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# Formation of a Hydroxo-bridged Dinuclear Ru(III)/Ru(III) Complex from *N*-Methylimidazole and [Ru*Cp*$(CH_3CN)_3$]$^+$

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**Summary.** The reaction of [Ru*Cp*$(CH_3CN)_3$]$PF_6$ with 1 equiv of *N-Me*-imidazole results in the quantitative formation of [Ru*Cp*($\kappa^1$*N-N′-Me*-imidazole)$(CH_3CN)_2$]$PF_6$ (**1**) featuring a $\kappa^1$*N* rather than a $\kappa^1$*C* bound *N-Me*-imidazole ligand. According to DFT/B3LYP calculations, $\kappa^1$*N* coordination of *N-Me*-imidazole is preferred over $\kappa^1$*C* coordination by 25.5 kJ/mol. Upon exposure to air **1** reacts with oxygen and water to afford the novel hydroxo-bridged dinuclear complex of [$Ru_2Cp_2$($\kappa^1$*N-N′-Me*-imidazole)$_2$($\mu$-OH)$_2$]$(PF_6)_2$ (**2**) featuring a metal-metal single bond. The dimeric nature of **2** was confirmed by a single-crystal X-ray structure analysis.

**Keywords.** Ruthenium; *N-Me*-imidazole; Dinuclear complexes; Structure analysis; DFT calculations.

## Introduction

Heteroatom-stabilized carbene complexes play a central role in organometallic chemistry [1]. They have found widespread applications as reactive intermediates in organic synthesis initiating a wide range of C–C and C-heteroatom bond forming reactions [2]. Moreover, heteroatom-stabilized carbenes, in particular N-heterocyclic ones based on imidazole derivatives, are recognized as extraordinarily useful spectator ligands in place of, or in addition to, phosphine ligands [3]. It is thus of some interest to find new synthetic routes to afford carbene complexes especially if available from simple organic precursors in a one pot-procedure. We have recently reported [4] a direct synthesis of amino carbenes from aldimines via a formal 1,2-hydrogen shift (Scheme 1).

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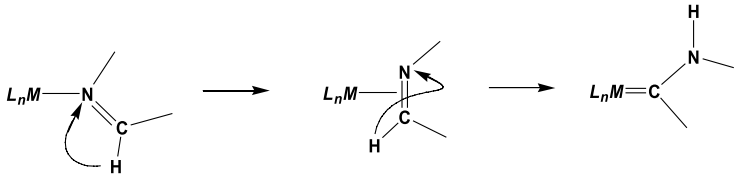
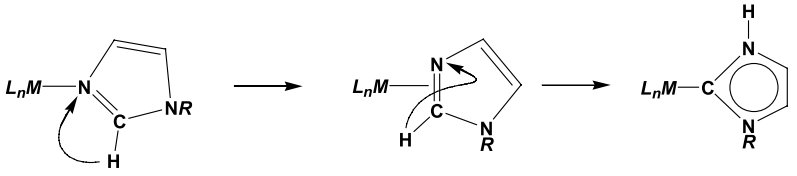


