

Synthesis and luminescence behaviour of rhenium(I) diyndyl complexes. X-Ray crystal structures of $[\text{Re}(\text{CO})_3(\text{tBu}_2\text{bpy})(\text{C}\equiv\text{C}-\text{C}\equiv\text{CH})]$ and $[\text{Re}(\text{CO})_3(\text{tBu}_2\text{bpy})(\text{C}\equiv\text{C}-\text{C}\equiv\text{CPh})]$

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Luminescent rhenium(I) diyndyl complexes $[\text{Re}(\text{CO})_3(\text{tBu}_2\text{bpy})(\text{C}\equiv\text{C}-\text{C}\equiv\text{CH})]$ and $[\text{Re}(\text{CO})_3(\text{tBu}_2\text{bpy})(\text{C}\equiv\text{C}-\text{C}\equiv\text{CPh})]$ were synthesized and their photophysical properties studied; the crystal structures have also been determined.

There has been a rapidly growing interest in the chemical and physical properties of C_n -bridged metal-containing materials,¹ in view of their potential applications as nonlinear optical materials, molecular wires, and molecular electronics. With the recent reports on the successful isolation of acetylide-bridged rhenium(I) organometallics^{1a-g,2} 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,³ we have extended our work to employ the diyndyl unit as the ligand to extend the carbon chain. Herein are reported the synthesis, structure and luminescence behaviour of two rhenium(I) diyndyl complexes, $[\text{Re}(\text{CO})_3(\text{tBu}_2\text{bpy})(\text{C}\equiv\text{C}-\text{C}\equiv\text{CH})]$ **1** and $[\text{Re}(\text{CO})_3(\text{tBu}_2\text{bpy})(\text{C}\equiv\text{C}-\text{C}\equiv\text{CPh})]$ **2**.

Reaction of a mixture of $[\text{Re}(\text{CO})_3(\text{tBu}_2\text{bpy})\text{Cl}]$,⁴ K₂CO₃, AgOTf and $\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3$ in a 1 : 1 : 1 : 3 ratio in MeOH under reflux conditions in an inert atmosphere of nitrogen for 24 h afforded $[\text{Re}(\text{CO})_3(\text{tBu}_2\text{bpy})(\text{C}\equiv\text{C}-\text{C}\equiv\text{CH})]$, which was isolated as orange crystals after purification by column chromatography on silica gel using dichloromethane as eluent, followed by recrystallization from dichloromethane–diethyl ether. On the other hand, reaction of a mixture of $[\text{Re}(\text{CO})_3(\text{tBu}_2\text{bpy})\text{Cl}]$, AgOTf, NEt₃ and $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{CH}$ ⁵ in a 1 : 1 : 2 : 1.5 ratio in refluxing THF under nitrogen for 24 h afforded $[\text{Re}(\text{CO})_3(\text{tBu}_2\text{bpy})(\text{C}\equiv\text{C}-\text{C}\equiv\text{CPh})]$. Purification by column chromatography on silica gel using dichloromethane–light petroleum (1 : 1 v/v) as eluent, followed by subsequent recrystallization from dichloromethane–light petroleum yielded $[\text{Re}(\text{CO})_3(\text{tBu}_2\text{bpy})(\text{C}\equiv\text{C}-\text{C}\equiv\text{CPh})]$ as yellow crystals. The identities of both complexes **1** and **2** have been confirmed by satisfactory elemental analyses, ¹H NMR spectroscopy, FAB-MS,[†] and X-ray crystallography.[‡]

Fig. 1 and 2 depict the perspective drawings of complexes **1** and **2** with atomic numbering, respectively. Both structures show a slightly distorted octahedral geometry about Re with the three carbonyl ligands arranged in a facial fashion. The N–Re–N bond angles of 74.6(2) and 73.9(1)° for **1** and **2**, respectively, are less than 90°, as required by the bite distance exerted by the steric demand of the chelating bipyridine ligand. The two C≡C bond lengths are 1.199(10) and 1.19(1) Å for **1** and 1.198(7) and 1.189(7) Å for **2**, which are comparable to those found for diyndyl systems.^{1a,6} The Re–C≡C–C units are essentially linear with bond angles of 175.2(6)–179.8(10) and 175.7(5)–178.6(6)° for **1** and **2**, respectively.

The electronic absorption spectra of **1** and **2** show intense absorption bands at ca. 404 and 416 nm, respectively, in tetrahydrofuran. With reference to previous spectroscopic work on rhenium(I) diimine systems,^{3,4,7} the intense low energy absorption is tentatively assigned as the $d\pi(\text{Re}) \rightarrow \pi^*(\text{tBu}_2\text{bpy})$ MLCT transition. The lower MLCT absorption energy for **2**

than **1** is consistent with the better σ - and π -donating abilities of $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{C}$ than $\text{HC}\equiv\text{C}-\text{C}\equiv\text{C}$,^{1j,8,9} which render the Re(I) centre more electron rich, and raise the Re $d\pi$ orbital energy. Similar trends have been observed in the related alkynyl system $[\text{Re}(\text{CO})_3(\text{tBu}_2\text{bpy})\text{X}]$,³ in which the MLCT absorption band occurs at higher energy for X = HC≡C than when X = PhC≡C.

