



Cite this: *Dalton Trans.*, 2015, 44, 18311

Received 25th August 2015,
Accepted 23rd September 2015

DOI: 10.1039/c5dt03285g

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C–H activation in Ir^{III} and *N*-demethylation in Pt^{II} complexes with mesoionic carbene ligands: examples of monometallic, homobimetallic and heterobimetallic complexes†‡

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Mononuclear Pt^{II} and the first dinuclear Pt^{II} complexes along with a cyclometalated heterobimetallic Ir^{III}/Pd^{II} complex bearing mesoionic carbene donor ligands are presented starting from the same bis-triazolium salt. The mononuclear Pt^{II} complex possesses a free triazole moiety which is generated from the corresponding triazolium salt through an *N*-demethylation reaction, whereas the mononuclear Ir^{III} complex features an unreacted triazolium unit.

N-Heterocyclic carbenes (NHCs) are fascinating ligands in organometallic chemistry.¹ Their unique properties have led to their use in various fields of research such as catalysis,² materials science,³ biologically active metal complexes⁴ and very recently also in metallosupramolecular chemistry.⁵ In addition to the classical NHC donors (imidazol-2-ylidenes⁶ or 1,2,4-triazol-5-ylidenes),⁷ a new class of mesoionic carbene (MIC) counterparts 1,2,3-triazol-5-ylidenes have also become popular in recent years.⁸ Many organic transformations have been successfully catalyzed by transition metal complexes comprising 1,2,3-triazol-5-ylidenes with catalytic transfer hydrogenation reactions,⁹ oxidation reactions,¹⁰ hydroarylation of alkynes,¹¹ Suzuki–Miyaura cross-coupling reactions,¹² click reactions¹³ and cyclization reactions¹⁴ constituting prominent examples. Metal complexes of such ligands have also been investigated for their photophysical properties.¹⁵

Recently, multinuclear complexes have also been reported with MIC ligands.^{5g,9b,c,16,17} We have recently demonstrated the synthesis of dinuclear Ir^{III} and Pd^{II} complexes (A and B) bearing a mesoionic dicarbene ligand (Fig. 1).^{9b,17} In complex A each Ir^{III} center is coordinated to a MIC donor and is additionally orthometalated to the central aryl ring of the ligand (Fig. 1). Here we demonstrate the synthesis of a mononuclear

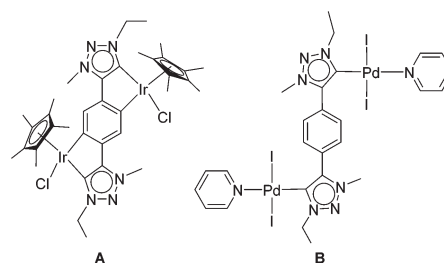


Fig. 1 Examples of dinuclear complexes with MIC ligands.

iridium(III) complex bearing a cyclometalated 1,2,3-triazol-5-ylidene ligand starting from the same 1,4-disubstituted bistriazolium salt, where one triazolium unit remains unreacted.

Although mononuclear platinum(II) complexes with 1,2,3-triazol-5-ylidene ligands have been reported, their polynuclear types are still unknown.^{8g,18} We also present here the synthesis of mononuclear and dinuclear Pt^{II} complexes with a 1,4-disubstituted phenylene derived mesoionic dicarbene ligand. Surprisingly, the mononuclear Pt^{II} complex contains a free triazole unit which is formed through the demethylation reaction from one of the corresponding triazolium units of the bis-triazolium salt. An intramolecular methylene shift from the pyridinium fragment to the benzyl group and subsequent insertion of a MeCN molecule has been demonstrated in the literature with Ir^{III} complexes containing triazolylidene ligands under specific conditions.¹⁹

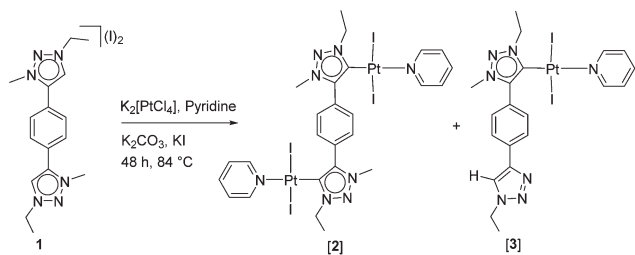
The reaction of the bis-triazolium salt **1** with 2 equiv. of K₂[PtCl₄] in the presence of K₂CO₃ in pyridine resulted in the formation of mono- and dinuclear platinum(II) complexes [2] and [3] in 33% and 44% yields, respectively (Scheme 1). Both complexes are stable under air and moisture. The complex [3] is well soluble in chlorinated solvents like dichloromethane and chloroform, however the complex [2] is only sparingly soluble in those solvents.

