## Dalton Transactions

## PAPER

**Cite this:** *Dalton Trans.*, 2014, **43**, 4313

Received 19th September 2013, Accepted 8th October 2013 DOI: 10.1039/c3dt52591k

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## Introduction

N-heterocyclic carbenes (NHCs) have been extensively applied in various research areas ranging from catalysis to small molecule activation and functional material applications.<sup>1</sup> Since the discovery of NHCs, multiple variations thereof have been investigated. Among these, cyclic alkyl-amino-carbenes (CAACs), in which one alkyl group replaces one amino group, have attracted increased interest since the first report by Bertrand et al. in 2005.<sup>2</sup> Metal-containing derivatives of CAACs featuring a metal atom within the heterocyclic framework have, to the best of our knowledge, not been described so far. Only very few examples of metallacyclic carbene derivatives exist in the literature, most of which are based on the NHC skeleton. Interest in metal-containing carbenes primarily arises from the possibility to employ these entities as "switchable" redoxactive ligands.<sup>3</sup> In particular, ferrocene-based diaminocarbene complexes reported almost simultaneously by the groups of Bielawski and Siemeling merit attention in this context.<sup>4</sup>

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# A metallacyclic alkyl-amido carbene complex (MCAAC)†‡

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The activation of the C=N moiety in the redox-active metalloligand [CpRu{ $\kappa^3 N_{pz}$ -1}][PF<sub>6</sub>] (2) (1: ambidentate hybrid ligand, N=C-C(pz)<sub>3</sub>, with pz = pyrazolyl) was observed in the reaction with [Ir(cod)Cl]<sub>2</sub> (cod = 1,5-cyclooctadiene). By performing detailed NMR spectroscopic and X-ray crystallographic investigations the product was found to be a bimetallic Ru<sup>II</sup>-Ir<sup>III</sup> complex of the composition [CpRu{ $\mu$ -1'}]r(cod)Cl<sub>2</sub>][PF<sub>6</sub>] (3) consisting of a chemically modified ligand 1'. Most notably, the heterobimetallic complex 3 features an unprecedented metallacyclic alkyl-amido carbene (MCAAC) core structure, which is coordinated to an Ir<sup>III</sup> centre. Density functional theory (DFT) calculations as well as cyclic voltammetry (CV) studies were performed in an effort to establish the formal oxidation states of the metal atoms in 3. Indeed, a quasi-reversible oxidation wave was detected at  $E_{1/2}^0 = 0.36$  V, which was attributed to the Ru<sup>II</sup>/Ru<sup>III</sup> redox couple, while two irreversible reduction of Ir<sup>III</sup> to Ir<sup>I</sup>. First efforts to elucidate the reaction mechanism have also been performed.

Furthermore, Ruiz and co-workers recently reported on a Mn/Au bimetallic complex, regarded as a Fischer carbene within an Arduengo carbene.<sup>5</sup> Herein we report on the synthesis and characterisation of an unprecedented metallacyclic alkyl-amido carbene complex (MCAAC) resulting from an unexpected reaction of a "next generation" scorpionate complex.<sup>6</sup>

## **Results and discussion**

As part of our investigations on ambidentate ligands,<sup>7</sup> we have employed donor-functionalised scorpionate ligands<sup>8</sup> for the synthesis of bimetallic complexes.<sup>9,10</sup> In particular, we pursued the introduction of a nitrile donor function as an additional binding site in a tripodal tris(pyrazolyl)methane (<sup>R</sup>Tpm) ligand scaffold.<sup>11</sup> To this end, lithium tris(pyrazolyl)methanide was reacted with phenyl cyanate to lead to the new ambidentate hybrid ligand N=C-C(pz)<sub>3</sub> (1, pz = pyrazolyl) in 85% isolated yield (Scheme 1).

Compound **1** has been fully characterised by standard analytical methods. In order to explore the potential of the new ambidentate ligand **1** as a precursor for the synthesis of redox-active metalloligands, it was treated with one equivalent of  $[CpRu(CH_3CN)_3][PF_6]$  at room temperature in  $CH_2Cl_2$ . Thus, the anticipated "mixed-sandwich" complex  $[CpRu(\kappa^3N_{pz}-1)]-[PF_6]$  (2) was obtained in 95% isolated yield in an analytically pure form (Scheme 1).<sup>12</sup>



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<sup>†</sup>This article is part of the Dalton Transactions themed issue, New Talent: Europe.