**Scheme 1**

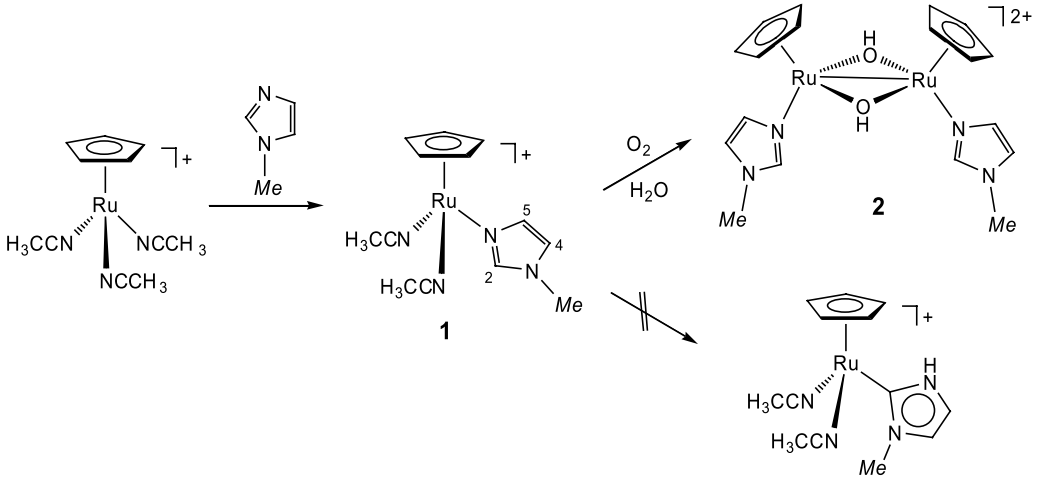


**Scheme 2**

Based on this imine to carbene conversion, it may be interesting whether or not a direct conversion of a $\kappa^1N$ coordinated imidazole ligand to the corresponding $\kappa^1C$ coordinated carbene mediated by transition metals according to Scheme 2 is feasible. Thus far, N-heterocyclic carbenes are commonly obtained by the reaction of the respective imidazolium salts with suitable transition metal complexes [5] or directly with the free carbene [3]. In the present contribution we report on the reaction of *N-Me*-imidazole with [Ru*Cp*$(CH_3CN)_3$]$PF_6$ with the objective to obtain the cationic carbene complex [Ru*Cp*($\kappa^1$*C-N-Me*-imidazole)$(CH_3CN)_2$]$PF_6$.

## Results and Discussion

Treatment of [Ru*Cp*$(CH_3CN)_3$]$PF_6$ with 1 equiv of *N-Me*-imidazole in acetone-$d_6$ results in the quantitative formation of [Ru*Cp*($\kappa^1$*N-N′-Me*-imidazole)$(CH_3CN)_2$]$PF_6$ (**1**) as monitored by $^1$H and $^{13}$C{$^1$H} NMR spectroscopy (Scheme 3). Characteristic $^1$H NMR signals include a singlet at 7.98 ppm and



**Scheme 3**

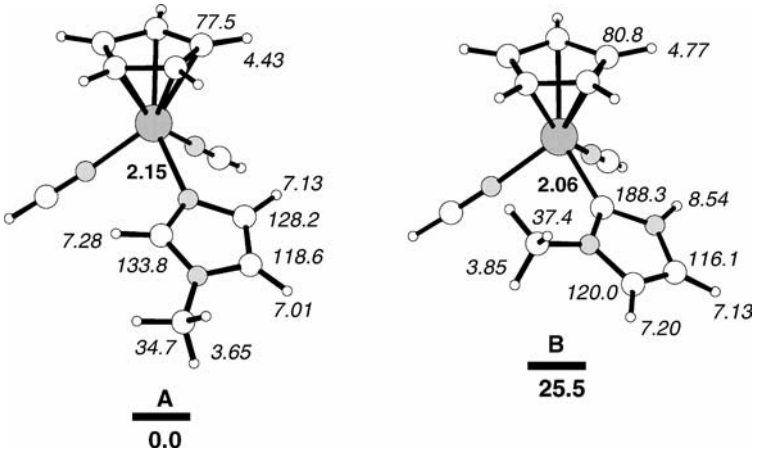



**Fig. 1.** Optimized DFT/B3LYP geometries (in Å, bold), relative energies (in kJ/mol), and calculated (DFT-GIAO) $^{1}$H and $^{13}$C chemical shifts $\delta$ (in ppm relative to Si*Me*$_4$, italic) of the model complexes [Ru*Cp*($\kappa^1$*N-N′-Me*-imidazole)(HCN)$_2$]$^+$ (**A**) and [Ru*Cp*($\kappa^1$*C-N′-Me*-imidazole)(HCN)$_2$]$^+$ (**B**) (basis set: Ru sdd; C, N, H 6–31 g$^{**}$)