The formation of these complexes was confirmed by ¹H, ¹³C{¹H}, 2D correlation NMR spectroscopy and ESI mass spectrometry. The ¹H NMR spectra of both complexes show the

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† Dedicated to Prof. Manfred Scheer on the occasion of his 60th birthday.

‡ Electronic supplementary information (ESI) available: Preparation and spectroscopic properties of complexes [2], [3], [4] and [5] and details of the crystal structure determination for [2]·2CH₂Cl₂. CCDC 1415685. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt03285g



Scheme 1 Synthesis of mono- and dinuclear Pt^{II} complexes.

absence of the triazolium C5–H signal which was observed at $\delta = 9.25$ ppm^{9b} for the original bis-triazolium salt. A resonance observed at $\delta = 8.03$ ppm in the ¹H NMR spectrum of complex [2] is attributed to the aryl C–H protons of the central phenyl ring of the ligand. However, a multiplet in the range of $\delta = 8.00$ – 8.04 ppm was observed for the aryl protons in complex [3].

The resonances for the C–H protons of pyridine rings appeared as multiplets at $\delta = 8.84$ – 8.89 , 7.48 – 7.52 and 7.09 – 7.20 ppm for complex [2] and at $\delta = 8.97$ – 8.99 , 7.67 and 7.25 – 7.28 ppm for complex [3]. The coordination of the pyridine to the Pt^{II} center was also supported by the downfield shift resonance of the pyridine α -hydrogen atoms ([2]: $\delta = 8.84$ – 8.89 ppm; [3]: $\delta = 8.97$ – 8.99 ppm) compared to their corresponding resonance in free pyridine ($\delta = 8.62$).²⁰ The resonance for the free triazole C–H proton appeared as a singlet at $\delta = 7.88$ ppm in the ¹H NMR spectrum of complex [3]. Two quartets were observed for the two different types of N–CH₂ protons at $\delta = 4.52$ and 4.96 ppm for complex [3], whereas only one expected quartet appeared at $\delta = 4.85$ ppm for four chemically equivalent N–CH₂ protons in complex [2]. The ¹H NMR spectrum of complex [3] also shows the absence of one of the N–CH₃ groups, and therefore only a singlet resonance appeared at $\delta = 4.01$ ppm with the expected integration ratio (Fig. 2).

The ¹³C{¹H} NMR spectrum of both complexes [2] and [3] showed the characteristic resonance for the carbene carbon atoms at $\delta = 124.9$ and 123.8 ppm, respectively. These resonances are slightly upfield shifted from the C5 resonance of the precursor bis-triazolium salt ($\delta = 129.6$ ppm).^{9b} The

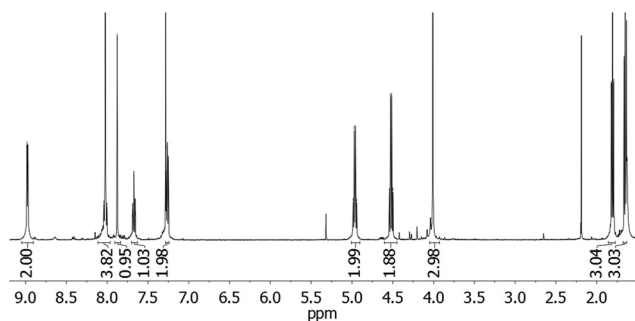


Fig. 2 ¹H NMR spectrum of complex [3] in CDCl₃.

resonance for the triazole carbon atom (C_{trz}–Ar) connected to the aryl ring appeared downfield shifted ([2]: $\delta = 143.8$ ppm; [3]: $\delta = 147.2$ and 144.1 ppm). The resonance for pyridine α -carbon atoms appeared at $\delta = 151.9$ ppm for [2] and at $\delta = 153.9$ ppm for [3], these resonances are downfield shifted compared to their equivalent resonance in a free pyridine atom ($\delta = 149.9$ ppm).¹⁹ A signal at $\delta = 119.6$ ppm is attributed to the triazole C–H carbon atom (Fig. 3). The 2D correlation NMR spectrum of complex [3] shows a correlation between the triazolylidene N–CH₂ ($\delta = 4.96$ ppm) protons and the carbene carbon atom ($\delta = 123.8$ ppm), whereas the other N–CH₂ protons ($\delta = 4.52$ ppm) from the free triazole moiety show a correlation with the triazole C–H carbon atom ($\delta = 119.6$ ppm) in the downfield region (Fig. 3).

