Unprecedented luminescence behaviour and structural characterization of a novel class of ruthenium(II) 2,2′-bipyridine complexes with orthometallated aminocarbene ligands

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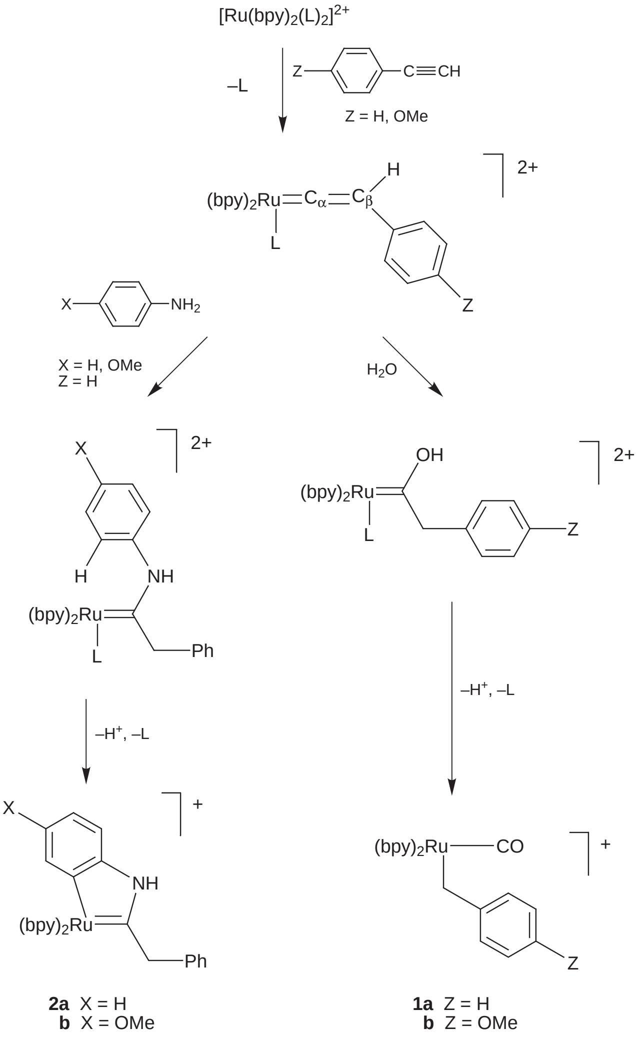
Novel luminescent ruthenium(II) bipyridine complexes with orthometallated aminocarbene ligands have been prepared and their photophysical properties studied.

The chemistry of metal σ-acetylide complexes has attracted considerable interest because of the unique properties of the delocalizable π systems. While most studies on ruthenium σ-acetylide complexes were focused on the use of phosphine ligands,[1] corresponding studies on nitrogen donor ligands are relatively rare.[2] In view of the rich photophysical and photochemical behaviour of ruthenium(II) polypyridyl complexes, we have started a program to design and synthesize luminescent organometallic ruthenium(II) σ-acetylide complexes containing polypyridyl ligands. In an attempt to prepare these complexes, we obtained the novel ruthenium(II) orthometallated aminocarbene complexes instead. Here we report the synthesis, characterization, electrochemistry, photophysical behaviour and X-ray crystal structure of this new class of ruthenium(II) orthometallated aminocarbene complexes with 2,2′-bipyridyl ligands, which represents the first of its kind.

Reaction of *cis*-$[Ru(bpy)_2(Me_2CO)_2](OTf)_2$ with phenylacetylene or 4-methoxyphenylacetylene in the presence of sodium ethoxide in ethanol, followed by metathesis reaction using NH_4PF_6 and subsequent recrystallization from MeCN–Et_2O, afforded *cis*-$[Ru(bpy)_2(CO)(\eta\text{-}CH_2Ph)]^+$ **1a**[3] or *cis*-$[Ru(bpy)_2(CO)(\eta\text{-}CH_2C_6H_4OMe)]^+$ **1b** as the PF_6^- salt in reasonable yield; the structure of **1b** was confirmed by X-ray diffraction studies.[4] On the other hand, treatment of *cis*-$[Ru(bpy)_2(Me_2CO)_2](OTf)_2$ with phenylacetylene in the presence of aniline in dry acetone under an inert atmosphere of nitrogen gave a stable orthometallated aminocarbene complex, $[Ru(bpy)_2{=}C(CH_2Ph)NHC_6H_4]^+$ **2a**. Similar reaction with *p*-anisidine in place of aniline gave $[Ru(bpy)_2{=}C(CH_2Ph)NHC_6H_3OMe]^+$ **2b** (Scheme 1).[5–7] The formulation of which were confirmed by satisfactory elemental analyses, FABMS, ^1H NMR and ^{13}C NMR spectroscopy† and the structure of **3b** was further established by X-ray crystallography (Fig. 1).‡