two triplets centered at 7.21 and 7.14 ppm, assignable to the ring hydrogen atoms of the imidazole ligand. In the $^{13}$C{$^{1}$H} NMR spectrum, the *N-Me*-imidazole ligand is characterized by signals at 140.8, 132.3, and 121.2 ppm which are assigned to C2, C5, and C4, respectively. Accordingly, the *N-Me*-imidazole ligand is $\kappa^1N$ rather than $\kappa^1C$ coordinated. In fact, a metal-bound carbon atom of imidazoles typically exhibits resonances in the range from 160 to 180 ppm [5]. In the absence of crystals suitable for X-ray structure determination, the structural assignment of **1** has been backed up by means of $^{1}$H and $^{13}$C NMR GIAO calculations based on optimum DFT/B3LYP models of [Ru*Cp*($\kappa^1$*N-N′-Me*-imidazole)(HCN)$_2$]$^+$ (**A**) and [Ru*Cp*($\kappa^1$*C-N′-Me*-imidazole)(HCN)$_2$]$^+$ (**B**). Gratifyingly, the calculated NMR spectra are in excellent agreement with experiment (Fig. 1). Moreover, DFT/B3LYP calculations suggest that the conversion of a $\kappa^1N$ coordinated imidazole ligand to the corresponding $\kappa^1C$ coordinated carbene is thermodynamically unavailable. The geometries and the relative energies of **A** and **B** are shown in Fig. 1. According to these calculations, the $\kappa^1C$ coordinated carbene complex is less stable by 25.5 kJ/mol than the corresponding complex with the $\kappa^1N$-coordinated *N-Me*-imidazole ligand.

Complex **1** turned out to be very air sensitive. All attempts to isolate **1** in pure form were unsuccessful. Upon exposure to air, the yellow solution of **1** in acetone turned rapidly dark green. NMR monitoring revealed the formation of a diamagnetic species which after work-up was isolated in 83% as the novel dinuclear complex of [Ru$_2$*Cp*$_2$($\kappa^1$*N-N′-Me*-imidazole)$_2$($\mu$-OH)$_2$](PF$_6$)$_2$ (**2**) as shown in Scheme 3. Support of this formulation comes from elemental analysis as well as from $^{1}$H and $^{13}$C{$^{1}$H} NMR spectroscopy. In the $^{1}$H NMR spectrum the hydrogen atoms of the *Cp* ring were shifted downfield to 5.83 ppm (*cf.* 4.21 ppm for **1**) indicative of an oxidation state higher than +II. The OH protons give rise to a characteristic low-field shifted signal at 9.08 ppm. Similarly, in the $^{13}$C{$^{1}$H} NMR spectrum the ring carbon atoms of the *Cp* ligand were found to be downfield shifted

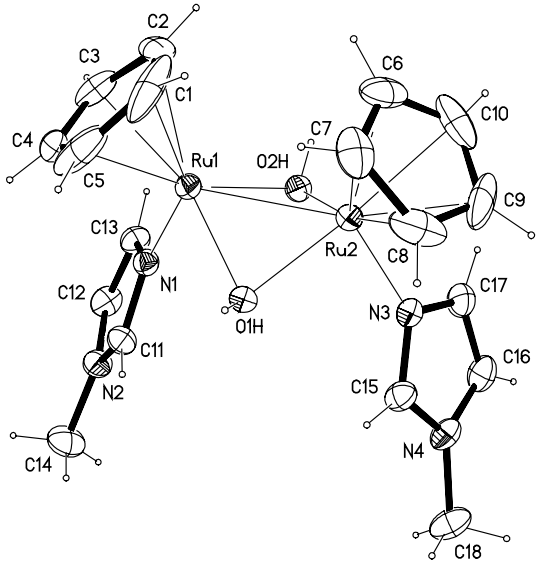



**Fig. 2.** Structural view of $[Ru_2Cp_2(\kappa^1N\text{-}N'\text{-}Me\text{-imidazole})_2(\mu\text{-OH})_2](PF_6)_2 \cdot (CH_3)_2CO \cdot H_2O$ ($\mathbf{2} \cdot (CH_3)_2CO \cdot H_2O$) showing 20% probability thermal ellipsoids ($PF_6$ and solvent molecules omitted for clarity); selected distances (Å) and angles (°): Ru(1)–C(1–5)$_{av}$ 2.167(4), Ru(2)–C(6–10)$_{av}$ 2.170(4), Ru(1)–Ru(2) 2.6297(4), Ru(1)–N(1) 2.038(2), Ru(2)–N(3) 2.080(2), Ru(1)–O(1) 2.040(2), Ru(1)–O(2) 2.041(2), Ru(2)–O(1) 2.038(2), Ru(2)–O(2) 2.045(2), O(1)–Ru(1)–O(2) 79.2(1), O(1)–Ru(2)–O(2) 79.1(1)

appearing as a singlet at 91.3 ppm (*cf.* 68.3 ppm for **1**). The *N-Me*-imidazole ligand exhibits resonances at 141.8, 131.3, and 122.0 ppm assignable to C2, C5, and C4, respectively. Based on these findings and the diamagnetic nature of **2**, the Ru(II) center was apparently oxidized to Ru(III) forming a binuclear hydroxo-bridged species with a metal-metal single bond. The hydroxo ligands, obviously, originate from adventitious water in the solvent.