<sup>‡</sup>Electronic supplementary information (ESI) available: Experimental, crystallographic and computational details; selected 2D NMR spectra. CCDC 961720. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt52591k



Scheme 1 Synthesis of 1 and 2.



Fig. 1 Cyclic voltammogram of 2 at room temperature in acetone vs. Fc/Fc<sup>+</sup> (internal standard). Two scans of the whole measurable solvent window. Inset: quasi-reversible oxidation wave centred at 0.47 V. Scan rate 100 mV s<sup>-1</sup>, Pt/[*n*Bu<sub>4</sub>N][PF<sub>6</sub>]/Ag;  $\Delta \phi_p = \phi_p^a - \phi_p^c = 98$  mV at 100 mV s<sup>-1</sup>.

2 is an air and thermally stable (m.p. = 220 °C, dec.), bright yellow solid, whose <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra in CD<sub>2</sub>Cl<sub>2</sub> show the expected sets of signals for a  $C_3$  symmetric "mixedsandwich" complex. The Cp protons appear as a singlet with a chemical shift of  $\delta$  = 4.53 ppm and the protons of the equivalent pyrazolyl heterocycles at  $\delta$  = 6.65, 8.30 and 8.37 ppm. Compared to the free ligand (1, CD<sub>3</sub>CN),<sup>13</sup> the signals are shifted to higher frequencies with the proton in the 3-position of the pz entities being most affected ( $\Delta \delta > 1$  ppm). Similar observations were made for the <sup>13</sup>C{<sup>1</sup>H} signals of the pyrazolyl carbon atoms.

In order to shed some light on the redox properties of 2, we performed some cyclic voltammetry studies in acetone at room temperature (Fig. 1). As expected for complexes of this type, 2 shows a quasi-reversible oxidation process centred at  $E_{1/2}^0 = 0.47$  V ( $\nu$ s. Fc/Fc<sup>+</sup>), which can be assigned to the Ru<sup>II</sup>/Ru<sup>III</sup> redox couple.

An X-ray crystallographic analysis performed on single crystals of 2, which were obtained from a CH<sub>2</sub>Cl<sub>2</sub>-hexane solution, confirmed the proposed  $\kappa^3 N_{\rm pz}$ ,  $\eta^5$ -Cp coordinated core structure.<sup>12</sup> However, several disordered solvent molecules in the crystal lattice prevented a detailed discussion of the structural parameters (see ESI<sup>‡</sup>).



Scheme 2 Synthesis of the MCAAC complex 3.



Fig. 2 (a) Molecular structure of 3 (cationic part; anisotropic displacement parameters at the 30% probability level). (b) Central core structure of 3 showing the basic MCAAC motif. Solvent molecules and the counter ion have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1–N2 2.084(5), Ru1–N4 2.079(5), Ru1–N7 2.107(4), Ru1–Cp<sub>cent</sub> 1.784(3), Ir1–C2 2.058(5), Ir1–N6 2.058(4), Ir1–C1 2.380(1), Ir1–Cl2 2.440(1), Ir1–cod<sub>cent</sub> 2.114(4), Ir1–cod<sub>cent</sub> 2.091(4), N1–C1 1.455(7), N3–C1 1.458(7), N5–C1 1.428(6), C1–C2 1.553(7), N7–C2 1.271(6), N4–Ru1–N2 82.7(2), N4–Ru1–N7 82.6(2), N2–Ru1–N7 81.0(2), C2–Ir1–N6 79.8(2), N7–C2–C1 111.5(4); Cp<sub>cent</sub> and cod<sub>cent</sub> denote the centroids of the Cp and the C=C double bonds of the cod ligands, respectively.

In order to explore the potential of complex **2** to act as a *metalloligand*<sup>10</sup> for the coordination of a second metal fragment *via* the apical nitrile functional group, we reacted **2** with  $[Ir(cod)Cl]_2$  (cod = 1,5-cyclooctadiene) in CH<sub>2</sub>Cl<sub>2</sub> (Scheme 2).

At room temperature, however, no reaction takes place. Only by heating the reaction mixture to 75  $^{\circ}C^{14}$  the formation of an orange-red precipitate was observed, which was straightforwardly collected by filtration and rinsed with CH<sub>2</sub>Cl<sub>2</sub>. Recrystallisation from a mixture of acetone and diethyl ether furnished block-like single crystals of 3 suitable for X-ray diffraction (isolated yield of 31%). The molecular structure is shown in Fig. 2; relevant bond lengths and angles are given in the caption.