Excitation of **1** and **2** both in the solid state and in fluid solutions at room temperature at $\lambda > 400$ nm resulted in strong orange luminescence, attributed to the ³MLCT phosphorescence. The excitation spectra of **1** and **2** in THF show excitation bands at ca. 400 nm and 410 nm, respectively, which closely resemble those of the MLCT absorption maxima. The photophysical data are summarized in Table 1. The slightly lower MLCT emission energy of **2** than **1** in THF is in line with the stronger σ - and π -donating abilities of the phenyldiyndyl unit than the butadiyndyl ligand, i.e. $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{C}$ (625 nm) < $\text{HC}\equiv\text{C}-\text{C}\equiv\text{C}$ (620 nm). Similar trends have been observed in the monoacetylide analogues [$\text{PhC}\equiv\text{C}$ (688 nm) < $\text{HC}\equiv\text{C}$ (670 nm)].³ It is interesting to note that both **1** and **2** emit at higher energies than their respective monoacetylide counterparts, i.e. in the $[\text{Re}(\text{CO})_3(\text{tBu}_2\text{bpy})\text{X}]$ system, the emission energies in THF follow the order: $\text{HC}\equiv\text{C}-\text{C}\equiv\text{C}$ (620 nm) > $\text{HC}\equiv\text{C}$ (670 nm); $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{C}$ (625 nm) > $\text{PhC}\equiv\text{C}$ (688 nm). The observation of a blue shift in emission energies upon increasing

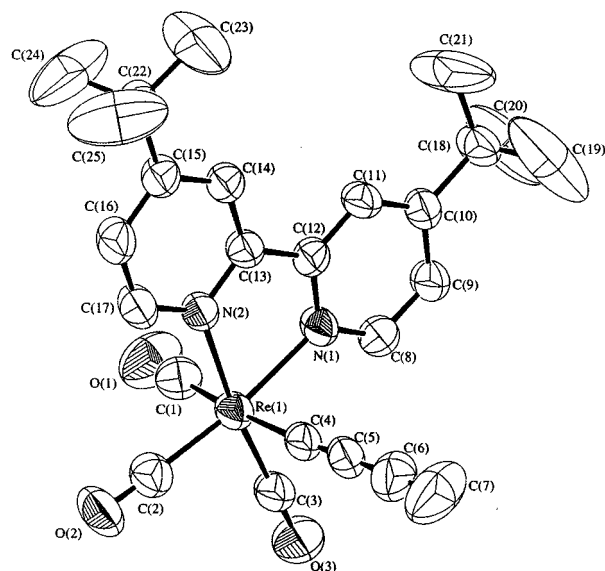


Fig. 1 Perspective drawing of complex **1** with atomic numbering. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond distances (Å) and bond angles (°): Re(1)–C(1) 1.946(9), Re(1)–N(1) 2.168(5), Re(1)–N(2) 2.183(4), Re(1)–C(4) 2.114(8), C(4)–C(5) 1.199(10), C(6)–C(7) 1.19(1), N(1)–Re(1)–N(2) 74.6(2), N(1)–Re(1)–C(2) 171.1(2), C(1)–Re(1)–C(4) 174.4(3), C(4)–C(5)–C(6) 178.3(8), C(5)–C(6)–C(7) 179.8(10).

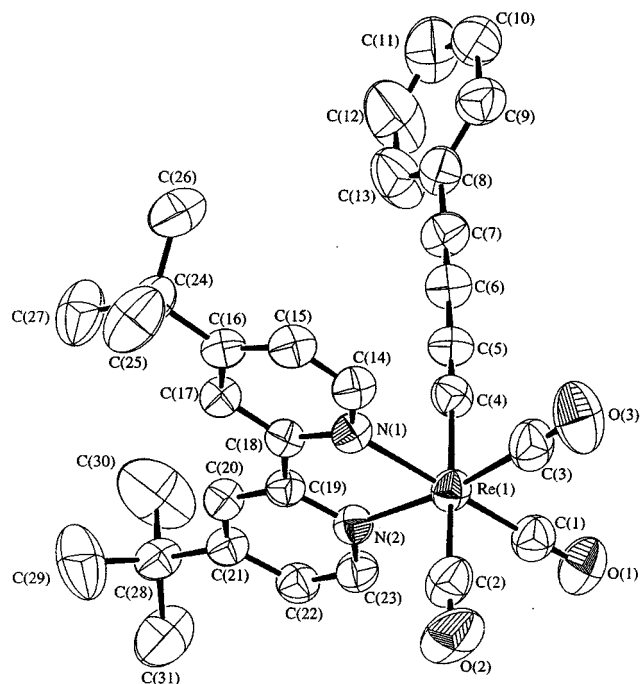


Fig. 2 Perspective drawing of complex **2** with atomic numbering. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids were shown at the 50% probability level. Selected bond distances (Å) and bond angles (°): Re(1)–C(1) 1.913(6), Re(1)–N(1) 2.188(4), Re(1)–N(2) 2.175(4), Re(1)–C(4) 2.126(5), C(4)–C(5) 1.198(7), C(6)–C(7) 1.189(7), N(1)–Re(1)–N(2) 73.9(1), N(1)–Re(1)–C(1) 171.8(2), C(2)–Re(1)–C(4) 176.3(2), C(4)–C(5)–C(6) 177.4(6), C(5)–C(6)–C(7) 178.6(6).

