

Synthesis and luminescence behaviour of mixed-metal rhenium(I)–copper(I) and –silver(I) alkynyl complexes. X-Ray crystal structures of $[\{\eta^2\text{-Re}(\text{CO})_3(\text{bpy})(\text{C}\equiv\text{CPh})\}_2\text{Cu}]\text{PF}_6$ and $[\{\eta^2\text{-Re}(\text{CO})_3(\text{bpy})(\text{C}\equiv\text{CPh})\}_2\text{Ag}]\text{PF}_6$

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Two mixed-metal rhenium(I)–copper(I) and –silver(I) alkynyl complexes, $[\{\eta^2\text{-Re}(\text{CO})_3(\text{bpy})(\text{C}\equiv\text{CPh})\}_2\text{Cu}]\text{PF}_6$ **1** and $[\{\eta^2\text{-Re}(\text{CO})_3(\text{bpy})(\text{C}\equiv\text{CPh})\}_2\text{Ag}]\text{PF}_6$ **2**, have been synthesized and shown to exhibit rich luminescence behaviour; the X-ray crystal structures of both complexes have also been determined.

There has been a rapidly growing interest in the chemical and physical properties of η^2 -alkynyl-coordinated complexes.^{1,2} Organometallic substituted alkynes $\text{L}_n\text{MC}\equiv\text{CR}^3$ exhibit a rich coordination chemistry with copper(I), silver(I) and gold(I) ions.² To the best of our knowledge, luminescence studies of π -bonded alkynyl complexes are rare^{2f} despite numerous works on the luminescence behaviour of the σ -bonded counterparts have been reported.⁴ With the recent reports on the successful isolation of acetylide-bridged rhenium(I) organometallics^{1a,2b,e,5} and our recent efforts in incorporating metal-to-ligand charge transfer (MLCT) excited states into rhenium(I) acetylide units to make luminescent rigid-rod materials,^{4d,6} we have extended our interest to utilize the luminescent alkynyl rhenium(I) complex, $\text{Re}(\text{CO})_3(\text{bpy})(\text{C}\equiv\text{CPh})$, to function as an η^2 -ligand towards Cu^{I} and Ag^{I} . Herein are reported the synthesis, structure and luminescence behaviour of two mixed-metal rhenium(I)–copper(I) and –silver(I) alkynyl complexes, $[\{\eta^2\text{-Re}(\text{CO})_3(\text{bpy})(\text{C}\equiv\text{CPh})\}_2\text{Cu}]\text{PF}_6$ **1** and $[\{\eta^2\text{-Re}(\text{CO})_3(\text{bpy})(\text{C}\equiv\text{CPh})\}_2\text{Ag}]\text{PF}_6$ **2**.

Reaction of $\text{Re}(\text{CO})_3(\text{bpy})(\text{C}\equiv\text{CPh})$ ^{6c} and $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ in THF at room temperature in an inert atmosphere of nitrogen for 0.5 h afforded $[\{\eta^2\text{-Re}(\text{CO})_3(\text{bpy})(\text{C}\equiv\text{CPh})\}_2\text{Cu}]\text{PF}_6$ **1**, which was isolated as yellow crystals after recrystallization from dichloromethane–*n*-hexane. Similarly, reaction of $\text{Re}(\text{CO})_3(\text{bpy})(\text{C}\equiv\text{CPh})$ and $[\text{Ag}(\text{MeCN})_4]\text{PF}_6$ in THF under similar conditions afforded $[\{\eta^2\text{-Re}(\text{CO})_3(\text{bpy})(\text{C}\equiv\text{CPh})\}_2\text{Ag}]\text{PF}_6$ **2** as yellow crystals. The identities of both have been confirmed by satisfactory ¹H NMR spectroscopy, IR, positive ESI-MS, elemental analyses,[†] and X-ray crystallography.[‡]