Rather unexpectedly, the structure determination did not correspond to the anticipated bimetallic complex [CpRu- $\{\mu-\kappa^3 N_{pz}:\kappa^1 N_{CN}-1\}$ Ir(cod)Cl][PF<sub>6</sub>] featuring a  $\mu-\kappa^3 N_{pz}:\kappa^1 N_{CN}$ -bridging ligand 1. Instead, a chemically modified ligand 1' in an uncommon coordination mode was observed. The Ru<sup>II</sup> cation is still *fac*-coordinated by three nitrogen atoms and one Cp ring, but only two of the N-donor groups are pyrazolyl rings  $\{avg. d(Ru-N_{pz}) = 2.090 \text{ Å}\}$ .<sup>12</sup> The third N-donor was found to be an amido functional group  $\{d(Ru-N7): 2.107(4) \text{ Å}\}$ <sup>15</sup> that originates from the former nitrile group (C1–C2–N7: 111.5°).

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The previous nitrile carbon atom (C2) coordinates as a carbene moiety to an iridium(III) cation, which is additionally coordinated by a 1,5-cyclooctadiene ligand, two chloro ligands and the nitrogen atom of the remaining one pyrazolyl group, forming a slightly distorted octahedral coordination environment around the Ir atom. The Ir1–C2 bond length of 2.058(5) Å is in good agreement with the known values for Ir<sup>III</sup>–NHC complexes.<sup>16</sup>

With the aid of 1D and 2D NMR spectroscopic methods (acetone- $d_6$ ) we were able to confirm that the structure of 3 found in the solid state is retained in solution (Fig. S3-5, ESI<sup>†</sup>). Hence, nine signals for three non-equivalent pyrazolyl heterocycles were observed in the <sup>1</sup>H and the <sup>13</sup>C{<sup>1</sup>H} NMR spectra. The carbon earbon atom C2 appears as a singlet in the <sup>13</sup>C{<sup>1</sup>H} spectrum with a chemical shift of  $\delta$  = 166.6 ppm – a typical value for carbene complexes.<sup>17</sup> <sup>1</sup>H,<sup>15</sup>N gHMQC experiments provided evidence for couplings between the pyrazolyl nitrogen atoms and the protons in 5-position, as well as a cross peak for the coupling of the amide nitrogen atom N7 with the directly bound proton. <sup>1</sup>H, <sup>1</sup>H gNOESY methods confirmed the close spatial arrangement of the amide proton ( $\delta$  = 13.27 ppm)<sup>18</sup> and three cod protons. Additionally, the Cp protons exhibit NOE contacts to the CHpz protons in the 3-position of two pyrazolyl moieties.

Having established the molecular structure of 3 in solution and the solid state as a cationic iridium(III) complex of a chelating MCAAC ligand featuring a ruthenium(II) atom as an additional transition metal entity in the backbone, we intended to further investigate its general characteristics and the mechanistic aspects of its formation. Some points merit attention in this context: (a) while the formal oxidation state of ruthenium in 3 remains +II, the oxidation state of iridium changes from +I in the precursor [Ir(cod)Cl]<sub>2</sub> to +III in 3; (b) the nitrile moiety in 2 is converted to an alkyl-amido carbene entity (C1-C2-N7) in 3 with the nitrogen atom bearing an additional hydrogen substituent. It is worth mentioning too that Woodward and Hiraki have independently reported on such a peculiar activation of nitriles by Ru<sup>II</sup> complexes in the presence of water or methanol, to yield cycloruthenated compounds.<sup>15a,c</sup> However, to the best of our knowledge, no mechanistic investigations of this process have been reported.

Although we were not able to isolate any pure by-product from the mother liquors of the reactions, attempts were made to further support the assignment of the formal oxidation states of the metal atoms in **3**. By performing cyclic voltammetry studies in acetone, we were able to detect a quasi-reversible oxidation wave at  $E_{1/2}^0 = 0.36$  V vs. Fc/Fc<sup>+</sup> (Fig. 3), which can be attributed to the Ru<sup>II</sup>/Ru<sup>III</sup> redox couple (*cf.*  $E_{1/2}^0 = 0.47$  V for 2). These results were supported by density functional theory calculations at the RI-DFT/BP86/def2-TZVP level of theory on the model compounds [**3q**]<sup>+</sup> and [**3q**]<sup>2+</sup> showing that the spin density of [**3q**]<sup>2+</sup> (HOMO of [**3q**]<sup>+</sup>) is primarily located on the ruthenium atom (Fig. 4; see also Fig. S1, ESI<sup>±</sup>).

