  salt was obtained by stirring **1** (1.80 g, 6.9 mmol) and  $(\text{NH}_4)\text{BF}_4$  (1.45 g, 14 mmol) in  $\text{H}_2\text{O}$  (20 mL) for 1 h. The solvent was removed under reduced pressure and the residue was suspended in  $\text{CH}_2\text{Cl}_2$  (30 mL) and filtered. The filtrate was dried over  $\text{MgSO}_4$ , and evaporated to dryness to yield the  $\text{BF}_4$  salt of **1** as a yellow solid (1.34 g, 6.1 mmol, 88%).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  8.65 (d,  $^3J_{\text{HH}} = 6.0$  Hz, 1H,  $H_{\text{py}}$ ), 8.06 (d,  $^3J_{\text{HH}} = 2.2$  Hz, 1H,  $H_{\text{imid}}$ ), 7.98–7.86 (m, 2H,  $H_{\text{py}}$ ), 7.82 (d,  $^3J_{\text{HH}} = 2.2$  Hz, 1H,  $H_{\text{imid}}$ ), 7.43 (ddd,  $^3J_{\text{HH}} = 7.2$  Hz,  $^3J_{\text{HH}} = 6.0$  Hz,  $^4J_{\text{HH}} = 1.0$  Hz, 1H,  $H_{\text{py}}$ ), 3.98 (s, 3H,  $\text{NCH}_3$ ).

**Complex 2a.** The imidazolium iodide **1** (100 mg, 0.46 mmol),  $[\text{IrCp}^*\text{Cl}_2]_2$  (180 mg, 0.23 mmol) and  $\text{Ag}_2\text{O}$  (53 mg, 0.23 mmol) were suspended in dry and degassed  $\text{CH}_2\text{Cl}_2$  (10 mL) and stirred at RT for 14 h. The suspension was filtered through Celite, and the filtrate layered with  $\text{Et}_2\text{O}$  (150 mL), which induced gradual formation of a redish precipitate. This precipitate was collected by filtration and dried in vacuo. Analysis of the residue by  $^1\text{H}$  NMR spectroscopy indicates **2a** as the major compound (76% spectroscopic yield). An analytically pure sample was obtained by purifying the residue by flash chromatography ( $\text{SiO}_2$ ;  $\text{CH}_2\text{Cl}_2/\text{acetone}$  1:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.96 (d, 1H,  $^3J_{\text{HH}} = 6.9$  Hz,  $H_{\text{py}}$ ), 7.44 (ddd,  $^3J_{\text{HH}} = 6.9$  Hz,  $^3J_{\text{HH}} = 9.0$  Hz,  $^4J_{\text{HH}} = 1.0$ , 1H,  $H_{\text{py}}$ ), 7.35 (dt,  $^3J_{\text{HH}} = 9.0$  Hz,  $^4J_{\text{HH}} = 1.0$  Hz, 1H,  $H_{\text{py}}$ ), 6.96 (s, 1H,  $H_{\text{imid}}$ ), 6.93 (td,  $^3J_{\text{HH}} = 6.9$  Hz,  $^4J_{\text{HH}} = 1.0$ , 1H,  $H_{\text{py}}$ ), 3.80 (s, 3H,  $\text{NCH}_3$ ), 1.61 (s, 15H,  $\text{C}_{\text{Cp}}-\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.4 ( $\text{C}_{\text{py}}$ ), 133.1 ( $\text{CH}_{\text{py}}$ ), 129.4 ( $\text{CH}_{\text{py}}$ ), 128.5 ( $\text{C}_{\text{imid}}-\text{Ir}$ ), 128.4 ( $\text{CH}_{\text{imid}}$ ), 113.2 ( $\text{CH}_{\text{py}}$ ), 108.2 ( $\text{CH}_{\text{py}}$ ), 87.4 ( $\text{C}_{\text{Cp}}$ ), 33.1 ( $\text{NCH}_3$ ), 8.9 ( $\text{C}_{\text{Cp}}-\text{CH}_3$ ). Anal. calcd. for  $\text{C}_{18}\text{H}_{23}\text{N}_2\text{IrCl}_2$  (530.51)  $\times$  0.25  $\text{CH}_2\text{Cl}_2$ : C, 39.73; H, 4.29; N, 5.08. Found: C, 39.98; H, 4.19; N, 4.74. HR-MS found 495.1201; calcd for  $\text{C}_{18}\text{H}_{23}\text{N}_2\text{IrCl}$   $[\text{M}-\text{Cl}]^+$ : 495.1179.

