

# Molecular rods based on a ruthenium(II) macrocyclic bis(acetylide) building block†

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Received (in Cambridge, UK) 4th April 2000, Accepted 22nd May 2000

Published on the Web 20th June 2000

The prototype of an organometallic linear-rod building block incorporating the saturated  $\sigma$ -donating 16-TMC macrocycle, peripheral pyridine moieties for versatile ligation, and the  $\pi$ -conjugated *trans*-[Ru(C $\equiv$ Cpy-4)<sub>2</sub>] fragment along the molecular axis, is described and applied to the assembly of trimetallic arrays.

The development of molecular rods and wires<sup>1,2</sup> has gained importance in view of their potential applications in the emerging fields of molecular-scale electronics and devices.<sup>3</sup> An attractive pursuit in this area is the design of rigid building blocks with readily tuneable electronic, steric and photophysical characteristics.<sup>4</sup> In this context, we became interested in metal-acetylide units as components in organometallic supermolecules. The unique nature of the M–C $\equiv$ CR interaction allows delocalisation of electron density in principle and has been harnessed in several active areas of material science,<sup>5</sup> but reports of supramolecular metal-acetylide systems are relatively sparse.<sup>6</sup>

We present the bis( $\sigma$ -pyridylacetylide) derivative *trans*-Ru(16-TMC)(C $\equiv$ Cpy-4)<sub>2</sub> (**Ru**, 16-TMC = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane) as a supramolecular bridging module for multinuclear rod-like assemblies.<sup>7</sup> The unique combination of properties that has been incorporated into the design of the neutral complex **Ru** include: (a) enhanced  $d_{\pi}(\text{Ru}) \rightarrow \pi^*(\text{C}\equiv\text{Cpy})$  back-bonding due to the saturated  $\sigma$ -donating 16-TMC amine ligand, as observed for the arylacetylide analogues;<sup>8</sup> (b) versatile coordination to adjacent units by the pendant pyridine moieties, to yield multicomponent systems with well-defined structures; (c) the electronic effect conferred upon **Ru** by the 16-TMC macrocycle and the  $\pi$ -overlapping Ru–C $\equiv$ Cpy interaction can afford anisotropic properties.

Reaction of a methanolic solution of [Ru(16-TMC)Cl<sub>2</sub>]Cl with zinc amalgam, sodium methoxide and 4-ethynylpyridine yielded **Ru** as a yellow crystalline solid.† We suggest that the sterically bulky nature of the 16-TMC ligand leads to preferential ligation of acetylide groups at the Ru(II) centre rather than pyridyl moieties. Treatment of **Ru** with two equivalents of [Re(N–N)(CO)<sub>3</sub>(MeCN)]OTf (OTf = CF<sub>3</sub>SO<sub>3</sub>) under reflux in THF afforded the trimetallic complexes [{Re(N–N)(CO)<sub>3</sub>]<sub>2</sub>{ $\mu$ -(4-pyC $\equiv$ C)<sub>2</sub>Ru(16-TMC)}](OTf)<sub>2</sub> (<sup>a</sup>-**Re<sub>2</sub>Ru**, see Fig. 1) as dark red solids in moderate yields (50–60%).‡ These derivatives are thermally stable > 200 °C (e.g. decomposition occurs at 220–222 °C for **Ru**; 207–210 °C for <sup>b</sup>-**Re<sub>2</sub>Ru**).

The IR spectrum of **Ru** displays an intense band at 1990 cm<sup>-1</sup> for the asymmetric C $\equiv$ C stretch. This value is slightly lower than that for the arylacetylide congeners (2002–2012 cm<sup>-1</sup>),<sup>8</sup> and is one of the lowest ever reported for a simple metal bis( $\sigma$ -acetylide) derivative.<sup>5</sup> The strongly electron-donating nature of 16-TMC is apparent, resulting in improved  $\pi$  back-bonding from the electron-rich Ru(II) core. The  $\nu_{\text{as}}(\text{C}\equiv\text{C})$  values