Complex **2b** shows a distorted octahedral structure. The N–Ru–N bond angles subtended by the chelating diimines are 77.0(2) and 77.6(2)°. A C(1)–Ru(1)–C(2) bond angle of 79.5(3)° subtended by the orthometallated *N*-arylcarbene has also been observed. The deviation from the ideal 90° for a regular octahedral geometry is a result of the steric requirement of the bidentate ligands. The bond angles around C(1) are 128.7(5), 116.9(5) and 114.3(6)°, consistent with the sp^2 hybridization of the carbene carbon. The bond distances of Ru(1)–N(1) [2.060(6) Å] and Ru(1)–N(4) [2.058(6) Å] are similar to those reported in other ruthenium(II) polypyridyl complexes (*ca.* 2.05 Å)[8] but those of Ru(1)–N(2) [2.141(5) Å] and Ru(1)–N(3) [2.120(5) Å] are longer than normal. This may be accounted for by the strong *trans* effect of the carbon atoms in the orthometallated *N*-arylcarbene ligand. The Ru(1)–C(2) bond distance [2.047(6) Å] is similar to that observed in other ruthenium(II) complexes with σ-bonded carbon ligands,[9] while the Ru(1)–C(1) bond distance [1.963(7) Å] is shorter than an average Ru–C bond [2.105(5) Å],[9e] which can be ascribed to the presence of Ru–C double bond character.[9f,10] A substantial double-bond character between the heteroatom and the carbene carbon is noticed as the C(1)–N(5) distance [1.318(9) Å] is reduced below that characteristic of a single bond between N and an sp^2 C, typical of Fischer type aminocarbenes (*ca.* 1.31 Å).[10]

The electronic absorption spectra of complexes **2a** and **2b** show moderately intense bands in the visible region which are tentatively assigned as MLCT transitions (Table 1). The intense absorptions in the UV region are assigned as intraligand



Scheme 1 Synthetic route to orthometallated ruthenium(II) aminocarbene complexes; L = Me_2CO

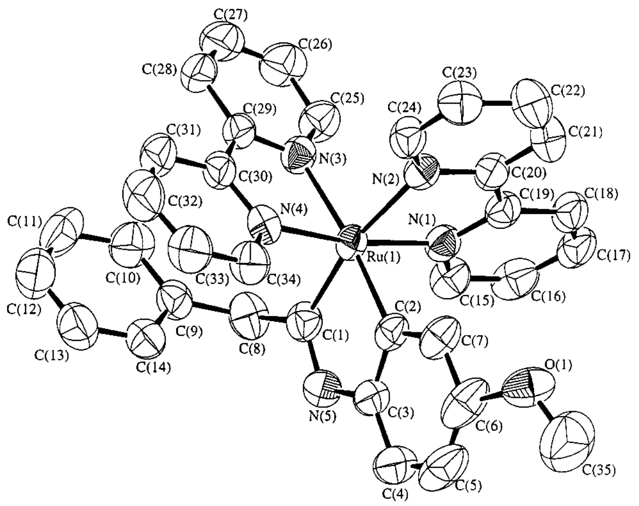


Fig. 1 Perspective drawing of the complex cation **2b** with atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability levels. Selected bond lengths (Å) and angles (°): Ru(1)–N(1) 2.060(6), Ru(1)–N(2) 2.141(5), Ru(1)–N(3) 2.120(5), Ru(1)–N(4) 2.058(6), Ru(1)–C(1) 1.963(7), Ru(1)–C(2) 2.047(6), C(1)–C(8) 1.514(9), C(8)–C(9) 1.519(10), C(1)–N(5) 1.318(9), C(3)–N(5) 1.426(9); N(1)–Ru(1)–N(2) 77.6(2), N(3)–Ru(1)–N(4) 77.0(2), C(1)–Ru(1)–C(2) 79.5(3), Ru(1)–C(1)–C(8) 128.7(5), C(8)–C(1)–N(5) 114.3(6), Ru(1)–C(1)–N(5) 116.9(5).