**Complex 2b.** The imidazolium iodide **1** (100 mg, 0.46 mmol),  $[\text{IrCp}^*\text{Cl}_2]_2$  (180 mg, 0.23 mmol),  $\text{Ag}_2\text{O}$  (106 mg, 0.46 mmol) and KI (225 mg, 1.4 mmol) were suspended in dry and degassed  $\text{CH}_2\text{Cl}_2$  (10 mL) and stirred at RT for 14 h. Purification was identical to that described for **2a** and afforded **2b** in 79% spectroscopic yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$

9.07 (d,  $^3J_{\text{HH}} = 6.9$  Hz, 1H,  $\text{H}_{\text{py}}$ ), 7.54–7.44 (m, 2H,  $\text{H}_{\text{py}}$   $\text{H}_{\text{imid}}$ ), 7.41 (dt,  $^3J_{\text{HH}} = 9.0$  Hz,  $^4J_{\text{HH}} = 1.0$  Hz, 1H,  $\text{H}_{\text{py}}$ ), 6.99 (dt,  $^3J_{\text{HH}} = 6.9$  Hz,  $^4J_{\text{HH}} = 1.0$  Hz, 1H,  $\text{CH}_{\text{py}}$ ), 4.01 (s, 3H,  $\text{NCH}_3$ ), 1.58 (s, 15H,  $\text{C}_{\text{Cp}}-\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  140.3 ( $\text{C}_{\text{py}}$ ), 132.5 ( $\text{CH}_{\text{py}}$ ), 128.8 ( $\text{CH}_{\text{imid}}$ ), 128.6 ( $\text{CH}_{\text{py}}$ ), 118.9 ( $\text{C}_{\text{imid}}-\text{Ir}$ ), 112.2 ( $\text{CH}_{\text{py}}$ ), 107.7 ( $\text{CH}_{\text{py}}$ ), 89.6 ( $\text{C}_{\text{Cp}}$ ), 31.9 ( $\text{NCH}_3$ ), 8.3 ( $\text{C}_{\text{Cp}}-\text{CH}_3$ ). HR-MS found 587.0524; calcd for  $\text{C}_{18}\text{H}_{23}\text{N}_2\text{IrI} [\text{M}-\text{I}]^+$ : 587.0535.