for <sup>a</sup>-**Re<sub>2</sub>Ru** are shifted to 2028–2030 cm<sup>-1</sup> upon coordination of Re(I) centres at the pyridyl sites. The FT Raman spectra of the trimetallic complexes show a symmetric C $\equiv$ C stretch at 2010–2024 cm<sup>-1</sup>. The electro spray mass spectra for <sup>a</sup>-**Re<sub>2</sub>Ru** are all dominated by two clusters of signals, the intensities of which correspond to the calculated isotope patterns of the [M]<sup>2+</sup> (peaks separated by 0.5 u) and [M + OTf]<sup>+</sup> species respectively. The <sup>13</sup>C NMR resonance for the  $\alpha$ -acetylide carbon in <sup>a</sup>-**Re<sub>2</sub>Ru** (assigned by <sup>1</sup>H–<sup>13</sup>C COSY, DEPT-135 and by comparison with precursors) appears at  $\delta$  155.4–156.7. This downfield shift compared to related Ru  $\sigma$ -acetylide complexes<sup>5,7</sup> again indicates strong ruthenium-to-acetylide  $\pi$  back-bonding. The cyclic voltammograms for **Ru** and <sup>a</sup>-**Re<sub>2</sub>Ru** all exhibit a well-defined reversible/quasi-reversible couple at –0.28 to –0.40 V vs. Cp<sub>2</sub>Fe<sup>0/+</sup> ( $\Delta E_p$  50–130 mV), which is assigned to the Ru(III/II) couple.

While numerous multinuclear molecular rods have been described, structural elucidations are rarely provided. X-Ray crystallographic analyses have been performed on **Ru** and <sup>a</sup>-**Re<sub>2</sub>Ru**·Et<sub>2</sub>O,<sup>§</sup> and their molecular structures are shown in Fig. 2. The metal atoms in **Ru** and <sup>a</sup>-**Re<sub>2</sub>Ru** all reside in distorted octahedral environments. The salient features of these structures are their linearity along the molecular axis and the coplanarity of the pyridine ring systems. The former illustrates the potential application of **Ru** as a linear rigid-rod motif, while the latter implies that the  $\pi$  orbitals within the *trans*-[Ru(C $\equiv$ Cpy-4)<sub>2</sub>] fragment are able to undergo favourable overlap in the crystal lattice. For <sup>a</sup>-**Re<sub>2</sub>Ru**, a facial arrangement of the carbonyl ligands is observed, while the end-to-end Re...Re distance is 19.1 Å. The Ru–C [**Ru**: 2.065(7) Å, <sup>a</sup>-**Re<sub>2</sub>Ru**: 2.040(10) Å] and C $\equiv$ C [**Ru**: 1.201(1) Å, <sup>a</sup>-**Re<sub>2</sub>Ru**: 1.207(13) Å] bond lengths are comparable to those reported for related Ru(II)  $\sigma$ -acetylide<sup>5</sup> and  $\sigma$ -pyridylacetylide<sup>7</sup> derivatives.

The UV-Vis absorption spectrum of **Ru** in dichloromethane (Fig. 3) contains an intense absorption band at  $\lambda_{\text{max}}$  430 nm ( $\epsilon = 4.7 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ). Because the saturated 16-TMC ligand is optically transparent in the UV-Vis spectral region, this absorption is assigned to a  $d_{\pi}(\text{Ru}) \rightarrow \pi^*(\text{C}\equiv\text{Cpy})$  metal-to-ligand charge transfer (MLCT) transition. The trimetallic derivatives <sup>a</sup>-**Re<sub>2</sub>Ru** display characteristic UV-Vis absorptions at  $\lambda_{\text{max}}$  355–430 (sh,  $\epsilon \approx 1 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) and 516 ( $\epsilon \approx 7 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) nm (Fig. 3 for <sup>a</sup>-**Re<sub>2</sub>Ru**). With