Furthermore, two irreversible reduction processes with cathodic peak potentials of  $E_{pc} = -1.17$  V and  $E_{pc} = -2.06$  V were observed (Fig. 3). It is reasonable to assume that these



**Fig. 3** Cyclic voltammograms of **3** obtained at ambient temperature in acetone vs. Fc/Fc<sup>+</sup>. Scan rate 100 mV s<sup>-1</sup>, Pt/[nBu<sub>4</sub>N][PF<sub>6</sub>]/Ag. (a) Two scans of the whole measurable solvent window. (b) Two scans of the quasi-reversible oxidation at  $E_{1/2}^0(1) = 0.36$  V ( $\Delta \phi_p = 78$  mV). (c) Two scans of the irreversible reductions at  $E_{pc}(2) = -1.71$  V and  $E_{pc}(3) = -2.06$  V.



Fig. 4 Calculated structure of  $[3q]^{2+}$  (a) and spin density of  $[3q]^{2+}$  (b) at the RI-DFT/BP86/def2-TZVP level.

irreversible redox processes correspond to the stepwise reduction of Ir<sup>III</sup> to Ir<sup>I</sup> and concomitant reductive splitting of the Ir–Cl bonds, explaining the irreversible nature of the reduction processes. However, attempts to perform the reduction on a preparative scale have failed so far.

In order to address the origin of the additional amido hydrogen substituent at N7, which may either stem from the solvent  $CH_2Cl_2$  or C–H moieties of the ligands in the precursor compounds, we performed the reaction of 2 with  $[Ir(cod)Cl]_2$ in  $CD_2Cl_2$  instead of  $CH_2Cl_2$ . 3 was isolated and purified as explained above. <sup>1</sup>H NMR spectroscopic monitoring quickly revealed that the NH function<sup>18</sup> with a chemical shift of  $\delta$  = 13.27 ppm was still visible and in the same intensity as observed before, which means that no deuterium was incorporated. We were thus able to exclude the solvent as a source for the additional amido hydrogen atom. Furthermore, the addition of lutidinium triflate as a proton source did not have any effect on the kinetics of the reaction. Considering that the formation of the amido fragment is accompanied by oxidation of the  $Ir^{I}$  centre, we investigated the possibility that this step would be the rate-determining one. To this end, we performed the reaction of 2 with either  $IrCl_3 \cdot H_2O$  or  $[Ir(tht)_3Cl_3]^{19}$  (tht = tetrahydrothiophene) as the starting material, both in the presence and absence of 1,5-cyclooctadiene. However, we were not able to isolate 3 or any analogous species from the complex mixtures observed in all cases. In the presence of cod, only traces of 3 were formed even after heating to 75 °C for extended periods of time.

Whereas further investigations are required in order to understand the mechanism of formation of 3, our current interpretation is that the amido H atom most likely stems from cod ligands, which would also explain the moderate (but reproducible) isolated yield of 31% of 3 (*i.e.*, parts of  $[Ir(cod)Cl]_2$  or other cod-containing species are consumed by H-abstracting processes). On the other hand, the origin of the additional chloride anion bound to the  $Ir^{III}$  center of 3 remains to be established.

## Conclusions

In summary, we have introduced the synthesis of the hybrid ligand  $N \equiv C-C(pz)_3$  (1), which proved to be a versatile  $\kappa^3 N$ -coordinating ligand for the synthesis of  $[CpRu\{\kappa^3 N_{pz}-1\}][PF_6]$  (2). The latter was found to undergo an unexpected reaction when treated with  $[Ir(cod)Cl]_2$  to produce a very unusual bimetallic complex (3) consisting of an unprecedented metallacyclic alkyl-amido carbene ligand (MCAAC). Studies in our laboratory continue to investigate a more general approach to MCAAC complexes of this type and to further explore the organometallic and coordination chemistry of this new class of bimetallic complexes.