**Complex 3.** Compound **1**· $\text{BF}_4$  (150 mg, 0.34 mmol),  $[\text{Ru}(p\text{-cym})\text{Cl}_2]_2$  (210 mg, 0.34 mmol), and  $\text{Ag}_2\text{O}$  (80 mg, 0.34 mmol) were suspended in dry and degassed  $\text{CH}_2\text{Cl}_2$  (15 mL) and stirred at RT for 14 h. The suspension was filtered through Celite and the solvent removed under reduced pressure. The resulting residue was purified by chromatography ( $\text{SiO}_2$ ; acetone). The orange band was collected and evaporated to dryness to afford complex **3** as an orange solid (52 mg, 0.12 mmol, 34%), which was recrystallized from  $\text{CH}_2\text{Cl}_2$ /pentane.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.89 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 1H,  $\text{H}_{\text{py}}$ ), 7.44 (dd,  $^3J_{\text{HH}} = 6.8$  Hz,  $^3J_{\text{HH}} = 8.4$  Hz, 1H,  $\text{H}_{\text{py}}$ ), 7.33 (d,  $^3J_{\text{HH}} = 8.4$  Hz, 1H,  $\text{H}_{\text{py}}$ ), 7.10 (s, 1H,  $\text{H}_{\text{imid}}$ ), 6.96 (t,  $^3J_{\text{HH}} = 8.4$  Hz, 1H,  $\text{H}_{\text{py}}$ ), 5.33, 5.19 (2  $\times$  d,  $^3J_{\text{HH}} = 6.0$  Hz, 2H,  $\text{H}_{\text{cym}}$ ), 3.78 (s, 3H,  $\text{NCH}_3$ ), 2.94 (septet,  $^3J_{\text{HH}} = 6.0$  Hz, 1H,  $\text{CHMe}_2$ ), 2.03 (s, 3H,  $\text{C}_{\text{cym}}-\text{CH}_3$ ), 1.29 (d,  $^3J_{\text{HH}} = 6.0$  Hz, 6H,  $\text{CH}-\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.9 ( $\text{C}_{\text{imid}}-\text{Ru}$ ), 141.1 ( $\text{C}_{\text{py}}$ ), 133.2 ( $\text{CH}_{\text{py}}$ ), 129.2 ( $\text{CH}_{\text{py}}$ ), 128.8 ( $\text{CH}_{\text{imid}}$ ), 113.4 ( $\text{CH}_{\text{py}}$ ), 108.9 ( $\text{CH}_{\text{py}}$ ), 104.4, 103.6 (2  $\times$   $\text{CH}_{\text{cym}}$ ), 84.2, 83.3 (2  $\times$   $\text{C}_{\text{cym}}$ ), 33.2 ( $\text{NCH}_3$ ), 30.6 ( $\text{CHMe}_2$ ), 22.4 ( $\text{C}_{\text{cym}}-\text{CH}_3$ ), 18.5 ( $\text{CH}-\text{CH}_3$ ). Anal. calcd. for  $\text{C}_{18}\text{H}_{22}\text{Cl}_2\text{N}_2\text{Ru}$  (438.36)  $\times$  0.8  $\text{CH}_2\text{Cl}_2$ : C, 44.60; H, 4.70; N, 5.53. Found: C, 44.34; H, 4.62; N, 5.26. HR-MS found 403.0535; calcd for  $\text{C}_{18}\text{H}_{22}\text{N}_2\text{RuCl} [\text{M}-\text{Cl}]^+$ : 403.0515.

**Complex 4.** Imidazolium salt **1** (100 mg, 0.40 mmol),  $[\text{Pd}(\text{allyl})\text{Cl}]_2$  (74 mg, 0.20 mmol) and  $\text{Ag}_2\text{O}$  (93 mg, 0.40 mmol) were suspended in  $\text{CH}_2\text{Cl}_2$  (10 mL) and stirred overnight at RT. The suspension was filtered through Celite, and the solvent was concentrated to 3 mL and layered with pentane. The greenish solid was collected and dried (47 mg, 0.11 mmol, 38%), and recrystallized from  $\text{CHCl}_3/\text{Et}_2\text{O}$ . Despite several recrystallization and other purification attempts, no satisfactory microanalytical data were obtained [88].  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.10 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 1H,  $\text{H}_{\text{py}}$ ), 7.43 (dt,  $^3J_{\text{HH}} = 8.8$  Hz,  $^3J_{\text{HH}} = 6.8$  Hz, 1H,  $\text{H}_{\text{py}}$ ), 7.31 (d,  $^3J_{\text{HH}} = 8.8$  Hz, 1H,  $\text{H}_{\text{py}}$ ), 6.95–6.91 (m, 2H,  $\text{H}_{\text{py}}+\text{H}_{\text{imid}}$ ), 3.75 (s, 3H,  $\text{NCH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.2 ( $\text{C}_{\text{imid}}-\text{Pd}$ ), 140.4 ( $\text{C}_{\text{py}}$ ), 134.2 ( $\text{CH}_{\text{py}}$ ), 129.9 ( $\text{CH}_{\text{py}}$ ), 129.4 ( $\text{CH}_{\text{imid}}$ ), 113.9 ( $\text{CH}_{\text{py}}$ ), 108.2 ( $\text{CH}_{\text{py}}$ ), 32.7 ( $\text{NCH}_3$ ). Anal. calcd. for  $\text{C}_{16}\text{H}_{16}\text{Cl}_2\text{N}_4\text{Pd}$

