Synthesis, luminescence and electrochemistry of novel pentanuclear rhenium(I)–copper(I) mixed-metal acetylide complexes. X-Ray crystal structure of $[Cu_3(\mu\text{-dppm})_3\{\mu_3\text{-}\eta^1\text{-C}{\equiv}\text{CC}_6\text{H}_4\text{C}{\equiv}\text{C-}p\text{–Re(bpy)(CO)}_3\}_2]^+$

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A series of luminescent mixed-metal acetylide complexes $[Cu_3(\mu\text{-LL})_3\{\mu_3\text{-}\eta^1\text{-C}{\equiv}\text{C–C}_6\text{H}_2\text{R}_2\text{-2,5–C}{\equiv}\text{C-}p\text{–Re(NN)(CO)}_3\}_2]^+$, (LL = dppm, Pr^{n}PNP; NN = bpy, Bu$^t{}_2$bpy; R = H, Me) have been synthesized and their electrochemical properties studied; the X-ray crystal structure of $[Cu_3(\mu\text{-dppm})_3\{\mu_3\text{-}\eta^1\text{-C}{\equiv}\text{C–C}_6\text{H}_4\text{C}{\equiv}\text{C-}p\text{–Re(bpy)(CO)}_3\}_2]^+$ has also been determined.

The highly conjugated polyynes and their transition metal complexes have attracted enormous attention in recent years owing to their potential technological applications as precursors for non-linear optical materials and rigid-rod molecular wires.[1] With our recent interest in the design and synthesis of luminescent Re^I [2] and Cu^I acetylide complexes,[3] it would be interesting to extend our studies to mixed-metal acetylide complexes using the 'metal complex as ligand' or metalloligand approach.[1c,4] Here, we report the synthesis of a series of Re^{I}Cu^I mixed-metal acetylide complexes (**1**–**5**), $[Cu_3(\mu\text{-LL})_3\{\mu_3\text{-}\eta^1\text{-C}{\equiv}\text{C–C}_6\text{H}_2\text{R}_2\text{-2,5–C}{\equiv}\text{C-}p\text{–Re(NN)(CO)}_3\}_2]^+$, {LL = bis(diphenylphosphino)methane (dppm), bis(diphenylphosphino)-*n*-propylamine (Pr^{n}PNP); NN = 2,2′-bipyridine (bpy), 4,4′-di-*tert*-butyl-2,2′-bipyridine (Bu$^t{}_2$bpy); R = H, Me} with a rigid-rod acetylide backbone employing Re^I acetylide as the metalloligand. We believe that these mixed-metal acetylide complexes would be ideal building blocks for the design of luminescent rigid-rod oligomers.

$[Cu_3(\mu\text{-LL})_3\{\mu_3\text{-}\eta^1\text{-C}{\equiv}\text{C–C}_6\text{H}_2\text{R}_2\text{-2,5–C}{\equiv}\text{C-}p\text{-Re(NN)(CO)}_3\}_2]^+$ {LL = dppm, NN = bpy, R = H (**1**); LL = dppm, NN = bpy, R = Me (**2**); LL = dppm, NN = Bu$^t{}_2$bpy, R = H (**3**); LL = Pr^{n}PNP, NN = bpy, R = H (**4**); LL = Pr^{n}PNP, NN = bpy, R = Me (**5**)} were prepared by reaction of the corresponding $[Cu_2(\mu\text{-LL})_2(\text{MeCN})_2]X_2$ (X = BF$_4$, PF$_6$)[3c,5] with $[\text{Re(NN)(CO)}_3(\text{C}{\equiv}\text{C–C}_6\text{H}_2\text{R}_2\text{-2,5–C}{\equiv}\text{CH-}p)]$[6] in a 3 : 4 molar ratio in the presence of an excess of KOH in CH_2Cl_2–MeOH at room temp. Recrystallization from CH_2Cl_2–Et_2O gave orange crystals of **1**–**5**. Complexes **1**–**5** have been characterized by elemental analyses, ^{1}H NMR, IR and Raman spectroscopy. The X-ray crystal structure of **1** has been determined.‡

Fig. 1 shows a perspective drawing of the complex cation of **1**. It consists of an isosceles triangular array of Cu atoms with a dppm ligand bridging each edge to form a roughly planar Cu_3P_6 core, with two Re acetylide metalloligands capping the triangular Cu^I in a μ_3-η^1 fashion. The bridging mode of the alkynyl group is asymmetric with Cu–C bond distances in the range 2.10(1)–2.34(2) Å. The C≡C bond distances are 1.17(2)–1.23(2) Å, typical of metal–acetylide σ bond.[7] The Cu···Cu separations in the range 2.556(2)–2.674(3) Å, which are shorter than the sum of van der Waals radii for Cu are suggestive of the presence of weak Cu···Cu interactions.