The single-crystal X-ray structure analysis of **2** in the form of its solvate $\mathbf{2} \cdot (CH_3)_2CO \cdot H_2O$, depicted in Fig. 2, confirms the dimeric nature of this compound. Selected bond distances and angles are reported in the caption. The complex contains two Ru*Cp* units in mutual *cis* configuration bridged by two hydroxo ligands. The *N-Me*-imidazole ligand is clearly $\kappa^1N$ bonded. The core of the dinuclear complex features a four-membered Ru–O–Ru–O ring. The O(1)–Ru(1)–O(2) and O(1)–Ru(2)–O(2) angles are 79.2(1) and 79.1(1)°, respectively. The Ru(1)–Ru(2) distance of 2.6297(4) Å is in line with a metal-metal single bond [6]. The Ru–O distances are in the range from 2.038 to 2.045(2) Å. This structure stands out by its two different solvent molecules, acetone and water, both of which are anchored via comparatively short hydrogen bonds of the OH-groups to the solvent oxygen atoms (to acetone: O(1H)···O(3) = 2.759(4) Å, to water: O(2H)···O(4W) = 2.732(4) Å). The water molecule in turn donates weak bifurcated hydrogen bonds to both $PF_6^-$ octahedra (O···F = 3.02–3.35 Å). Only very few dinuclear hydoxo-bridged Ru(III)–Ru(III) complexes have been structurally characterized so far with all of them comprising of donor ligands. Examples are

the compounds CODCUT, FADVAH, PILMAY, POSPAO, and WATRUE of the Cambridge Structural Database [7]. The present compound is the first one with the $Cp/Cp^*$ ligand.

## Experimental Section

*General Methods*

All manipulations were performed under an inert atmosphere of argon by using *Schlenk* techniques. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures [8]. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. [Ru*Cp*$(CH_3CN)_3$]$PF_6$ was prepared according to Ref. [9]. $^1$H and $^{13}$C{$^1$H} spectra were recorded on a Bruker AC-250 spectrometer operating at 250.13 and 62.86 MHz, respectively, and were referenced to Si*Me*$_4$.

*[RuCp($\kappa^1$N-N′-Me-imidazole)($CH_3CN)_2$]$PF_6$ (**1**)*

A 5 mm NMR tube was charged with a solution of [Ru*Cp*$(CH_3CN)_3$]$PF_6$ (100 mg, 0.230 mmol) in acetone-$d_6$ (0.5 cm$^3$) and was capped with a septum. *N*-Methylimidazole (18.4 mm$^3$, 0.230 mmol) was added by syringe and the sample was transferred to a NMR probe. $^1$H and $^{13}$C{$^1$H} NMR spectra were recorded after keeping the solution for 2 h at room temperature revealing the quantitative formation of **1**. $^1$H NMR (acetone-$d_6$, 20°C): $\delta = 7.98$ (s, 1H, Im$^2$), 7.21 (d, $J = 1.52$ Hz, 1H, Im$^4$), 7.14 (d, $J = 1.37$ Hz, 1H, Im$^3$), 4.21 (s, 5H, RuCp), 3.79 (s, 3H, Im-$CH_3$), 2.50 (s, 6H, NC$CH_3$) ppm; $^{13}$C{$^1$H} NMR (acetone-$d_6$, 20°C): $\delta = 140.8$ (Im$^2$), 132.3 (Im$^5$), 125.2 (N*C*$CH_3$), 121.3 (Im$^4$), 68.3 (RuCp), 34.1 (Im–*C*$H_3$), 4.1 (NC*C*$H_3$) ppm.