Figs. 1 and 2 depict perspective drawings of the complex cations of **1** and **2**, respectively, with atomic numbering. The C≡C bond lengths are in the range 1.20(1)–1.23(1) Å in **1** and 1.199(8)–1.203(8) Å in **2**, which are slightly longer than that of their precursor complex $[\text{Re}(\text{CO})_3(\text{bpy})(\text{C}\equiv\text{CPh})]$ of 1.199(9) Å.^{6c} The bend-back angles (C–C–R) at the coordinated triple bond are 13.1(9)–18.2(9)° in **1** and 13.1(6)–14.4(6)° in **2** which are also larger than that of their precursor complex $[\text{Re}(\text{CO})_3(\text{bpy})(\text{C}\equiv\text{CPh})]$ of 3.7(7)°.^{6c} The interplanar angles between the $\text{MC}\equiv\text{C}$ planes are 98.7 and 96.0° in the two independent molecules of **1** which is close to the expected 90° for a tetrahedrally coordinated Cu^{I} atom, and 149.0° in **2**. In addition, the bond weakening observed by IR spectroscopy of the C≡C triple bonds in **1** and **2** relative to the precursor complex (2083 cm^{−1}) further supports the π coordination mode of the alkynyl group to the d¹⁰ metal centres.

The electronic absorption spectra of **1** and **2** both show an intense absorption band at ca. 396 nm in dichloromethane solution. With reference to previous spectroscopic work on rhenium(I) diimine systems,^{4d,6,7} the intense low energy

absorption in the visible region is tentatively assigned as the $\text{d}_{\pi}(\text{Re}) \rightarrow \pi^*(\text{bpy})$ MLCT transition. The observation of the

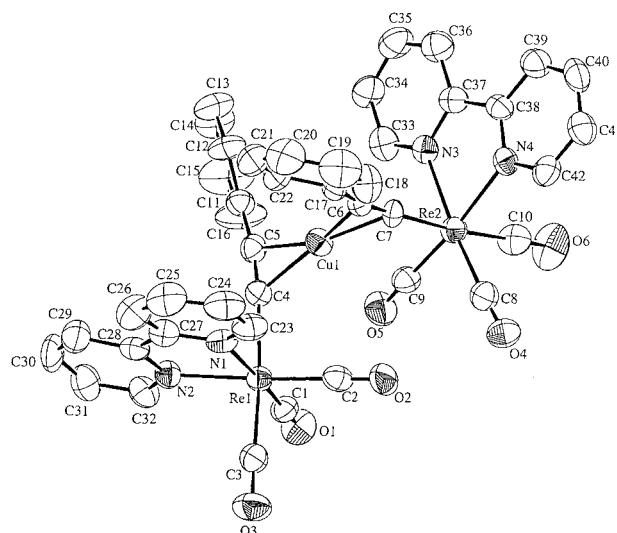


Fig. 1 Perspective drawing of the complex cation of **1** with atomic numbering. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids were shown at the 40% probability level. Selected bond distances (Å) and bond angles (°): Re(1)–C(4) 2.139(8), C(11)–C(5) 1.46(1), C(4)–C(5) 1.23(1), C(4)–Cu(1) 1.997(8), C(5)–Cu(1) 2.093(8), C(6)–Cu(1) 2.076(8), C(7)–Cu(1) 2.004(7), C(6)–C(7) 1.20(1), C(17)–C(6) 1.47(1), Re(2)–C(7) 2.143(8), C(5)–C(4)–Re(1) 171.3(7), C(4)–C(5)–C(11) 166.9(9), C(6)–C(7)–Re(2) 178.4(7), C(7)–C(6)–C(17) 164.9(8).