(441.65)  $\times$  0.8 CHCl<sub>3</sub>: C, 37.56; H, 3.15; N, 10.43. Found: C, 37.95; H, 2.72; N, 9.93. HR-MS found 439.9788; calcd for C<sub>16</sub>H<sub>16</sub>N<sub>4</sub>PdCl<sub>2</sub> [M]<sup>+</sup>: 439.9787.

**Typical catalytic procedure.** A mixture of complex **2a** (2.6 mg, 5  $\mu$ mol), *i*PrOH (10 mL) and aqueous KOH (2M, 0.05 mL, 0.1 mmol) was stirred at reflux for 10 minutes. Benzophenone (91 mg, 0.5 mmol) was added and heating was continued. Aliquots (0.1 mL) were taken at indicated times, poured into cyclohexane (0.2 mL), and evaporated to dryness. Yields were determined by <sup>1</sup>H NMR spectroscopy using CDCl<sub>3</sub> as solvent.

### Crystallographic details.

Crystal data for complexes **2a**, **2b**, and **4** were collected by using an Agilent Technologies SuperNova. A diffractometer fitted with an Atlas detector that uses monochromated Mo-K $\alpha$  radiation (0.71073 Å). A complete dataset was collected, assuming that the Friedel pairs are not equivalent. An analytical numeric absorption correction was performed [89]. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares fitting on F<sup>2</sup> for all data using SHELXL-97 [90]. Hydrogen atoms were added at calculated positions and refined by using a riding model. Anisotropic thermal displacement parameters were used for all nonhydrogen atoms. Complex **4** cocrystallised with one molecule of CHCl<sub>3</sub> and the unit cell contained a partially occupied molecule of H<sub>2</sub>O. Crystallographic details are summarized in Table 2. CCDC numbers 976513–976515 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table 2.** Crystal data and structure refinement for complexes **2a**, **2b**, and **4**.

	<b>2a</b>	<b>2b</b>	<b>4</b>
CCDC number	976513	976514	976515
Empirical formula	C <sub>18</sub> H <sub>23</sub> N <sub>2</sub> Cl <sub>2</sub> Ir	C <sub>18</sub> H <sub>23</sub> N <sub>2</sub> I <sub>2</sub> Ir	C <sub>17</sub> H <sub>17.29</sub> N <sub>4</sub> O <sub>0.145</sub> Cl <sub>5</sub> Pd <sup>a)</sup>
Formula weight	530.48	713.38	563.64
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2 <sub>1</sub> /c (#14)	P2 <sub>1</sub> /c (#14)	C2/c (#15)
Unit cell dimensions	a = 7.1510(2) Å b = 17.4375(4) Å c = 14.8259(3) Å	a = 9.1068(1) Å b = 13.8960(2) Å c = 15.3864(1) Å	a = 17.4655(4) Å b = 14.7960(2) Å c = 16.2258(3) Å

