

# A Ru–carbene complex with a metallacycle involving a 1,8-naphthylidene framework

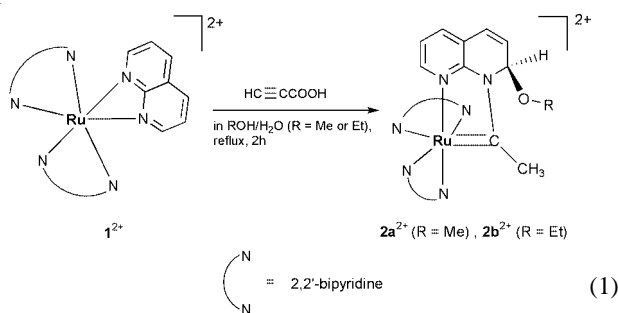
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The reaction of [Ru(bpy)<sub>2</sub>(napy-κ<sup>2</sup>N,N′)](PF<sub>6</sub>)<sub>2</sub> [**1**](PF<sub>6</sub>)<sub>2</sub> (napy = 1,8-naphthylidene) with propiolic acid yielded a Ru–carbene complex with a five-membered metallacycle involving a 1,8-naphthylidene framework.

Reactions of transition metal complexes with terminal alkynes have been utilized to prepare vinylidene complexes,<sup>1</sup> which are characterized by the electrophilicity of the α carbon. In fact, vinylidene–metal complexes are converted to alkoxy–alkyl carbene complexes by reaction with alcohols.<sup>2</sup> We have reported that the non-bonded nitrogen of napy-κN of [Ru(bpy)<sub>2</sub>(napy-κN)(CO)]<sup>2+</sup> attacks the carbonyl carbon to form a five-membered metallacycle upon one-electron reduction of the napy moiety (napy = 1,8-naphthylidene).<sup>3</sup> Moreover, [Ru(bpy)<sub>2</sub>(napy-κ<sup>2</sup>N,N′)]<sup>2+</sup> exists in equilibrium with [Ru(bpy)<sub>2</sub>(napy-κN)(solvent)]<sup>2+</sup> in polar solutions.<sup>4</sup> Thus [Ru(bpy)<sub>2</sub>(napy-κ<sup>2</sup>N,N′)]<sup>2+</sup> readily forms a 1:1 adduct with various substrates upon opening of the chelate ring. The reaction of [Ru(bpy)<sub>2</sub>(napy-κ<sup>2</sup>N,N′)](PF<sub>6</sub>)<sub>2</sub> [**1**](PF<sub>6</sub>)<sub>2</sub> with propiolic acid in alcohol was conducted to elucidate whether the non-bonded nitrogen of napy or alcohol attacks the α carbon of the vinylidene moiety. Here we report the isolation of a Ru–carbene complex with a metallacycle **2a**<sup>2+</sup> (eqn. 1), and the reversible conversion between **2a**<sup>2+</sup> and the vinyl complex **3**<sup>+</sup> upon acid–base treatment.