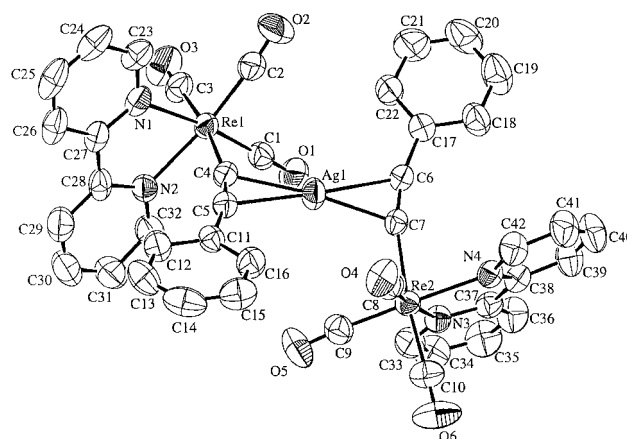


Fig. 2 Perspective drawing of the complex cation of **2** with atomic numbering. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids were shown at the 40% probability level. Selected bond distances (Å) and bond angles (°): Re(1)–C(4) 2.159(6), C(11)–C(5) 1.444(8), C(4)–C(5) 1.203(8), C(4)–Ag(1) 2.257(6), C(5)–Ag(1) 2.378(6), C(6)–Ag(1) 2.382(6), C(7)–Ag(1) 2.244(6), C(6)–C(7) 1.199(8), C(17)–C(6) 1.477(8), Re(2)–C(7) 2.138(6), C(5)–C(4)–Re(1) 166.2(5), C(4)–C(5)–C(11) 166.9(6), C(6)–C(7)–Re(2) 165.9(5), C(7)–C(6)–C(17) 165.6(6).

MLCT absorption band at higher energy than that found in the related $\text{Re}(\text{CO})_3(\text{bpy})(\text{C}\equiv\text{CPh})$ precursor, which absorbs at ca. 420 nm in dichloromethane, is supportive of a lower-lying $d_{\pi}(\text{Re})$ orbital in **1** and **2**, resulted from the weaker π -donating ability of the acetylide ligand upon π -coordination to the d^{10} metal ions.

Excitation of **1** and **2** both in the solid state and in fluid solutions resulted in orange luminescence,[†] with emission lifetimes of 0.18 and 0.16 μs in dichloromethane solutions, respectively, which are attributed to the ³MLCT phosphorescence. Similar to the absorption studies, the close resemblance of the MLCT emission energies of **1** and **2** is suggestive of the similar σ - and π -donating properties of the acetylide ligand upon coordination to Cu^{I} and Ag^{I} . It is also interesting that both **1** and **2** emit at higher energies than their precursor complex, i.e. the emission energies in CH_2Cl_2 follow the order: **1** (590 nm) \cong **2** (600 nm) > $\text{Re}(\text{CO})_3(\text{bpy})(\text{C}\equiv\text{CPh})$ (654 nm).^{6c} The observation of a blue shift in emission energies on going from $\text{Re}(\text{CO})_3(\text{bpy})(\text{C}\equiv\text{CPh})$ to **1** and **2** is in line with the assignment of a ³MLCT [$d_{\pi}(\text{Re}) \rightarrow \pi^*(\text{bpy})$] origin and disfavours the assignment of a ³MLCT [$d_{\pi}(\text{Re}) \rightarrow \pi^*(\text{C}\equiv\text{CPh})$] origin. Such a trend can be rationalized by the fact that the acetylide ligand would become a poorer electron donor upon coordination to Cu^{I} or Ag^{I} , and as a result, the energy of the $\text{Re } d_{\pi}$ orbitals would be lowered, leading to a higher ³MLCT emission energy.