## **Experimental**

#### General considerations

All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon. Solvents were freshly distilled under argon from the appropriate drying agent. Deuterated solvents were refluxed over the appropriate drying agent, and distilled and stored under argon in Teflon valve ampoules. Elemental analyses were recorded at the institutional technical laboratories of the Karlsruhe Institute of Technology (KIT). NMR samples were prepared under an inert atmosphere in 5 mm NMR tubes. Solution NMR spectra were recorded using Bruker Avance instruments operating at <sup>1</sup>H Larmor frequencies of 300 and 400 MHz. Chemical shifts are given relative to TMS for <sup>1</sup>H and <sup>13</sup>C and MeNO<sub>2</sub> in CDCl<sub>3</sub> for <sup>15</sup>N. Coupling constants J are given in hertz as positive values regardless of their real individual signs. Assignments were confirmed as necessary with the use of 2D NMR correlation experiments. Due to the low solubility of 1 in CD<sub>3</sub>CN, the corresponding <sup>1</sup>H, <sup>15</sup>N gHMBC spectrum

was obtained in DMSO- $d_6$ . Standard IR spectra were measured using the ATR technique (attenuated total reflection) on a Bruker Vertex 70 or a Bruker ALPHA IR spectrometer in the range from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>. The intensity of the absorption band is indicated as vw (very weak), w (weak), m (medium), s (strong), vs (very strong), and br (broad). Cyclic voltammetry measurements were performed in a dry-box with a Metrohm Autolab Potentiostat–Galvanostat PGSTAT101 and a typical three-electrode electrochemical cell. We used a freshly polished Pt disk as the working electrode, a Pt wire as the counter electrode, and an Ag wire as the (pseudo) reference electrode ([ $nBu_4N$ ][PF<sub>6</sub>] (0.1 M) as the electrolyte). Potentials given for 2 and 3 were calibrated against the Fc/Fc<sup>+</sup> couple (internal standard).<sup>20</sup>

#### **Computational details**

The calculations were performed with the TURBOMOLE program package.<sup>21</sup> The geometries were optimized without symmetry restrictions at the BP86<sup>22</sup> level in the def2-TZVP basis.<sup>23</sup> Analytical frequency calculations<sup>24</sup> were performed at the BP86/def2-TZVP level. Species  $[\mathbf{3q}]^+$  showed one small imaginary eigenvalue (-6.34 cm<sup>-1</sup>) and  $[\mathbf{3q}]^{2+}$  represents a true minimum on the respective potential-energy surface. The coordinates of the calculated structures of  $[\mathbf{3q}]^+$  and  $[\mathbf{3q}]^{2+}$  are compiled in the ESI.<sup>‡</sup>

#### Crystal structure determination

Crystal data for 3 ( $C_{24}H_{27}N_7F_6PCl_2IrRu$ ·acetone):  $M_r = 980.74$ , monoclinic, space group  $P2_1/c$ ,<sup>25</sup> T = 200 K, a = 13.478(3), b =12.446(3), c = 20.633(4) Å,  $\beta = 108.49(3)^\circ$ , V = 3283(1) Å<sup>3</sup>, Z = 4,  $\rho$  = 1.985 g cm<sup>-3</sup>, total data = 23 939, independent reflections 6419  $[R_{(int)} = 0.0724]$ ,  $\mu = 4.791 \text{ mm}^{-1}$ , 417 parameters,  $R_1 =$ 0.0400 for  $I \ge 2\sigma(I)$  and w $R_2 = 0.1056$ . In order to avoid quality degradation the single crystal was mounted in perfluoropolyalkyletheroil on top of the edge of an open Mark tube and then brought into the cold nitrogen stream of a low-temperature device so that the oil solidified. Data collection for the X-ray structure determination was performed on a STOE STADI 4 diffractometer with a CCD area detector using graphitemonochromated Mo-Kα (0.71073 Å) radiation and a low temperature device. All calculations were performed using SHELXTL (ver. 6.12) and SHELXL-97.26 The structure was solved by direct methods and successive interpretation of the difference Fourier maps, followed by full matrix least-squares refinement (against  $F^2$ ). All non-hydrogen atoms were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. This also holds true for the NH hydrogen atom, which could also be located in the difference Fourier map. Upon convergence, the final Fourier difference map of the X-ray structures showed no significant peaks (largest res. el. dens. close to the iridium atom; numerical absorption corrections did not furnish better datasets). A full listing of atomic coordinates, bond lengths and angles and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC 961720).