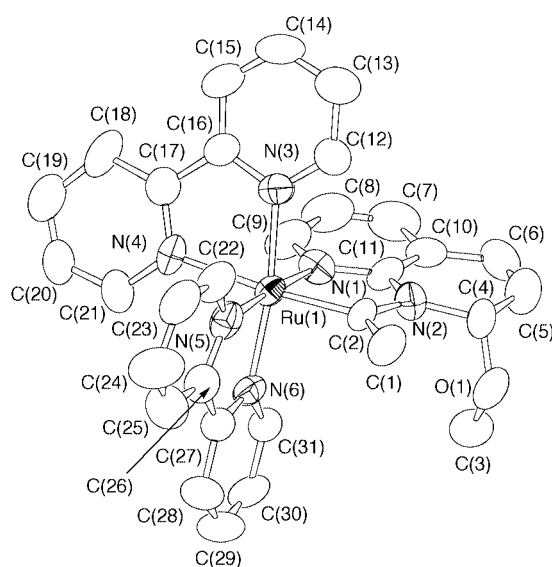


A CH<sub>3</sub>OH/H<sub>2</sub>O (3:2 v/v) solution containing [**1**](PF<sub>6</sub>)<sub>2</sub> (60 mg, 72 μmol) and HCCC(O)OH (7 mg, 100 μmol) was refluxed for 2 h, and [**2a**](PF<sub>6</sub>)<sub>2</sub> was obtained from the solution (eqn. 1). Recrystallization of the crude product from CH<sub>3</sub>CN/CH<sub>3</sub>OH (4:1 v/v) gave single crystals of [**2a**](PF<sub>6</sub>)<sub>2</sub>·CH<sub>3</sub>CN in 64% yield.† The similar reaction between [**1**](SbF<sub>6</sub>)<sub>2</sub> and HCCC(O)OH in C<sub>2</sub>H<sub>5</sub>OH/H<sub>2</sub>O (4:1 v/v) under similar reaction conditions afforded [**2b**](SbF<sub>6</sub>)<sub>2</sub> in 56% yield (eqn. 1).†

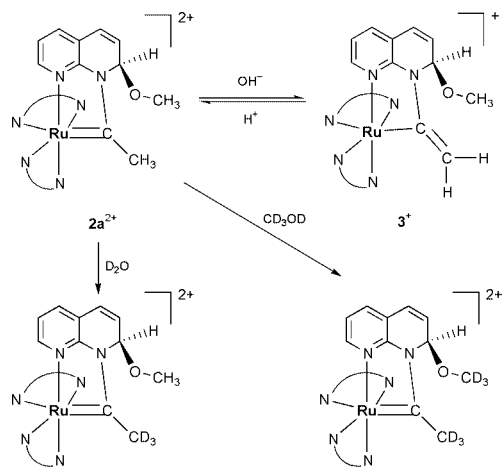
The molecular structure of **2a**<sup>2+</sup> determined by X-ray diffraction analysis is shown in Fig. 1.<sup>5</sup> The ruthenium atom of **2a**<sup>2+</sup> has octahedral geometry with four nitrogen atoms of two bpy ligands, one nitrogen from napy and one carbon of the CCH<sub>3</sub> group. The characteristic features of **2a**<sup>2+</sup> are the C–N bond formation between the CCH<sub>3</sub> group and one nitrogen of napy, and the attachment of the CH<sub>3</sub>O group to the 2-position of the napy moiety. The resultant five-membered metallacycle consisting of Ru, N(1), C(11), N(2), and C(2) atoms in an almost

planar structure, and the sum of the bond angles around the five-membered ring is almost 360°. Despite the attachment of CH<sub>3</sub>O to the 2-position of the napy moiety, the resultant ligand still maintains the planar structure in **2a**<sup>2+</sup>. As a result, the napy moiety and the five-membered metallacycle are co-planar. The Ru–N(4) (2.156(9) Å) bond *trans* to Ru–C(2) is substantially longer than the other Ru–N bonds of **2a**<sup>2+</sup> (2.03(1)–2.08(1) Å), suggesting a strong *trans* effect of the carbene ligand. The Ru–C(2) bond distance (1.93(1) Å) is in the expected range of hexacoordinated ruthenium carbene bonds (1.941–1.98 Å),<sup>6</sup> and the bond length is longer than those expected for penta-coordinated ruthenium carbene complexes (1.810–1.861 Å).<sup>7</sup> The <sup>13</sup>C NMR spectrum of **2a**<sup>2+</sup> also showed the α-carbon signal of the Ru–CCH<sub>3</sub> group at δ 293 as a singlet, similar to most Ru carbene complexes.<sup>2,6a–c,7e,f</sup>