	$\beta = 92.875(2)^\circ$	$\beta = 95.512(1)^\circ$	$\beta = 97.765(2)^\circ$
Volume	1846.40(8) Å <sup>3</sup>	1938.12(4) Å <sup>3</sup>	4154.61(13) Å <sup>3</sup>
Z	4	4	8
Density (calculated)	1.908 g cm <sup>-3</sup>	2.445 g cm <sup>-3</sup>	1.802 g cm <sup>-3</sup>
Absorption coefficient	7.521 mm <sup>-1</sup>	10.076 mm <sup>-1</sup>	1.548 mm <sup>-1</sup>
F(000)	1024	1312	2236
Crystal size	0.11 × 0.08 × 0.04 mm <sup>3</sup>	0.12 × 0.10 × 0.06 mm <sup>3</sup>	0.31 × 0.20 × 0.16 mm <sup>3</sup>
data collection $\theta$ range	2.85 to 29.46°	2.90 to 29.56°	2.98 to 29.76°
Reflections collected	21858	55028	46652
Independent reflections	4691 [R(int) = 0.0338]	5144 [R(int) = 0.0351]	5481 [R(int) = 0.0292]
Completeness $\theta = 27.50^\circ$	99.2 %	99.7 %	99.2 %
Absorption correction	Analytical	Analytical	Analytical
Max., min. transmission	0.765, 0.496	0.588, 0.394	0.925, 0.871
Restraints, parameters	0, 214	0, 214	0, 249
Goodness-of-fit on F <sup>2</sup>	1.165	1.059	1.022
R1, wR2 [ $I > 2\sigma(I)$ ]	0.0281, 0.0619	0.0147, 0.0265	0.0496, 0.1176
R1, wR2 [all data]	0.0331, 0.0635	0.0173, 0.0273	0.0631, 0.1294
Largest diff. peak, hole	1.487, -1.146 e Å <sup>-3</sup>	0.563, -0.589 e Å <sup>-3</sup>	2.478, -1.502 e Å <sup>-3</sup>

<sup>a)</sup> The hydrogen atoms of the water molecule could not be detected.

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## References

- [1] D. Bourissou, O. Guerret, F. P. Gabbai, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39.
- [2] W. A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1290.
- [3] F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3122.
- [4] A. T. Normand, K. J. Cavell, *Eur. J. Inorg. Chem.* **2008**, 2781.
- [5] M. Poyatos, J. A. Mata, E. Peris, *Chem. Rev.* **2009**, *109*, 3677.
- [6] S. Diez-Gonzalez, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612.
- [7] M.-L. Teyssot, A.-S. Jarrousse, M. Manin, A. Chevy, S. Roche, F. Norre, C. Beaudoin, L. Morel, D. Boyer, R. Mahiou, A. Gautier, *Dalton Trans.* **2009**, 6894.
- [8] L. Mercks, M. Albrecht, *Chem. Soc. Rev.* **2010**, *39*, 1903.
- [9] A. Monney, M. Albrecht, *Coord. Chem. Rev.* **2013**, *257*, 2420.
- [10] W. Liu, R. Gust, *Chem. Soc. Rev.* **2013**, *42*, 755.
- [11] L. Oehninger, R. Rubbiani, I. Ott, *Dalton Trans.* **2013**, *42*, 3269.