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Notes and references

[†] **1**: ¹H NMR (300 MHz, acetone- d_6 , 298 K, relative to SiMe_4): δ 6.80 (d, 2H, J 7.5 Hz, aryl H *meta* to ethynyl group), 7.15 (m, 3H, aryl H *ortho* and *para* to ethynyl group), 7.70 (t, 2H, J 7.2 Hz, bpy H), 8.30 (t, 2H, J 7.8 Hz, bpy H), 8.60 (d, 2H, J 8.2 Hz, bpy H), 9.15 (d, 2H, J 5.3 Hz, bpy H). IR (Nujol mull, cm^{-1}): 2029, 1999, 1932, 1911 $\nu(\text{C}=\text{O}, \text{C}\equiv\text{C})$. Positive ESI-MS: ion cluster at m/z 1119 $[\text{M}]^+$. UV-VIS [λ/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): CH_2Cl_2 , 246(28160), 288(29000), 396(6050). Emission [λ/nm ($\tau/\mu\text{s}$): CH_2Cl_2 (298 K), 590 (0.18); solid (298 K), 550 (0.35); solid (77 K), 540; EtOH-MeOH glass (4:1 v/v) (77 K), 555. Found: C, 39.07, H, 2.07, N, 4.29. Calc. for $1 \cdot 0.5\text{CH}_2\text{Cl}_2$: C, 39.17; H, 1.94, N, 4.31%. **2**: ¹H NMR (300 MHz, acetone- d_6 , 298 K, relative to SiMe_4): δ 6.80 (d, 2H, J 7.2 Hz, aryl H *meta* to ethynyl group), 7.10 (m, 3H, aryl H *ortho* and *para* to ethynyl group), 7.60 (t, 2H, J 6.5 Hz, bpy H), 8.20 (t, 2H, J 7.4 Hz, bpy H), 8.55 (d, 2H, J 8.1 Hz, bpy H), 9.0 (d, 2H, J 5.5 Hz, bpy H). IR (Nujol mull, cm^{-1}): 2033, 2006, 1921, 1888 $\nu(\text{C}=\text{O}, \text{C}\equiv\text{C})$. Positive ESI-MS: ion cluster at m/z 1163 $[\text{M}]^+$. UV-VIS [λ/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): CH_2Cl_2 , 250(26890), 292(28240), 396(5930). Emission [λ/nm ($\tau/\mu\text{s}$): CH_2Cl_2 (298 K), 600 (0.16); solid (298 K), 535 (<0.1); solid (77 K), 533; EtOH-MeOH glass (4:1 v/v) (77 K), 540. Found: C, 38.53, H, 1.99, N, 4.28. Calc. for **2**: C, 38.44, H, 1.87, N, 4.26%.

[‡] Crystal data for **1**: $[(\text{C}_{42}\text{H}_{26}\text{N}_4\text{O}_6\text{CuRe}_2)^+\text{PF}_6^-\cdot\text{CH}_2\text{Cl}_2]$, $M = 1348.55$, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.806(1)$, $b = 17.408(2)$, $c = 25.199(2)$ Å, $\alpha = 81.432(7)$, $\beta = 82.688(7)$, $\gamma = 88.139(7)^\circ$, $V = 4648(1)$ Å³, $Z = 4$, $D_c = 1.927 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 58.74 \text{ cm}^{-1}$, $F(000) = 2576$, $T = 301 \text{ K}$. One crystallographic asymmetric unit consists of two independent formula units. Convergence for 1111 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.036F_o^2)^2]$ for 10761 reflections with $I > 3\sigma(I)$ was reached at $R = 0.032$ and $wR = 0.045$ with a goodness-of-fit of 1.46. The F atoms in both PF_6 counter ions were refined isotropically.

For **2**: $[(\text{C}_{42}\text{H}_{26}\text{N}_4\text{O}_6\text{AgRe}_2)^+\text{PF}_6^-\cdot(\text{CH}_3)_2\text{CO}]$, $M = 1366.02$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.485(1)$, $b = 13.368(1)$, $c = 17.259(1)$ Å, $\alpha = 102.048(6)$, $\beta = 107.155(6)$, $\gamma = 103.476(6)^\circ$, $V = 2549.8(10)$ Å³, $Z = 2$, $D_c = 1.931 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 56.63 \text{ cm}^{-1}$, $F(000) = 1304$, $T = 301 \text{ K}$. Convergence for 575 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.024F_o^2)^2]$ for 5957 reflections with $I > 3\sigma(I)$ was reached at $R = 0.026$ and $wR = 0.034$ with a goodness-of-fit of 1.33.

CCDC 182/1239. See <http://www.rsc.org/suppdata/cc/1999/1013/> for crystallographic files in .cif format.

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