The complex [**2a**](PF<sub>6</sub>)<sub>2</sub> was stable in CH<sub>3</sub>OH/(CH<sub>3</sub>)<sub>2</sub>CO and H<sub>2</sub>O/(CH<sub>3</sub>)<sub>2</sub>CO. On the other hand, the methyl signals of the CH<sub>3</sub>O and the Ru–CCH<sub>3</sub> groups of **2a**<sup>2+</sup> (δ 2.95 and 2.85, respectively) gradually weakened with time in the <sup>1</sup>H NMR spectrum in (CD<sub>3</sub>)CO/CD<sub>3</sub>OD (1:1 v/v). The Ru–CCH<sub>3</sub> signal vanished in 30 min at ambient temperature, and the CH<sub>3</sub>O one disappeared after 12 h at 65 °C. At the same time, the methyl signal of free methanol appeared at δ 3.33. Moreover, **2a**<sup>2+</sup> was



**Fig. 1** An ORTEP view of complex **2a**<sup>2+</sup>. Selected intramolecular distances (Å): Ru(1)–N(1), 2.03(1); Ru(1)–N(3), 2.061(9); Ru(1)–N(4), 2.156(9); Ru(1)–N(5), 2.08(1); Ru(1)–N(6), 2.052(9); Ru(1)–C(2), 1.93(1); C(1)–C(2), 1.53(2); C(2)–N(2), 1.41(1); C(4)–O(1), 1.40(2); C(3)–O(1), 1.40(2). Selected bond angles (degrees): N(1)–Ru(1)–C(2), 79.8(5); Ru(1)–C(2)–C(1), 127.1(9); Ru(1)–C(2)–N(2), 116.3(8); C(1)–C(2)–N(2), 117(1); C(2)–N(2)–C(4), 123(1); C(2)–N(2)–C(11), 114(1); C(4)–N(2)–C(11), 122(1); N(2)–C(4)–O(1), 112(1); N(2)–C(4)–C(5), 112(1); C(5)–C(4)–O(1), 111(1).



Scheme 1

converted to  $2b^{2+}$  in  $C_2H_5OH/(CH_3)_2CO$  for 1 week at room temperature. Thus, the Ru–CCH<sub>3</sub> and CH<sub>3</sub>O groups of  $2a^{2+}$  underwent H/D exchange and substitution, respectively, by CD<sub>3</sub>OD (Scheme 1). The rate of the H/D exchange was faster than substitution by CD<sub>3</sub>OD, and the H/D exchange reaction was greatly enhanced in D<sub>2</sub>O, since the Ru–CCH<sub>3</sub> signal ( $\delta$  2.78) disappeared after 5 min in the <sup>1</sup>H NMR spectrum of  $2a^{2+}$  in (CD<sub>3</sub>)<sub>2</sub>CO/D<sub>2</sub>O (10:1 v/v). On the other hand, treatment of [2a](PF<sub>6</sub>)<sub>2</sub> with an equiv. amount of aqueous NaOH in CD<sub>2</sub>Cl<sub>2</sub> caused the appearance of new signals at  $\delta$  4.96 and 2.99, and  $\delta$  92.5 in the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra, respectively, and the proton and carbon signals of the Ru–CCH<sub>3</sub> group of  $2a^{2+}$  completely disappeared. The addition of 1 equiv. of HPF<sub>6</sub> to the solution regenerated the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of  $2a^{2+}$ . Such complete recovery of  $2a^{2+}$  in the cycle of the acid–base treatments without producing CH<sub>3</sub>OH is indicative of the reversible conversion between the carbene complex  $2a^{2+}$  and the vinyl complex  $3^+$  without opening the five-membered metallacycle (Scheme 1).

The carbene complex  $2a^{2+}$  is probably formed *via* a Ru–vinylidene intermediate formed by the reaction of  $1^{2+}$  with HCCC(O)OH, though it is not clear whether the decarboxylation takes place before or after the formation of the Ru–vinylidene framework. Although vinylidene complexes react with alcohols to produce a variety of alkoxy–alkyl carbene complexes, the  $\alpha$ -carbon of the carbene moiety of  $2a^{2+}$  linked exclusively with the non-bonded nitrogen of napy in MeOH. Such novel N–C bond formation must be assisted by the attachment of the CH<sub>3</sub>O<sup>−</sup> group at the 2-position of the napy ligand, since intra-molecular attack of the non-bonded nitrogen

of napy to the carbonyl carbon of [Ru(bpy)<sub>2</sub>(napy- $\kappa$ N)(CO)]<sup>2+</sup> is initiated by the ligand localized one-electron reduction.

