



Iridium, ruthenium, and palladium complexes containing a mesoionic fused imidazolylidene ligand



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ARTICLE INFO

Article history:

Received 26 December 2013

Received in revised form

12 March 2014

Accepted 20 March 2014

Available online 29 March 2014

Keywords:

N-heterocyclic carbene

Mesoionic

Fused abnormal carbene

Ruthenium(II)

Iridium(III)

Palladium(II)

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 Ag₂O, *i.e.* at the imidazolium carbon that is proximal to the pyridine nitrogen. While the silver carbene complex is unstable, transmetallation with [IrCp*Cl₂]₂, [RuCl₂(cym)₂], and [PdCl(allyl)]₂ 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 centre 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.

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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].

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 [IrCp*Cl₂]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

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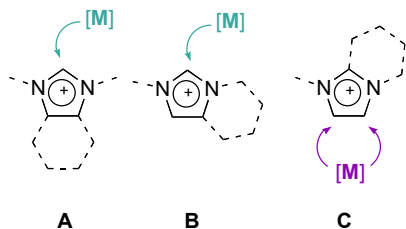


Fig. 1. Schematic representation of ring-annulated imidazolium salts and their most probably site of metallation (arrows), green arrows lead to normal carbene complexes, purple arrows to mesoionic/abnormal carbene complexes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

useful for transmetalation [51–53]. Upon reaction of **1** with Ag_2O , indeed, a silver carbene complex formed as inferred from the disappearance of the resonance of one imidazolium proton at δ_{H} 8.2 ppm in the ^1H 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 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_2O , and the transmetalating 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 transmetalation of the in-situ generated silver carbene intermediate with $[\text{IrCp}^*\text{Cl}_2]_2$, 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 $[\text{RuCl}_2(\text{cym})]_2$ for transmetalation. Both complexes formed in high spectroscopic yield (>90% according to ^1H 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.

Complex **2a** and **2b** have very similar analytical features. Complex **2a** was characterized by ^1H NMR spectroscopy and showed a

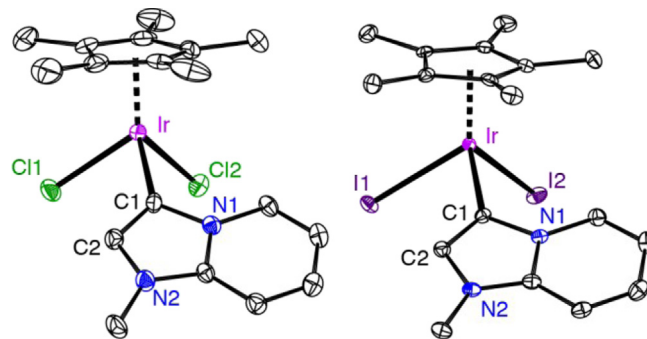
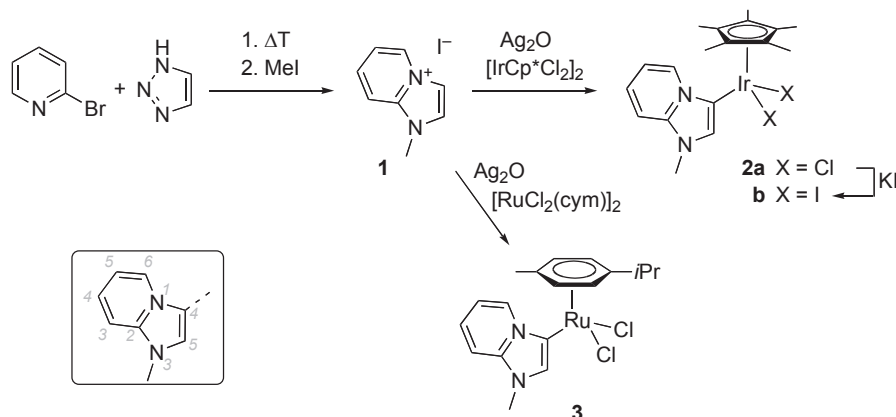


Fig. 2. ORTEP presentation of the molecular structures of **2a** (a) and **2b** (b; 50% probability, H atoms omitted for clarity).

singlet for the CH_{imid} at δ_{H} 6.96 ppm, which is substantially upfield compared to the imidazolium precursor (δ_{H} 8 ppm). Also the pyridinic protons shift to slightly higher field upon metallation ($\Delta\delta$ 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 ^1H and ^{13}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 labelling). The significant deshielding of the pyridinic C6-bound proton points to an interaction of this site with the IrCp^*Cl_2 fragment and hence metallation at the imidazole C5 position. Moreover, the singlet at δ_{H} 3.80 ppm attributed to the NCH_3 group shows a nuclear Overhauser effect (nOe) with the singlet of the imidazole heterocycle at δ_{H} 6.96 ppm as well as with the doublet due to the pyridinic C3-bound proton at δ_{H} 7.35 ppm, providing evidence that the site *ortho* to the 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 α -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



Scheme 1.

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