#### Synthetic procedures

 $N \equiv C - C(pz)_3$  (1). A 1.6 M solution of *n*-butyl lithium (8.75 ml, 14 mmol) is added dropwise to a solution of  $HC(pz)_3$  (3.00 g, 14 mmol) dissolved in 100 ml THF at -78 °C. A white precipitate forms instantly. After one hour of stirring in the cold, phenyl cyanate is added dropwise to the cooled slurry. After stirring for an additional 16 h at room temperature, the white precipitate is collected by filtration, washed with 40 ml of THF and dried in vacuum. Crystals were obtained from a CH<sub>3</sub>CN- $Et_2O$  solution. Yield: 2.8 g (85%); m.p. (sealed tube under Ar): 180 °C (dec.); elemental analysis (%) calcd for C<sub>11</sub>H<sub>9</sub>N<sub>7</sub> (239.24): C 55.22, H 3.79, N 40.98, found: C 55.21, H 3.91, N 40.87; <sup>1</sup>H NMR (300 MHz, 298 K, CD<sub>3</sub>CN):  $\delta$  6.52 (dd, <sup>3</sup> $J_{\rm HH}$  = 2.8 Hz,  ${}^{3}J_{HH} = 1.7$  Hz, 3H, 4-CH<sub>pz</sub>), 7.18 (d,  ${}^{3}J_{HH} = 2.8$  Hz, 3H, 3- $CH_{pz}$ ), 7.84 (d,  ${}^{3}J_{HH}$  = 1.7 Hz, 3H, 5- $CH_{pz}$ ) ppm;  ${}^{13}C{}^{1}H$  NMR (75 MHz, 298 K, CD<sub>3</sub>CN): δ 83.5 (s, C<sub>apical</sub>), 109.7 (s, 4-CH<sub>pz</sub>), 111.9 (s, -C=N), 131.1 (s, 3-CH<sub>pz</sub>), 144.6 (s, 5-CH<sub>pz</sub>) ppm; <sup>15</sup>N NMR (<sup>1</sup>H, <sup>15</sup>N gHMBC, 30 MHz, 298 K, DMSO- $d_6$ ):  $\delta$  208.4 (s,  $N_{pz}$ ), 305.0 (s,  $N_{pz}$ ); IR (solid, ATR, cm<sup>-1</sup>):  $\nu = 1508$  (vw), 1419 (w), 1379 (m), 1328 (m), 1249 (m), 1199 (w), 1097 (m), 1081 (m), 1031 (m), 934 (w), 913 (w), 870 (s), 756 (vs), 654 (w), 601 (m), 479 (w); EI-MS (70 eV): m/z (%): 239 (25)  $[M]^+$ , 213 (3)  $[HC(pz)_3]^+$ , 172 (100)  $[NCC(pz)_2]^+$ , 106 (87)  $[NCC(pz)]^+$ .