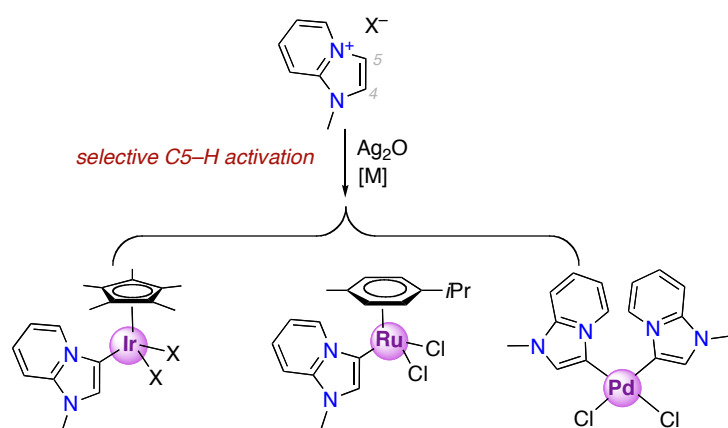
- [12] M. C. Perry, K. Burgess, *Tetrahedron: Asymmetry* **2003**, *14*, 951.
- [13] M. Albrecht, *Chem. Commun.* **2008**, 3601.
- [14] E. Aldeco-Perez, A. J. Rosenthal, B. Donnadieu, P. Parameswaran, G. Frenking, G. Bertrand, *Science* **2009**, *326*, 556.
- [15] L. Yang, O. Schuster, H. G. Raubenheimer, M. Albrecht, *Chem. Rev.* **2009**, *109*, 3445.
- [16] M. Melaimi, M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2010**, *49*, 8810.
- [17] K. F. Donnelly, A. Petronilho, M. Albrecht, *Chem. Commun.* **2013**, *49*, 1145.
- [18] R. H. Crabtree, *Coord. Chem. Rev.* **2013**, *257*, 755.
- [19] J. J. Dunsford, D. S. Tromp, K. J. Cavell, C. J. Elsevier, B. M. Karluki, *Dalton Trans.* **2013**, *42*, 7318.
- [20] M. Poyatos, J. A. Mata, E. Peris, *Chem. Sci.* **2014**, *5*, in press.
- [21] M. C. Jahnke, F. E. Hahn, in *N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools* (Ed. S. Diez-Gonzalez), RSC Catalysis Series (Royal Society of Chemistry, London), 2011, pp 1–41.
- [22] O. Köhl, *Functionalised N-Heterocyclic Carbene Complexes*, Wiley-VCH (Weinheim, Germany), 2010.
- [23] M. C. Jahnke, F. E. Hahn, *Top. Organomet. Chem.* **2010**, *30*, 95.
- [24] A. J. Boydston, C. W. Bielawski, *Dalton Trans.* **2006**, 4073.
- [25] S. Ruiz-Botella, G. Guisado-Barrios, J. A. Mata, E. Peris, *Organometallics* **2013**, *32*, 6613.
- [26] R. Weiss, S. Reichel, M. Handke, F. Hampel, *Angew. Chem. Int. Ed.* **1998**, *37*, 344.
- [27] M. Alcarazo, S.J. Roseblade, A.R. Cowley, R. Fernández, J. M. Brown, J. M. Lassaletta, *J. Am. Chem. Soc.* **2005**, *127*, 3290.
- [28] M. Nonnenmacher, D. Kunz, F. Rominger, T. Oeser, *Chem. Commun.* **2006**, 1378.
- [29] M. Nonnenmacher, F. Rominger, D. Kunz, *Organometallics* **2008**, *27*, 1561.
- [30] G. Song, Y. Zhang, X. Li, *Organometallics* **2008**, *27*, 1936.
- [31] A. John, M. M. Shaikh, P. Gosh, *Dalton Trans.* **2009**, 10581.
- [32] V. Gierz, A. Seyboldt, C. Maichle-Mössmer, R. Fröhlich, F. Rominger, D. Kunz, *Eur. J. Inorg. Chem.* **2012**, 1423.
- [33] V. Gierz, C. Maichle-Mössmer, D. Kunz, *Organometallics* **2012**, *31*, 739.
- [34] A. J. Hubert, H. Reimlinger, *Chem. Ber.* **1970**, *103*, 3811.
- [35] E. S. Hand, W. W. Paudler, *J. Org. Chem.* **1978**, *43*, 2900.
- [36] H. Galons, I. Bergerat, C. Combet Farnoux, M. Miocque, *Synthesis* **1982**, 1103.
- [37] H.-J. Knölker, R. Boese, R. Hitzmann, *Chem. Ber.* **1990**, *123*, 327.