The electronic absorption spectra of **1**–**5** in CH_2Cl_2 show high-energy absorption bands at *ca.* 250–300 nm, tentatively assigned as ligand-localized transitions. Absorptions at *ca.* 348–378 nm appear as vibronically structured bands with vibrational progressional spacings of *ca.* 1350–1500 cm^{-1}, typical of $\nu(\text{C}\overset{\cdot\cdot}{-}\text{C})$ stretching modes of the aromatic ring in the excited state. In addition, a low-energy absorption is observed at *ca.* 440 nm, which is likely to arise from a $[d_\pi(\text{Re}) \rightarrow \pi^*(\text{NN})]$ MLCT transition,[8] since the mononuclear Re^I diimine acetylide complexes $\text{HC}{\equiv}\text{C–C}_6\text{H}_2\text{R}_2\text{-2,5–C}{\equiv}\text{C-}p\text{-Re(NN)(CO)}_3$ (NN = bpy, Bu$^t{}_2$bpy; R = H, Me) absorb in a similar region.[2,6]

Excitation of **1**–**5** in the solid state and in fluid solutions resulted in strong orange luminescence. The photophysical data are summarized in Table 1. All spectra showed a low-energy emission band at *ca.* 600–660 nm. With reference to previous spectroscopic studies on Re^I diimine acetylide systems,[2,6] the low-lying emission band in **1**–**5**, which resembles that of the corresponding mononuclear Re^I diimine acetylide, is assigned as derived from an emissive state of $[d_\pi(\text{Re}) \rightarrow \pi^*(\text{NN})]$ MLCT character. The shift in emission energy upon changing the bipyridine and the acetylide ligands lends further support to the MLCT assignment. A blue shift in energy of the lowest lying emission band of 0.09 eV from **1** to **3** in CH_2Cl_2 is in accord with the higher π* orbital energy of Bu$^t{}_2$bpy than bpy. A similar blue shift in emission energy (0.11 eV) has also been observed

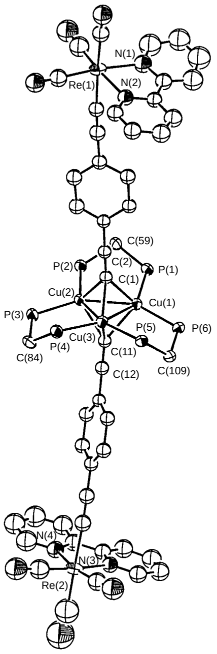

Fig. 1 Perspective drawing of the complex cation of **1** with the atomic numbering scheme. Hydrogen atoms and phenyl rings have been omitted for clarity. Thermal ellipsoids are shown at the 40% probability level. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.20(2), C(11)–C(12) 1.21(2), Cu(1)···Cu(2) 2.556(2), Cu(2)···Cu(3) 2.674(3), Cu(1)···Cu(3) 2.674(3); Cu(1)–Cu(2)–Cu(3) 61.44(7), Cu(2)–Cu(1)–Cu(3) 61.47(7), Cu(1)–Cu(3)–Cu(2) 57.09(6).

Table 1 Photophysical and electrochemical data for complexes **1**–**5**

Complex	Medium (T/K)	λ_{abs}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1})	$\lambda_{em}{}^{a}$/nm (τ_o/μs)	$E_{1/2}{}^{ox,c}$	$E_{1/2}{}^{red,c}$
1	CH_2Cl_2 (298)	262sh (102 600), 300sh (78 400), 354sh (69 300), 372 (77 400), 440sh (5110)	642 (< 0.1)	+0.39	−1.82
	Solid (298)		616 (< 0.1)		
	Solid (77)		605		
2	CH_2Cl_2 (298)	298 (51 800), 360sh (50 700), 378 (53 000), 440sh (4920)	650 (< 0.1)	+0.31	−1.83
	Solid (298)		615 (0.14)		
	Solid (77)		608		
3	CH_2Cl_2 (298)	296 (103 100), 356sh (101 200), 374 (117 000), 440sh (9230)	615 (< 0.1)	+0.33	−1.91
	Solid (298)		613 (0.1)		
	Solid (77)		605		
4	CH_2Cl_2 (298)	276sh (91 800), 292 (94 300), 348sh (95 400), 370 (145 100), 440sh (5310)	660 (< 0.1)	+0.34	−1.90
	Solid (298)		616 (0.12)		
	Solid (77)		623^{b}		
5	CH_2Cl_2 (298)	244sh (23 400), 278sh (41 600), 294 (16 100), 350sh (15 500), 372 (22 100), 440sh (950)	650 (< 0.1)	+0.30	−1.93
	Solid (298)		618 (0.13)		
	Solid (77)		615		