 $[CpRu{\kappa^3N_{pz}-1}][PF_6]$  (2). Ligand 1 (550 mg, 2.3 mmol) in 20 ml CH<sub>2</sub>Cl<sub>2</sub> is added dropwise to a solution of [CpRu-(CH<sub>3</sub>CN)<sub>3</sub> [PF<sub>6</sub>] (1 g, 2.3 mmol) in 20 ml CH<sub>2</sub>Cl<sub>2</sub> at room temperature. The orange solution is stirred for three hours. The solution is then concentrated in vacuo to about half its original volume and layered with n-hexane to give orange, diamondshaped crystals. Yield: 1.2 g (95%); m.p. (sealed tube under Ar): 220 °C (decomposition); elemental analysis (%) calcd for C16H14F6N7PRu (550.36): C 34.92, H 2.56, N 17.81, found: C 34.71, H 2.59, N 17.77; <sup>1</sup>H NMR (400 MHz, 298 K,  $CD_2Cl_2$ ):  $\delta$ 4.53 (s, 5H, Cp-*H*), 6.65 (dd,  ${}^{3}J_{HH}$  = 3.0 Hz,  ${}^{3}J_{HH}$  = 2.2 Hz, 3H, 4-C $H_{pz}$ ), 8.30 (dd,  ${}^{3}J_{HH}$  = 3.1 Hz,  ${}^{3}J_{HH}$  = 0.6 Hz, 3H, 3-C $H_{pz}$ ), 8.37 (dd,  ${}^{3}J_{HH} = 2.2$  Hz,  ${}^{3}J_{HH} = 0.6$  Hz, 3H, 5-CH<sub>pz</sub>) ppm;  ${}^{1}H$ NMR (300 MHz, 298 K, CD<sub>3</sub>CN):<sup>13</sup> δ 4.58 (s, 5H, Cp-H), 6.60  $(dd, {}^{3}J_{HH} = 3.0 \text{ Hz}, {}^{3}J_{HH} = 2.3 \text{ Hz}, 3H, 4-CH_{pz}), 8.38 (d, {}^{3}J_{HH} =$ 3.2 Hz 3H, 3- $CH_{pz}$ ), 8.47 (dd,  ${}^{3}J_{HH}$  = 2.3 Hz 3H, 5- $CH_{pz}$ ) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  70.5 (s, Cp–C), 78.3 (s, C<sub>apical</sub>), 107.5 (s, -C=N), 110.3 (s, 4-CH<sub>pz</sub>), 132.1 (s, 3-CH<sub>pz</sub>), 150.5 (s, 5- $CH_{pz}$ ) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, 298 K, CD<sub>3</sub>CN):<sup>13</sup>  $\delta$  70.7 (s, Cp–C), 78.8 (s, C<sub>apical</sub>), 107.7 (s, –C=N), 109.9 (s, 4-CH<sub>pz</sub>), 134.3 (s, 3-CH<sub>pz</sub>), 151.0 (s, 5-CH<sub>pz</sub>) ppm; <sup>31</sup>P {<sup>1</sup>H} NMR (120 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -144.5 (sept, <sup>1</sup>J<sub>PF</sub> = 709 Hz,  $PF_6$ ) ppm; <sup>19</sup>F NMR (280 MHz, 298 K,  $CD_2Cl_2$ ):  $\delta$  -72.3 (d,  ${}^{1}J_{\rm PF}$  = 709 Hz, PF<sub>6</sub>) ppm;  ${}^{15}$ N NMR ( ${}^{1}$ H,  ${}^{15}$ N gHMBC, 40 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  204.9 (s,  $N_{pz}$ ), 236.1 (s,  $N_{pz}$ ); <sup>15</sup>N NMR (<sup>1</sup>H, <sup>15</sup>N gHMBC, 30.4 MHz, 298 K, CD<sub>3</sub>CN):<sup>13</sup>  $\delta$  205.6 (s,  $N_{\rm pz}$ ), 234.6 (s,  $N_{\rm pz}$ ); IR (solid, ATR, cm<sup>-1</sup>):  $\nu$  = 1320 (m), 1222 (w), 1100 (m), 823 (vs), 739 (s), 594 (m), 555 (s); ESI-MS (70 eV): m/z (%): 208 (100)  $[Ru(NCCpz)]^+$ , 249 (29)  $[Ru(C(pz)_2)]^+$ , 406 (98)  $[MPF_6]^+$ ; UV/Vis (MeCN, nm):  $\lambda_{max} = 210 \ (\varepsilon = 23500 \ dm^3 \ mol^{-1} \ cm^{-1})$ , 270 ( $\varepsilon$  = 5300 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>), 313 ( $\varepsilon$  = 6500 dm<sup>3</sup> mol<sup>-1</sup>  $cm^{-1}$ ), 380 (sh).