- [38] M. P. Groziak, S. R. Wilson, G. L. Clauson, N. J. Leonard, *J. Am. Chem. Soc.* **1986**, *108*, 8002.
- [39] K. Groebke, L. Weber, F. Mehlin, *Synlett* **1998**, 661.
- [40] A. R. Katritzky, Y.-J. Xu, H. Tu, *J. Org. Chem.* **2003**, *68*, 4935.
- [41] E. Kluser, A. Neels, M. Albrecht, *Chem. Commun.* **2006**, 4495.
- [42] M. Heckenroth, E. Kluser, A. Neels, M. Albrecht, *Angew. Chem. Int. Ed.* **2007**, *46*, 6293.
- [43] M. Heckenroth, A. Neels, M. G. Garnier, P. Aebi, A. Ehlers, M. Albrecht, *Chem. Eur J.* **2009**, *15*, 9375.
- [44] P. Mathew, A. Neels, M. Albrecht, *J. Am. Chem. Soc.* **2008**, *130*, 13534.
- [45] A. Krüger, M. Albrecht, *Chem. Eur. J.* **2012**, *18*, 652.
- [46] A. Krüger, L. J. L. Häller, H. Müller-Bunz, O. Serada, A. Neels, S. A. Macgregor, M. Albrecht, *Dalton Trans.* **2011**, *40*, 9911.
- [47] D. Canseco-Gonzalez, A. Gniewek, M. Szulmanowicz, H. Müller-Bunz, A. Treziak, M. Albrecht, *Chem. Eur. J.* **2012**, *18*, 6055.
- [48] D. Canseco-Gonzalez, A. Petronilho, H. Müller-Bunz, K. Ohmatsu, T. Ooi, M. Albrecht, *J. Am. Chem. Soc.* **2013**, *135*, 13193.
- [49] I. J. B. Lin, C. S. Vasam, *Coord. Chem. Rev.* **2007**, *251*, 642.
- [50] J. M. Hayes, M. Viciano, E. Peris, G. Ujaque, A. Lledos, *Organometallics* **2007**, *26*, 6170.
- [51] A. R. Chianese, B. M. Zeglis, R. H. Crabtree, *Chem. Commun.* **2004**, 2176.
- [52] A. R. Chianese, A. Kovacevic, B. M. Zeglis, J. W. Faller, R. H. Crabtree, *Organometallics* **2004**, *23*, 2461.
- [53] A. Prades, M. Viciano, M. Sanau, E. Peris, *Organometallics* **2008**, *27*, 4254
- [54] L. Yang, A. Krüger, A. Neels, M. Albrecht, *Organometallics* **2008**, *27*, 3161.
- [55] R. Daniels, O. L. Salerni, *Proc. Chem. Soc.* **1960**, 286.
- [56] I.; Zugravescu, M. Petrovanu, *N-Ylid Chemistry*, McGraw Hill (New York), 1976.
- [57] D. Lloyd, M. I. C. Singer, *J. Chem. Soc. C* **1971**, 2939.
- [58] J. E. Jackson, N. Soundararajan, M. S. Platz, *J. Am. Chem. Soc.* **1988**, *110*, 5595.
- [59] J. C. Garrison, W. J. Youngs, *Chem. Rev.* **2005**, *105*, 3978.
- [60] Chianese, A. R.; Li, X. W.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663.
- [61] M. Viciano, M. Feliz, R. Corberan, J. A. Mata, E. Clot, E. Peris, *Organometallics* **2007**, *26*, 5304.