The formation of both the complexes was further supported by ESI mass (positive ions) spectrometry, which shows the peaks at $m/z = 1374.7840$ (calcd for [[2] + Na]⁺ 1374.7958), 1216.7014 (calcd for [[2] – 2Py + Na]⁺ 1216.7112), 832.9613 (calcd for [[3] + Na]⁺ 832.9651) and 753.9229 (calcd for [[3] – Py + Na]⁺ 753.9192). These data thus conclusively prove the formation of the diplatinum complex [2] and more intriguingly of the monoplatinum complex [3] which results from an *N*-demethylation reaction of the parent bis-triazolium salt. Although we cannot conclusively show the exact mechanistic pathway for the demethylation reaction, the methyl group is certainly taken up by the pyridine molecules as the NMR spectrum of the crude reaction mixture shows the peaks for the 1-methylpyridinium iodide salt (ESI; Fig. S20†). The formation of the 1-methylpyridinium iodide salt was further supported by the ESI mass (positive ions) spectrum (ESI; Fig. S21†), which shows a peak at $m/z = 94.06512$ (calcd for [C₆H₈N]⁺ 94.06513). The reaction of the dinuclear Pt^{II} complex [2] with excess KI in the presence of pyridine and K₂CO₃ did not lead to the formation of the mononuclear Pt^{II} complex [3]. However, a partial demethylation reaction was also observed when the bis-triazolium salt was treated with pyridine in the absence of Pt^{II} under the mentioned reaction conditions in Scheme 1.

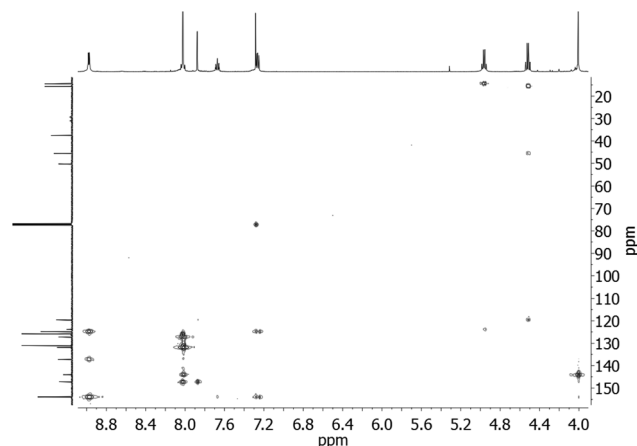


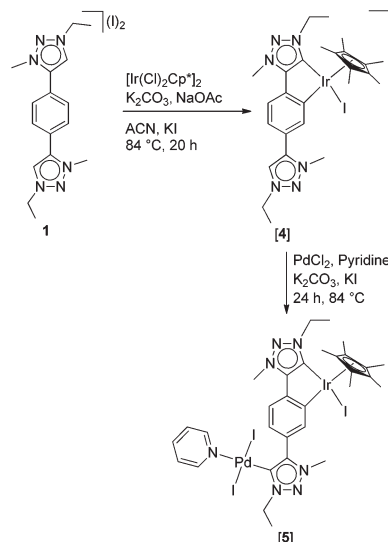
Fig. 3 HMBC NMR spectrum of complex [3] in CDCl₃.

Single crystals suitable for an X-ray diffraction study were obtained by slow evaporation of the solvents from a saturated dichloromethane : chloroform solution of [2] at ambient temperature. The molecular structure analysis with these crystals confirmed the formation of dinuclear platinum(II) complex [2], where each platinum atom is coordinated by an MIC donor and one pyridine donor in a *trans*-fashion, whereas the remaining coordination sites of the platinum atom are occupied by iodido donors (Fig. 4). The coordination geometry around the Pt atom is distorted square planar. The distance between Pt and C_{MIC} atoms measures to be 1.971(5) Å, which falls in the range previously described for platinum MIC complexes.¹⁸ The Pt–N_{Py} distance (2.094(4) Å) is slightly longer compared to the Pt–C_{MIC} bond distance.

The MIC donor planes are rotated out of the central aryl ring plane to coordinate to platinum centers. The torsion angle between the MIC plane and the central aryl ring plane measures to be –37.13°. Two [Pt₂(Py)] moieties are oriented in an opposite direction relative to the central aryl ring plane and thus feature an *anti*-orientation of the complex.