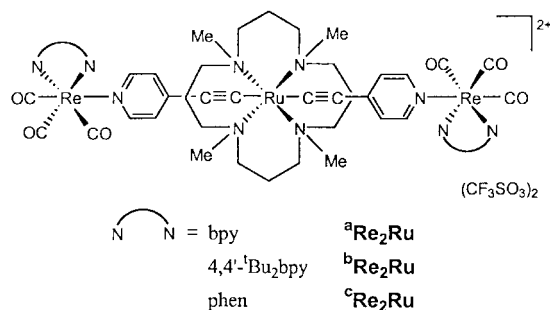
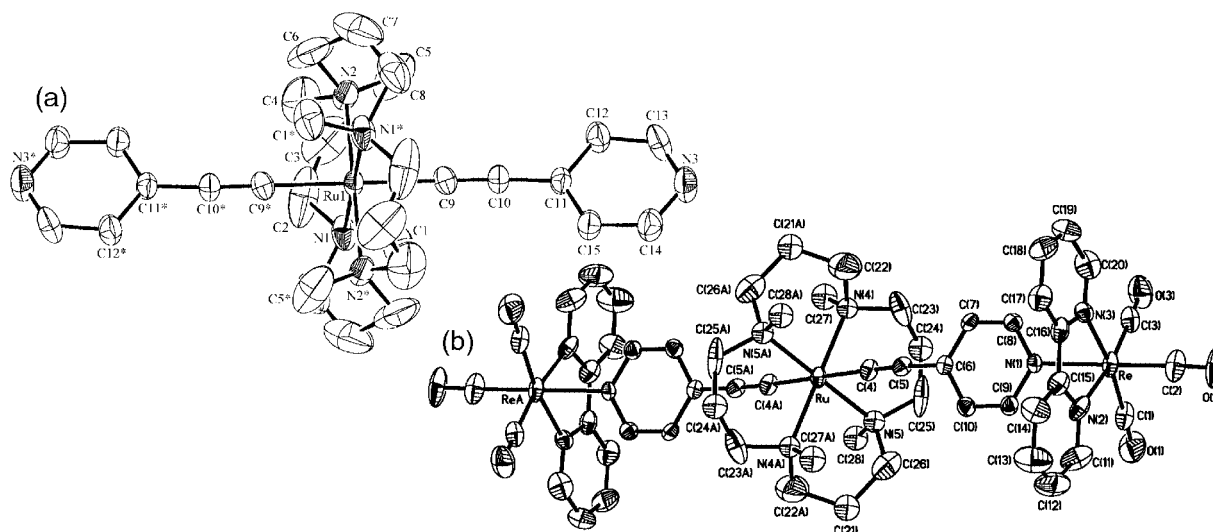
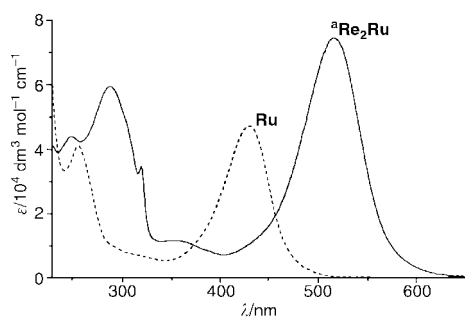


Fig. 1

† Electronic supplementary information (ESI) available: experimental details, characterisation details. See <http://www.rsc.org/suppdata/cc/b0/b002674n/>



**Fig. 2** (a) Perspective view of **Ru** (40% probability ellipsoids). Selected bond distances (Å) and angles (°): Ru–N(1) 2.249(6), Ru–N(2) 2.292(6), Ru–C(9) 2.065(7), C(9)–C(10) 1.20(1), C(10)–C(11) 1.43(1); N(1)–Ru–C(9) 92.0(3), Ru–C(9)–C(10) 173.5(7), C(9)–C(10)–C(11) 174.1(9). (b) Perspective view of cation in **a-Re<sub>2</sub>Ru-Et<sub>2</sub>O** (30% probability ellipsoids). Selected bond distances (Å) and angles (°): Ru–N(4) 2.28(2), Ru–C(4) 2.040(10), C(4)–C(5) 1.207(13), C(5)–C(6) 1.410(13), Re–N(1) 2.208(7); N(4)–Ru–C(4) 88.0(5), Ru–C(4)–C(5) 174.0(9), C(4)–C(5)–C(6) 172.9(11).