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

Complex	Medium (T/K)	Emission, λ_{em}/nm ($\tau_e/\mu s$)
1	THF (298)	620 (<0.1)
	CH ₂ Cl ₂ (298)	604 (<0.1)
	Solid (298)	565 (<0.1)
	Solid (77)	580
	EtOH–MeOH glass (4 : 1 v/v) (77)	540
2	THF (298)	625 (<0.1)
	Solid (298)	570 (<0.1)
	Solid (77)	570

the C=C unit is in line with the assignment of a ³MLCT [$d\pi(\text{Re}) \rightarrow \pi^*(\text{tBu}_2\text{ppy})$] origin and disfavours the assignment of a ³MLCT [$d\pi(\text{Re}) \rightarrow \pi^*(\text{C}\equiv\text{C}-\text{C}\equiv\text{CR})$] or a metal-perturbed ³IL [$\pi(\text{C}\equiv\text{C}-\text{C}\equiv\text{CR}) \rightarrow \pi^*(\text{C}\equiv\text{C}-\text{C}\equiv\text{CR})$] origin. Given the similar σ -donating properties of the monoacetylide versus the diyanyl unit,⁹ the much better π -accepting ability of RC≡C–C≡C than RC≡C would become the dominating factor, stabilizing the Re $d\pi$ orbitals to a greater extent, and hence give rise to a higher energy ³MLCT emission.

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

Notes and References

† **1**: ¹H NMR (300 MHz, acetone-*d*₆, 298 K, relative to TMS): δ 1.40 (s, 18H, ^tBu), 1.75 (s, 1H, C≡CH), 7.70 (dd, 2H, 5- and 5'-pyridyl Hs), 8.60 (d, 2H, 3- and 3'-pyridyl Hs), 8.80 (d, 2H, 6- and 6'-pyridyl Hs). Positive FAB-MS: ion clusters at m/z 588 {M}⁺, 560 {M – CO}⁺, 539 {M – [C≡C–C≡CH]}⁺. UV–VIS [λ/nm ($\epsilon/dm^3\text{mol}^{-1}\text{cm}^{-1}$): THF, 248(16410), 284(17130), 404(3470); CH₂Cl₂, 310(6100), 396(2690). Elemental analyses. Found: C 50.44, H 4.31, N 4.31. Calc. for 1·0.5H₂O: C 50.29, H 4.36, N 4.69%. ¹H NMR (300 MHz, acetone-*d*₆, 298 K, relative to TMS): δ 1.50 (s, 18H, ^tBu), 7.25 (s, 5H, Ph Hs), 7.80 (dd, 2H, 5- and 5'-pyridyl Hs), 8.70 (d, 2H, 3- and 3'-pyridyl Hs), 8.90 (d, 2H, 6- and 6'-pyridyl Hs). Positive FAB-MS: ion clusters at m/z 665 {M}⁺, 636 {M – CO}⁺, 539 {M – [C≡C–C≡CPh]}⁺. UV–VIS [λ/nm ($\epsilon/dm^3\text{mol}^{-1}\text{cm}^{-1}$): THF, 298(48570), 340(14610), 416(3220).

‡ **Crystal data for 1**: [C₂₅H₂₅O₃N₂Re], $M = 587.69$, monoclinic, space group $P2_1/n$ (no. 14), $a = 11.273(3)$, $b = 12.748(1)$, $c = 17.168(2)$ Å, $\beta = 97.60(4)^\circ$, $V = 2445.7(7)$ Å³, $Z = 4$, $D_c = 1.596$ g cm^{–3}, $\mu(\text{Mo-K}\alpha) = 49.97$ cm^{–1}, $F(000) = 1152$, $T = 301$ K. Convergence for 280 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.025F_o^2)^2]$ for 2847 reflections with $I > 3\sigma(I)$ was reached at $R = 0.028$ and $wR = 0.034$ with a goodness-of-fit of 1.22. For **2**: [C₃₁H₂₉O₃N₂Re], $M = 663.79$, monoclinic, space group $P2_1/c$ (no. 14), $a = 11.048(2)$, $b = 11.795(2)$, $c = 21.935(3)$ Å, $\beta = 94.23(2)^\circ$, $V = 2859.9(7)$ Å³, $Z = 4$, $D_c = 1.542$ g cm^{–3}, $\mu(\text{Mo-K}\alpha) = 42.83$ cm^{–1}, $F(000) = 1312$, $T = 301$ K. Convergence for 334 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.030F_o^2)^2]$ for 3876 reflections with $I > 3\sigma(I)$ was reached at $R = 0.031$ and $wR = 0.040$ with a goodness-of-fit of 1.40. CCDC 182/995.

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Received in Cambridge, UK, 23rd June 1998; 8/04775H