The reaction of the bistriazolium salt **1** with one or two equiv. of [Ir(Cl)₂Cp*]₂ in the presence of K₂CO₃ and NaOAc in acetonitrile at 84 °C resulted in the formation of the mononuclear cyclometalated complex [4], featuring one unreacted triazolium unit (Scheme 2). The complex [4] has a very good solubility in chlorinated solvents (dichloromethane and chloroform) and is stable towards air and moisture.

The formation of the complex was easily monitored by ¹H NMR spectroscopy, which shows the resonance at δ = 9.69 ppm for the unreacted triazolium C–H proton. The ¹H NMR spectrum also shows three different resonances at δ = 7.24, 7.51 and 7.79 ppm for chemically non-equivalent aryl C–H protons. In addition two set of signals were also observed for methyl and methylene protons in complex [4]. The resonance for the characteristic carbene carbon atom appeared at δ = 152.9 ppm along with two additional downfield resonances at δ = 159.0 and 154.4 ppm attributed to the cyclometalated aryl carbon and triazolylidene carbon atom connected to the



Scheme 2 Synthesis of the heterobimetallic Ir^{III}/Pd^{II} complex [5].

aryl ring, respectively. These resonances are in the range reported for iridium(III) complexes with cyclometalated 1,2,3-triazol-5-ylidene ligands.^{9b,16,21} The signal for the aryl C–H carbon atom near to the cyclometalated carbon atom appeared more downfield shifted (δ = 139.0 ppm) compared to the resonances for the other two aryl C–H carbon atoms (δ = 123.3 and 120.6 ppm). The formation of the complex [4] was further confirmed by the ESI-HRMS (positive ions) spectrum, which shows a peak at *m/z* = 751.1591 (calcd for [[4] – I]⁺ 751.1598) as the strongest signal. It is thus possible to selectively generate a cyclometalated Ir^{III} complex with an additional MIC donor starting from a completely symmetrical bis-triazolium salt. Such bis-triazolium salts are otherwise usually prone to the formation of dinuclear complexes.^{9b}

The free triazolium unit in complex [4], however, can also be metalated under suitable reaction conditions. Treatment of [4] with PdCl₂ delivers the heterobimetallic complex [5] (Scheme 2) which was characterized by ¹H and ¹³C{¹H} NMR spectroscopy. The ¹H NMR spectrum of complex [5] features no resonance for the triazolium C5–H proton anymore. The ¹³C{¹H} NMR spectrum of complex [5] revealed the characteristic resonances for the carbene carbon atoms at δ = 152.3 ppm for the Ir–C_{MIC} carbon atom and at δ = 130.9 ppm for the Pd–C_{MIC} carbon atom. These resonances compare well to the equivalent resonances reported for the M–C_{MIC} atoms in iridium(III) and palladium(II) complexes.^{9b,16} Formation of complex [5] was further supported by ESI mass spectrometry. The ESI mass spectrum (positive ions) showed a strong peak at *m/z* = 982.9516 (calcd for [[5] – Py – I]⁺ 982.9600).

In conclusion, we have presented the synthesis of mono- and dinuclear Pt^{II} complexes ([2] and [3]) along with a cyclometalated Ir^{III} complex [4] starting from the same bis-triazolium salt. The complex [2] is the first example of a dinuclear Pt^{II} complex with a mesoionic dicarbene ligand. In addition, the mononuclear complex [2] possesses a free triazole moiety,

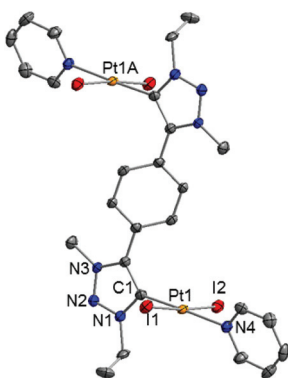


Fig. 4 ORTEP plot of [2] in [2]·2CH₂Cl₂. Ellipsoids are drawn at 50% probability. Hydrogen atoms and solvent molecules have been omitted for clarity.

which is generated from the parent triazolium unit through an *N*-demethylation reaction. Only one triazolium unit of the bis-triazolium salt could be metalated to Ir^{III} upon C5 deprotonation, while the other triazolium unit remained unreacted under the mentioned reaction conditions for the synthesis of complex [4]. However, the unreacted triazolium moiety could be metalated with a Pd^{II} unit to yield a heterobimetallic Ir^{III}/Pd^{II} complex [5]. Further research work in our laboratory will be directed towards the synthesis of a large number of heterobimetallic complexes suitable for tandem catalytic applications.

The authors thank the Fonds der Chemischen Industrie (FCI) and the Freie Universität Berlin for financial support.

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