**Fig. 3** UV-Vis absorption spectra of **Ru** ( $\text{CH}_2\text{Cl}_2$ ) and **a-Re<sub>2</sub>Ru** ( $\text{CH}_3\text{CN}$ ) at 298 K.

reference to previous spectroscopic studies on rhenium(i) diimine systems,<sup>9</sup> the former are attributed to  $d_{\pi}(\text{Re}) \rightarrow \pi^*(\text{diimine})$  MLCT transitions. The highly intense 516 nm absorption band is tentatively assigned to be  $d_{\pi}(\text{Ru}) \rightarrow \pi^*(\text{C}\equiv\text{Cpy})$  MLCT in nature. The observed red shift from **Ru** is in accordance with the Lewis acidity of the pyridine-bound Re(i) centres. Furthermore, the identical  $\lambda_{\text{max}}$  value of this band for **a-c-Re<sub>2</sub>Ru** suggests that the transition concerned contains negligible contribution from the different diimine ligands. Complex **Ru** is non-emissive in solution or solid states. While  $[\text{Re}(\text{diimine})(\text{CO})_3(\text{py})]^+$  complexes are known to exhibit a long-lived  $\text{Re} \rightarrow \pi^*(\text{diimine})$  MLCT excited state in solution at room temperature, this photoluminescence is quenched in the trinuclear arrays **a-c-Re<sub>2</sub>Ru**. A possible mechanism for the quenching process involves fast inter-component energy transfer ( $\text{Re}^{\text{I}}-\text{Ru}^{\text{II}}-\text{Re}^{\text{I}} \rightarrow \text{Re}^{\text{I}}-\text{Ru}^{\text{II*}}-\text{Re}^{\text{I}}$ ), leading to a non-radiative  $\text{Ru} \rightarrow \pi^*(\text{C}\equiv\text{Cpy})$  charge transfer excited state.<sup>10</sup>

We are grateful for financial support from The University of Hong Kong and the Research Grants Council of the Hong Kong SAR, China [HKU 501/96P]. We thank Prof. K. Y. Wong for assistance in electrochemical measurements.

## Notes and references

† Satisfactory elemental analyses were obtained for all new complexes. Detailed characterisation is provided in the electronic supplementary information.

§ *Crystal data for Ru*:  $\text{C}_{30}\text{H}_{44}\text{N}_6\text{Ru}$ ,  $M = 589.79$ , monoclinic,  $P2_1/c$ ,  $a = 8.763(2)$ ,  $b = 10.534(2)$ ,  $c = 15.243(2)$  Å,  $\beta = 97.31(2)^\circ$ ,  $V = 1395.6(5)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.403$  g cm<sup>-3</sup>,  $\mu = 5.92$  cm<sup>-1</sup>,  $T = 301$  K. A total of 2741 unique reflections ( $R_{\text{int}} = 0.074$ ) was collected on a MAR diffractometer ( $2\theta_{\text{max}} = 56^\circ$ ). The structure was solved by direct methods and refined by

least-squares treatment on  $F^2$  using the TeXsan program:  $R = 0.064$ ,  $wR = 0.078$  for 1530 reflections with  $I > 3\sigma(I)$  and 169 parameters. For **a-Re<sub>2</sub>Ru-Et<sub>2</sub>O**:  $\text{C}_{62}\text{H}_{70}\text{F}_6\text{N}_{10}\text{O}_{13}\text{Re}_2\text{RuS}_2$ ,  $M = 1814.89$ , triclinic,  $P\bar{1}$ ,  $a = 8.3284(2)$ ,  $b = 10.5843(3)$ ,  $c = 20.8961(5)$  Å,  $\alpha = 84.370(1)$ ,  $\beta = 84.973(1)$ ,  $\gamma = 88.998(1)^\circ$ ,  $V = 1826.0(1)$  Å<sup>3</sup>,  $Z = 1$ ,  $D_c = 1.650$  g cm<sup>-3</sup>,  $\mu = 3.65$  mm<sup>-1</sup>,  $T = 295$  K. A total of 7455 unique reflections ( $R_{\text{int}} = 0.097$ ) were collected on a Siemens SMART CCD diffractometer ( $\omega$  scans,  $2\theta_{\text{max}} = 53^\circ$ ). The structure was solved by direct methods and refined by least-squares treatment on  $F^2$  using the SHELXL-93 program (the 16-TMC ligand is disordered, with major and minor occupancies of 0.6:0.4 respectively for positions rotated by  $45^\circ$ ):  $R = 0.065$ ,  $wR = 0.133$  for 4349 absorption-corrected (SADABS, transmission 0.379–0.648) reflections with  $I > 2\sigma(I)$  and 416 parameters.

CCDC 182/1600. See <http://www.rsc.org/suppdata/cc/b0/b002674n/> for crystallographic files in .cif format.

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