[a] Excitation at 400 nm. [b] Excitation at 510 nm. [c] In MeCN (0.1 M $NBu^n{}_4PF_6$), glassy carbon electrode, scan rate 100 mV s^{-1}, 298 K. $E_{1/2}$ (V *vs.* Fc–Fc$^+$) is taken to be the average of E_{pa} and E_{pc}.

on going from $[Re(bpy)(CO)_3Cl]$[8b] to $[Re(Bu^t{}_2bpy)(CO)_3Cl]$.[2a] A comparison of the emission energies for the complexes with the same Re acetylide but different bidentate phosphine ligands, that is, between **1** and **4** and **2** and **5**, showed that a slight red shift in energy occurred on going from **1** to **4** and **2** to **5**. Such a trend may be rationalized by the fact that the Pr^{n}PNP ligand is more electron rich than dppm, which upon coordination to Cu^I would render the Cu^I-coordinated acetylide more electron rich, which in turn raises the energy of the Re d orbitals, causing a lower energy ^{3}MLCT emission. Similar findings have been reported in Re^I-acetylide and Re^I-alkyl systems.[2,9] On the contrary, an acetylide-to-Cu LMCT origin would predict an opposite trend since a more electron rich diphosphine on Cu^I would lower the electron-accepting ability of Cu, raising its acceptor orbital energy, leading to a higher emission energy. Furthermore, the lifetime in the range of submicroseconds is typical of ^{3}MLCT emission.

The electrochemistry of complexes **1**–**5** has been studied by cyclic voltammetry and the electrochemical data are listed in Table 1. Complexes **1**–**5** in MeCN (0.1 M $NBu^n{}_4PF_6$) show both a quasi-reversible oxidation couple and a quasi-reversible reduction couple. In general, complexes with electron rich ligand are found to be more easily oxidized, with the potential values decreasing for the series with dppm as bridging ligand: **1** > **3** > **2** and the series with Pr^{n}PNP as bridging ligand: **4** > **5**. These trends are consistent with the greater electron richness of the 2,5-dimethyl-1,4-diethynylbenzene than the unsubstituted 1,4-diethynylbenzene and Bu$^t{}_2$bpy than bpy. The oxidation couples are tentatively assigned as the one-electron oxidation of the Cu^I center, with the more electron rich ligands preferentially stabilizing the Cu^{II} center to a larger extent. Oxidation couples at similar potential values have also been observed in the trinuclear Cu^I acetylide systems.[3a–c]

The quasi-reversible reduction couple for **1**–**5** has been assigned as the one-electron reduction couple of bpy ligands[10] on the basis of the similarity of their reduction potential. The greater ease of reduction in **1** and **2** than **3** is in line with the greater π-acceptor ability of bpy than Bu$^t{}_2$bpy.

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Notes and References

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‡ *Crystal data* for **1**: $\{[R\underline{e}_2Cu_3P_6O_6N_4C_{121}H_{90}]^+PF_6{}^-\}$; M_w = 2589.92, triclinic, space group $P1$ (no. 2), a = 19.635(3), b = 22.083(4), c = 14.703(3) Å, α = 92.82(2), β = 102.04(2), γ = 89.06(2)°, U = 6227(2) Å^3, Z = 4, μ(Mo-Kα) = 25.91 cm^{-1}, $F(000)$ = 1352, T = 301 K. Convergence for 1040 variable parameters by least-squares refinement on F with $w = 4\,F_o{}^2/\sigma^2(F_o{}^2)$, where $\sigma^2(F_o{}^2) = [\sigma^2(I) + (0.040F_o{}^2)^2]$ for 10 336 reflections with $I > 3\sigma(I)$ was reached at R = 0.067 and wR = 0.103 with a goodness-of-fit of 2.88. CCDC 182/784.

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