Table 1 Photophysical data for complexes **2a** and **2b**

Complex	λ_{abs}/nm (ε/dm^3 mol^{-1} cm^{-1})	Medium	T/K	$\lambda_{em}{}^a$/nm	τ_0/μs
2a	250 (37 960), 298 (46 400), 370 (11 630), 484 (6230), 572 (6605)	MeCN	298	808	< 0.1
		Solid	298	775	< 0.1
		Solid	77	704	
		Glass^b	77	742	
2b	250 (37 680), 298 (52 720), 370 (12 645), 482 (6850), 571 (7090)	MeCN	298	813	< 0.1
		Solid	298	767	< 0.1
		Solid	77	701	
		Glass^b	77	745	

^{a} Excitation wavelength at 580 nm. Emission maxima are corrected values. ^{b} EtOH–MeOH (4 : 1, v/v).

transitions. Excitation of **2a** and **2b** at $\lambda > 350$ nm at room temperature produces red luminescence. It is likely that the origin of the emission is ^{3}MLCT in nature, arising from states derived from either a $d_\pi(Ru) \rightarrow \pi^*(bpy)$ or a $d_\pi(Ru) \rightarrow \pi^*(alkylidene)$ MLCT transition. The close similarity of the absorption and emission characteristics of complexes **2a** and **2b** suggests that the methoxy substituent on the *N*-aryl ring of the aminocarbene unit has relatively little influence on the charge-transfer transition in these complexes.

The redox properties of the complexes **2a** and **2b** are investigated by cyclic voltammetry in acetonitrile using 0.1 mol dm^{-3} NBu$_4$PF$_6$ as the supporting electrolyte. Reversible to quasi-reversible reduction couples are observed at -1.66 and -1.89 V *vs.* SCE for **2a** and -1.65 and -1.88 V *vs.* SCE for **2b**; the potentials of which are relatively independent of the scan rate with $\Delta(E_{pa} - E_{pc})$ values of *ca.* 60–90 mV, assigned to the successive reduction of the bipyridine ligand. The relative insensitivity of the reduction potentials to the substituent effect on the aminocarbene unit in **2a** and **2b** further confirms its assignment as bpy-centered reduction. A quasi-reversible oxidation couple is observed at +1.42 V *vs.* SCE for **2b** and an irreversible oxidation wave is noted at $E_{pa} = +1.67$ V *vs.* SCE for **2a**, which are assigned as metal-centered oxidation. The irreversible nature of the oxidation in **2a** is indicative of the instability of the Ru(III) aminocarbene complex in which the electron-rich methoxy substituent capable of stabilizing the electron-deficient Ru(III) metal center is absent, which may lead to its decomposition.

Further spectroscopic studies to elucidate the nature of the lowest lying excited state are in progress.

V. W.-W. Y. acknowledges financial support from the Research Grants Council and The University of Hong Kong. B. W.-K. C. acknowledges the receipt of a postgraduate studentship, administered by The University of Hong Kong.

Notes and References

† **2a**: Elemental analysis: Calc. for **2a** (found) %: C 54.18 (54.22), H 3.85 (3.56), N 9.30 (9.23); positive FABMS: m/z 607 $[M - PF_6]^+$; ^{1}H NMR (300 MHz, CD$_3$CN, 298 K): δ 4.3 (s, 2H, CH$_2$), 6.2–8.3 (m, 25H, aromatic H), 11.2 (s, 1H, NH); ^{13}C NMR (67.8 MHz, CD$_3$CN, 298 K): δ 52.71 (CH$_2$), 113.98–176.58 (aromatic C), 266.01 (Ru=C). **2b** : Elemental analysis: Calc. for **2b** (found) (%): C 57.07 (57.24), H 4.08 (4.08), N 9.51 (9.74); ^{1}H NMR (300 MHz, CD$_3$CN, 298 K): δ 3.5 (s, 3H, OCH$_3$), 4.3 (s, 2H, CH$_2$), 5.8–8.3 (m, 24H, aromatic H), 11.2 (s, 1H, NH); ^{13}C NMR (125.76 MHz, CD$_3$CN, 298 K): δ 53.25 (OCH$_3$), 55.70 (CH$_2$), 105.90–180.09 (aromatic C), 262.70 (Ru=C).