## Notes and references

† *Spectroscopic data* for [2a](PF<sub>6</sub>)<sub>2</sub>·CH<sub>3</sub>CN: <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN):  $\delta$  8.52–6.33 (m, 22H, aromatic H), 2.84 (s, 3H, OCH<sub>3</sub>), 2.68 (s, 3H, CCH<sub>3</sub>). <sup>13</sup>C NMR (270 MHz, CD<sub>3</sub>CN):  $\delta$  293.6 (Ru=CCH<sub>3</sub>), 157.5–119.0 (aromatic C), 82.8 (OCH<sub>3</sub>), 50.2 (Ru=CCH<sub>3</sub>). IR (KBr): 2252, 1659, 1605 cm<sup>−1</sup>. ESI-MS:  $m/z$  = 301 (M<sup>2+</sup>). Anal. Calcd. for C<sub>33</sub>H<sub>31</sub>N<sub>7</sub>OF<sub>12</sub>P<sub>2</sub>Ru: C, 42.50; H, 3.35; N, 10.51. Found: C, 42.31; H, 3.37; N, 10.39%. [2b](SbF<sub>6</sub>)<sub>2</sub>: <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN):  $\delta$  8.50–6.45 (m, 22H, aromatic H), 3.76 and 3.59 (q, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.69 (s, 3H, CCH<sub>3</sub>), 1.28 (t, 3H, OCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (270 MHz, CD<sub>3</sub>CN):  $\delta$  294.7 (Ru=CCH<sub>3</sub>), 157.3–121.1 (aromatic C), 81.8 (OCH<sub>2</sub>CH<sub>3</sub>), 61.8 (Ru=CCH<sub>3</sub>), 15.4 (OCH<sub>2</sub>CH<sub>3</sub>). IR (KBr): 1653, 1605 cm<sup>−1</sup>. ESI-MS:  $m/z$  = 308 (M<sup>2+</sup>). Anal. Calcd. for C<sub>32</sub>H<sub>30</sub>N<sub>6</sub>OF<sub>12</sub>Sb<sub>2</sub>Ru: C, 35.35; H, 2.78; N, 7.73. Found: C, 35.15; H, 2.90; N, 7.45%. [3](PF<sub>6</sub>): <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  9.12–5.84 (m, 22H, aromatic H), 4.96 and 2.99 (s, 2H, C=CH<sub>2</sub>), 2.54 (s, 3H, OCH<sub>3</sub>). <sup>13</sup>C NMR (270 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  184.6 (C=CH<sub>2</sub>), 157.2–114.6 (aromatic C), 92.5 (C=CH<sub>2</sub>), 79.9 (OCH<sub>3</sub>). ESI-MS:  $m/z$  = 601 (M<sup>+</sup>).

*Crystal data* for [2a](PF<sub>6</sub>)<sub>2</sub>·CH<sub>3</sub>CN: C<sub>33</sub>H<sub>31</sub>F<sub>12</sub>N<sub>7</sub>OP<sub>2</sub>Ru,  $M$  = 932.65, orthorhombic, space group  $Pna2_1$  (no. 33),  $a$  = 12.495(2),  $b$  = 19.134(4),  $c$  = 15.602(3) Å,  $V$  = 3729(1) Å<sup>3</sup>,  $T$  = 296 K,  $Z$  = 4,  $D_c$  = 1.661 g cm<sup>−3</sup>,  $\mu$ (Mo–K $\alpha$ ) = 6.06 cm<sup>−1</sup>, 4889 reflections measured, 4778 unique reflections, 2566 observed reflections [ $I > 3.00\sigma(I)$ ]. Final  $R$  = 0.051 and  $R_w$  = 0.071. CCDC reference number 157684. See <http://www.rsc.org/suppdata/cc/b1/b101045j/> for crystallographic data in .CIF or other electronic format.

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