MCAAC complex 3. In a thick-walled Schlenk tube, 2 (550 mg, 1.0 mmol) and [Ir(cod)Cl]<sub>2</sub> (672 mg, 1.0 mmol) are dissolved in 50 ml CH<sub>2</sub>Cl<sub>2</sub> and heated to 75 °C for 120 h. The resulting orange precipitate is collected by filtration, washed with 25 ml CH<sub>2</sub>Cl<sub>2</sub> and dried in vacuum. Layering of a solution of 3 in acetone with diethyl ether furnished red cubic-shaped crystals. Yield: 321 mg (31%); m.p. (sealed tube under Ar): 250 °C (decomposition); elemental analysis (%) calcd for C<sub>24</sub>H<sub>27</sub>Cl<sub>2</sub>F<sub>6</sub>N<sub>7</sub>PIrRu (921.67): C 31.24, H 2.95, N 10.63, found: C 30.96, H 2.95, N 10.45; <sup>1</sup>H NMR (400 MHz, 298 K, acetone $d_6$ :  $\delta$  1.53–1.83 (m, 3H, cod-H), 2.41–2.50 (m, 1H, cod-H), 2.52-2.69 (m, 2H, cod-H), 2.84-2.59 (m, 1H, cod-H), 3.28-3.43 (m, 1H, cod-H), 3.92-4.0 (m, 1H, cod-H), 4.81 (s, 5H, Cp-H), 4.99-5.08 (m, 1H, cod-H), 5.17-5.26 (m, 1H, cod-H), 5.48-5.55 (m, 1H, cod-*H*), 6.53 (dd,  ${}^{3}J_{HH} = 3.1$  Hz,  ${}^{3}J_{HH} = 2.2$  Hz, 1H,  $CH_{pz}$ ), 6.70 (dd,  ${}^{3}J_{HH}$  = 2.9 Hz,  ${}^{3}J_{HH}$  = 2.3 Hz, 1H,  $CH_{pz}$ ), 7.38–7.42 (m, 2H,  $CH_{pz}$ ), 7.83 (d,  ${}^{3}J_{HH}$  = 3.1 Hz, 1H,  $CH_{pz}$ ), 8.63 (d,  ${}^{3}J_{HH} = 2.0$  Hz, 1H,  $CH_{pz}$ ), 8.80 (d,  ${}^{3}J_{HH} = 2.0$  Hz, 1H,  $CH_{pz}$ ), 9.06 (d,  ${}^{3}J_{HH}$  = 2.2 Hz, 1H,  $CH_{pz}$ ), 9.24 (d,  ${}^{3}J_{HH}$  = 3.0 Hz, 1H,  $CH_{pz}$ ), 13.27 (s, 1H, NH) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, 298 K, acetone- $d_6$ ):  $\delta$  27.7 (s, cod-C), 29.1 (s, cod-C), 32.9 (s, cod-C), 34.2 (s, cod-C), 72.8 (s, Cp-C), 89.4 (s, cod-C), 92.4 (s, C(pz)<sub>3</sub>), 93.7 (s, cod-C), 94.4 (s, cod-C), 104.7 (s, cod-C), 109.7 (s, pz-C), 110.7 (s, pz-C), 114.4 (s, pz-C), 132.7 (s, pz-C), 133.6 (s, pz-C), 137.6 (s, pz-C), 144.2 (s, pz-C), 149.6 (s, pz-C), 149.9 (s, pz-C), 166.6 (s, -CN) ppm; <sup>31</sup>P{<sup>1</sup>H} NMR (120 MHz, 298 K, acetone $d_6$ ):  $\delta$  -144.5 (sept,  ${}^{1}J_{PF}$  = 709 Hz,  $PF_6$ ) ppm;  ${}^{19}F$  NMR (280 MHz, 298 K, acetone- $d_6$ ):  $\delta$  -72.3 (d,  ${}^{1}J_{PF}$  = 709 Hz, PF<sub>6</sub>) ppm; <sup>15</sup>N NMR (<sup>1</sup>H, <sup>15</sup>N gHMBC, 40 MHz, 298 K, acetone- $d_6$ ):  $\delta$ 202.5 (s,  $N_{pz}$ ), 205.9 (s,  $N_{pz}$ ), 206.3 (s,  $N_{pz}$ ), 212.0 (s,  $N_{pz}$ ), 232.6 (s, N<sub>pz</sub>), 236.5 (s, N<sub>pz</sub>), 250.7 (s, N<sub>amide</sub>) ppm; IR (solid, ATR,  $cm^{-1}$ ):  $\nu = 1401$  (m), 1359 (m), 1318 (m), 1273 (m), 1217 (m), 1102 (m), 1062 (w), 877 (w), 830 (vs), 771 (s), 755 (s), 740 (s), 598 (m), 556 (s), 502 (w), 418 (w); ESI-MS (70 eV): m/z (%): 778  $(100) [M - PF_6]^+$ , 742 (10)  $[M - PF_6 - Cl]^+$ ; UV/Vis (MeCN, nm):  $\lambda_{\text{max}} = 220$  (shoulder), 307 ( $\varepsilon = 19300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), 399  $(\varepsilon = 9500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}).$ 

## Acknowledgements

Financial support by the DFG-funded transregional collaborative research centre SFB/TRR 88 "Cooperative effects in homo- and heterometallic complexes (3MET)" is gratefully acknowledged.

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