‡ *Crystal data* for **2b** : $\{[C_{35}H_{30}ON_5Ru]^+ClO_4^-\}$, $M_r = 737.18$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.398(4)$, $b = 12.843(4)$, $c = 14.994(4)$ Å, $\alpha = 67.74(3)$, $\beta = 77.36(3)$, $\gamma = 71.07(3)°$, $V = 1574(1)$ Å^3, $Z = 2$, $D_c = 1.555$ g cm^{-3}, μ(Mo-Kα) = 6.35 cm^{-1}, $F(000) = 752$, $T = 301$ K. Convergence for 436 variable parameters by least-squares refinement on F with $w = 4\,F_o{}^2 / \sigma^2(F_o{}^2)$, where $\sigma^2(F_o{}^2) = [\sigma^2(I) + (0.018F_o{}^2)^2]$ for 3911 reflections with $I > 3\sigma(I)$ was reached at $R = 0.049$ and $wR = 0.066$ with a goodness-of-fit of 2.75. CCDC 182/1023.

1 See, for example: P. H. Dixneuf, D. Touchard, P. Haquette, N. Pirio and L. Toupet, *Organometallics*, 1993, **12**, 3132; Z. Atherton, C. W. Faulkner, S. L. Ingham, A. K. Kakkar, M. S. Khan, J. Lewis, N. J. Long and P. R. Raithby, *J. Organomet. Chem.*, 1996, **462**, 265; Y. Sun, N. J. Taylor and A. J. Carty, *J. Organomet. Chem.*, 1992, **423**, C43; G. Jia, J. C. Gallucci, A. L. Rheingold, B. S. Haggerty and D. W. Meek, *Organometallics*, 1991, **10**, 3459.

2 See, for example: Y. Degani and T. Willner, *J. Chem. Soc., Chem. Commun.*, 1985, 648; A. M. Echavarren, J. Lopez, A. Santos, A. Romero, J. A. Hermoso and A. Vegas, *Organometallics*, 1991, **10**, 2371; J. Montoya, A. Santos, J. Lopez, A. M. Echavarren, J. Ros and A. Romero, *J. Organomet. Chem.*, 1992, **426**, 383; T. Rappert and A. Yamamoto, *Organometallics*, 1994, **13**, 4984; M. A. Esteruelas, A. Miguel, F. J. Lahoz, A. M. Lopez, E. Onate and L. A. Oro, *Organometallics*, 1994, **13**, 1669; A. Pedersen, M. Tilset, K. Folting and K. G. Caulton, *Organometallics*, 1995, **14**, 875; C. M. Che, S. M. Yang, M. C. W. Chan, K. K. Cheung and S. M. Peng, *Organometallics*, 1997, **16**, 2819; Y. Zhu, O. Clot, M. O. Wolf and G. P. A. Yap, *J. Am. Chem. Soc.*, 1998, **120**, 1812; A. Klose, E. Solari, C. Floriani, S. Geremia and L. Randaccio, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 148.

3 T. J. Meyer, B. P. Sullivan, R. B. Smythe and E. M. Kober, *J. Am. Chem. Soc.*, 1982, **104**, 4701.

4 V. W. W. Yam and B. W. K. Chu, unpublished work.

5 C. Bianchini, J. A. Casares, M. Peruzzini, A. Romerosa and F. Zanobini, *J. Am. Chem. Soc.*, 1996, **118**, 4585.

6 M. I. Bruce and A. G. Swincer, *Aust. J. Chem.*, 1980, **33**, 1471.

7 M. I. Bruce, in *Comprehensive Organometallic Chemistry*, Pergamon, Oxford, vol. 7, pp. 350.

8 D. Schomburg, S. Neumann and R. Schmutzler, *J. Chem. Soc., Chem. Commun.*, 1979, 848.

9 See, for example: (*a*) R. J. Doedens and J. A. Moreland, *Inorg. Chem.*, 1976, **15**, 2486; (*b*) U. A. Gregory, S. D. Ibekwe, B. T. Kilbourn and D. R. Russell, *J. Chem. Soc. A*, 1971, 1118; (*c*) J. D. Edwards, R. Goddard, S. A. R. Knox, R. J. McKinney, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1975, 828; (*d*) R. J. Sundberg, R. F. Bryan, I. F. Taylor and H. Taube, *J. Am. Chem. Soc.*, 1974, **96**, 381; (*e*) P. B. Hitchcock, M. F. Lappert, P. L. Pye and S. Thomas, *J. Chem. Soc., Dalton Trans.*, 1979, 1929; (*f*) M. F. Lappert, P. B. Hitchcock and P. L. Pye, *J. Chem. Soc., Dalton Trans.*, 1978, 826.

10 F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, 1972, **16**, 487.

Received in Cambridge, UK, 20th July 1998; revised manuscript received 15th Setpember 1998; 8/07281G