- [62] R. Maity, H. Koppetz, A. Hepp, F. E. Hahn, *J. Am. Chem. Soc.* **2013**, *135*, 4966.
- [63] R. Maity, A. Rit, C. Schulte to Brinke, C. G. Daniliuc, F. E. Hahn, *Chem. Commun.* **2013**, *49*, 1011.
- [64] W. Zuo, P. Braunstein, *Organometallics* **2010**, *29*, 5535.
- [65] J. S. Owen, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2004**, *126*, 8247.
- [66] E. Alvarez, S. Conejero, M. Paneque, A. Petronilho, M. L. Poveda, O. Serrano, E. Carmona, *J. Am. Chem. Soc.* **2006**, *128*, 13060.
- [67] M. A. Esteruelas, F. J. Fernandez-Alvarez, E. Onate, *J. Am. Chem. Soc.* **2006**, *128*, 13044.
- [68] E. Stander, O. Schuster, G. Heydenrych, S. Cronje, E. Tosh, M. Albrecht, G. Frenking, H. G. Raubenheimer, *Organometallics* **2010**, *29*, 5721.
- [69] M. S. Viciu, R. F. Germaneau, O. Navarro-Fernandez, E. D. Stevens, S. P. Nolan, *Organometallics* **2002**, *21*, 5470.
- [70] K. J. Cavell, A. Stasch, L.-L. Ooi, K. J. Cavell, *Organometallics* **2008**, *27*, 6507.
- [71] B.-L. Lin, P. Kang, T. D. P. Stack, *Organometallics* **2010**, *29*, 3683.
- [72] B. Cetinkaya, E. Cetinkaya, M. F. Lappert, *J. Chem. Soc., Dalton Trans.* **1973**, 906.
- [73] D. S. McGuinness, M. J. Green, K. J. Cavell, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **1998**, *565*, 165.
- [74] F. E. Hahn, M. Foth, *J. Organomet. Chem.* **1999**, *585*, 241.
- [75] D. S. McGuinness, K. J. Cavell, *Organometallics* **2000**, *19*, 741.
- [76] A. Poulain, D. Canseco-Gonzalez, R. Hynes-Roche, H. Müller-Bunz, O. Schuster, H. Stoeckli-Evans, A. Neels, M. Albrecht, *Organometallics* **2011**, *30*, 1021.
- [77] M. Prinz, M. Grosche, E. Herdtweck, W. A. Herrmann, *Organometallics* **2000**, *19*, 1692.
- [78] F. Hanasaka, Y. Tanabe, K. Fujita, R. Yamaguchi, *Organometallics* **2006**, *25*, 826.
- [79] A. Petronilho, M. Rahman, J. A. Woods, H. Al-Sayyed, H. Mueller-Bunz, D. J. MacElroy, S. Bernhard, M. Albrecht, *Dalton Trans.* **2012**, *41*, 13074.
- [80] A. Petronilho, H. Mueller-Bunz, M. Albrecht, *Chem. Commun.* **2012**, *48*, 6499.
- [81] M. Albrecht, J. Miecznikowski, A. Samuel, J. W. Faller, R. H. Crabtree, *Organometallics* **2002**, *21*, 3596.
- [82] F. E. Hahn, C. Holtgrewe, T. Pape, M. Martin, E. Sola, L. A. Oro, *Organometallics* **2005**, *24*, 2203.
- [83] R. Corberan, E. Peris, *Organometallics* **2008**, *27*, 1954.

- [84] D. Gnanamgari, E. L. O. Sauer, N. D. Schley, C. Butler, C. D. Incarvito, R. H. Crabtree, *Organometallics* **2009**, *28*, 321.
- [85] A. Zanardi, J. A. Mata, E. Peris, *J. Am. Chem. Soc.* **2009**, *131*, 14531.
- [86] W. W. N. O, A. J. Lough, R. H. Morris, *Organometallics* **2012**, *31*, 2152.
- [87] W. W. N. O, A. J. Lough, R. H. Morris, *Organometallics* **2013**, *32*, 3208.
- [88] While complex **4** was by far the predominant product, we cannot exclude minor impurities from dinuclear  $[\text{PdCl}_2(\text{carbene})]_2$  species and from  $\text{PdCl}(\text{allyl})(\text{carbene})$ -type complexes, which we were unable to separate and which obviously affect the microanalytical measurements.
- [89] R. C. Clark and J. S. Reid, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 1995, **51**, 887–897.
- [90] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112–122.

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Imidazo[1,2-*a*]pyridine undergoes selective C–H bond activation to afford mesoionic carbene complexes with  $[\text{IrCp}^*\text{Cl}_2]$ ,  $[\text{RuCl}_2(\text{cym})]$ , and  $[\text{PdCl}_2]$ ; the N-substituents of these new carbenes are unusually remote from the metal coordination sphere.

## Highlights

- A fused mesoionic pyrido-imidazolylidene was metallated with Ir, Ru, Pd
- Metallation occurs selectively at the carbon proximal to the pyridine
- Little steric protection of the mesoionic carbenes destabilizes the M–C bond