*[$Ru_2Cp_2$($\kappa^1$N-N′-Me-imidazole)$_2$($\mu$-OH)$_2$]($PF_6)_2$ (**2**)*

To a solution of [Ru*Cp*$(CH_3CN)]_3PF_6$ (0.150 g, 0.345 mmol) in acetone (10 cm$^3$) *N*-methylimidazole (27.5 mm$^3$, 0.345 mmol) was added and stirred for 10 min. The solution was then exposed to air and stirred overnight, whereupon the color of the solution changed from yellow to green. After removal of the solvent under reduced pressure, a dark green microcrystalline compound was obtained which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 0.117 g (83%); $^1$H NMR (acetone-$d_6$, 20°C): $\delta = 9.08$ (bs, 2H, OH), 7.82 (s, 2H, Im$^2$), 7.21 (d, $J = 1.52$ Hz, 2H, Im$^4$), 6.94 (d, $J = 1.22$ Hz, 2H, Im$^5$), 5.83 (s, 10H, Cp), 3.76 (s, 6H, Me) ppm; $^{13}$C{$^1$H} NMR (acetone-$d_6$, 20°C): $\delta =$ 141.8 (Im$^2$), 131.3 (Im$^5$), 122.0 (Im$^4$), 91.3 (Cp), 34.1 (Me) ppm; Anal. calcd. for $C_{18}H_{24}F_{12}N_4O_2P_2Ru_2$: C 26.35, H 2.95, N 6.83; found: C 26.29, H 2.83, N 6.90.

*Computational Details*

All calculations were performed using the Gaussian98 software package [10] on the Silicon Graphics Power Challenge of the Vienna University of Technology. The geometry and energy of the complexes [Ru*Cp*($\kappa^1$*N-N′-Me*-imidazole)$(HCN)_2]^+$ (**A**) and [Ru*Cp*($\kappa^1$*C-N′-Me*-imidazole)$(HCN)_2]^+$ (**B**) were optimized at the B3LYP level [11] with the Stuttgart/Dresden ECP (sdd) basis set [12] to describe the electrons of the ruthenium atom. For the H, C, and N atoms the 6–31g** basis set was employed [13]. A vibrational analysis was performed to confirm that the structures of the model compounds have no imaginary frequency. The geometries were optimized without constraints ($C_1$ symmetry). $^1$H and $^{13}$C chemical shifts were calculated at the B3LYP level of theory for the optimized structures of **A** and **B** using the gauge independent atomic orbital (GIAO) method in Gaussian 98 with the above basis sets. Chemical shifts are given with respect to Si*Me*$_4$ at the same computational level.

*X-Ray Structure Determination*

Crystals of $[Ru_2Cp_2(\kappa^1N\text{-}N'\text{-}Me\text{-imidazole})_2(\mu\text{-}OH)_2](PF_6)_2 \cdot (CH_3)_2CO \cdot H_2O$ ($\mathbf{2} \cdot (CH_3)_2CO \cdot H_2O$) were obtained by diffusion of pentane into an acetone solution. X-Ray data were collected on a Bruker Smart CCD area detector diffractometer (graphite monochromated MoK$\alpha$ radiation, $\lambda = 0.71073$ Å, 0.3°$\omega$-scan frames covering a complete sphere of the reciprocal space). Corrections for crystal decay and for absorption were applied. The structure was solved with direct methods using the program SHELXS97 [14]. Structure refinement on $F^2$ was carried out with program SHELXL97 [15]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of OH groups and $H_2O$ were refined in x, y, z using a O–H distance restraint. All other hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. Complete structure data have been deposited [16]. Salient crystal data are: $\mathbf{2} \cdot (CH_3)_2CO \cdot H_2O$: $C_{21}H_{32}F_{12}N_4O_4P_2Ru_2$, $M_r = 896.59$, monoclinic, space group $P2_1/c$, $T = 297(2)$ K, $a = 17.595(3)$ Å, $b = 10.740(2)$ Å, $c = 18.399(1)$ Å, $\beta = 109.682(3)°$, $V = 3273.6(8)$ Å$^3$, $Z = 4$, $\mu = 1.123$ mm$^{-1}$. Of 45821 reflections collected up to $\theta = 30°$, 9429 were independent, $R_{int} = 0.0253$; final R indices: $R_1 = 0.051$ (all data), $wR_1 = 0.093$ (all data).

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[16] Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 226888. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ ccdc.cam.ac.uk)