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Diruthenium σ-alkynyl complexes as potential building blocks for heterometallic molecular rods †

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Diruthenium(III) bis(σ-pyridylacetylide) complexes can be utilized for axially connecting to monometallic organometallic units in order to construct heterobimetallic building blocks for molecular rods; the synthesis and characterization of an exemplary rhenium–diruthenium–rhenium complex is described, which is stable to air, moisture and a broad variety of organic solvents and which displays electron delocalisation along the propagation axis.

The development of molecular rods and wires has attracted considerable attention due to their potential applications in the emerging fields of molecular electronics and devices.[1,2] Particularly, oligomers and polymers containing metal–metal bonds in the backbone may display novel optical and magnetic properties.[3,4] In principle two methods exist to connect the metal–metal subunits to oligomers or polymers.[3] The M–M axis associated with the M–M bond can be perpendicular[5] or parallel[6] to the propagating axis. The bridging ligands used to date in the axial position of M–M bonds are essentially organic compounds[5,6] while derivatives containing organometallic spacing groups are rare.[7] However, the use of organometallic bridges between metal–metal units enlarges the variety of accessible compounds significantly and may combine polymers containing bimetallic metal units with polymers containing solely monometallic building blocks. The drawback of building blocks for macromolecules of this type reported before was that they only contained M–M–N units which were relatively labile, since axial M–M–N interactions are usually comparatively weak.[7] Here we report on complexes with stable M–M–C interactions as building blocks for heterobimetallic oligomers. The concept of attaching axial organometallic groups to M–M units by means of M–M–C bonds has, to the best of our knowledge, not yet been used to combine bimetallic and monometallic building blocks within one molecular rod.[3,6,7]

Treatment of $Ru_2(form)_4Cl$ (form = *N*,*N′*-di-*p*-tolylformamidinate ion) or $Ru_2(dpf)_4Cl$ (dpf = *N*,*N′*-diphenylformamidinate ion) with an excess of lithiated 4-ethynylpyridine in THF yields **1** and **2**, respectively (see ESI). † Both complexes are soluble in common organic solvents. Formation of the diruthenium(III) bis(σ-pyridylacetylide) complexes was established by elemental analysis, FAB-mass- and IR-spectrometry. The stretching frequencies of the C≡C bonds are located at 2064 and 2097 cm^{-1} for complex **1**, 2062 and 2099 cm^{-1} for complex **2**, which is consistent with the bent configuration of the axial pyridylacetylide ligands. Reaction of compound **1** with two equivalents of $Re(CO)_3(t\text{-}Bu_2bipy)(MeCN)(CF_3SO_3)$ [t-Bu_2bipy = 4,4′-bis(*tert*-butyl)-2,2′-bipyridine] in THF afforded the tetrametallic complexes **3** as dark brown solid (Scheme 1). ‡ The ν_{as} (C≡C) values for **3** are slightly shifted to 2067 and 2092 cm^{-1} due to the coordination of Re(I) centres at the pyridyl N donor atoms. There are two main clusters of signals in the electrospray mass spectrum, which correspond to the calculated isotope patterns of the $[M]^{2+}$ (peaks separated by 0.5 atom mass units) and $[M + OTf]^+$ species respectively.

The UV-Vis absorption spectrum of **1** in dichloromethane (Fig. 1) contains three absorption bands at 504, 553 and 996 nm.

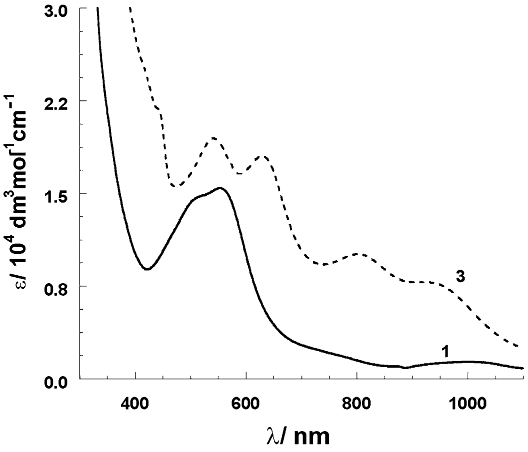

Fig. 1 UV-Vis absorption spectra of complexes **1** and **3** (in CH_2Cl_2) at 298 K.

The intense peak at 553 nm might be assigned to the σ(RuC) to δ*(Ru_2) transition. The peak at 996 nm may be due to the π(Ru_2) to π*(RuN) transition in analogy to related cases mentioned in the literature.[8] The peak at around 504 nm is tentatively assigned as the LMCT (Ligand to Metal Charge Transfer) from π(N–C–N) to the δ*(Ru_2) transition.[8] The tetranuclear complex **3** displays four very intense absorption bands at 546, 630, 805 and 955 nm. A band at a lower energy cannot be clearly observed, probably due to overlapping with the intense peak at 955 nm. Due to the lack of proper MO calculations, a precise assignment of the observed bands in complex **3** is currently not possible. The higher number of peaks may be the result of a splitting of the original peaks due to electronic coupling across the bridges between the metal centres.

An essential feature for a building block of molecular wires is the ability to function as an electron reservoir and to undergo reversibly both oxidation and reduction.[1–3] This is clearly the case for the new building block **1**, as revealed in the cyclic voltammograms (Fig. 2). Cyclic voltammetry measurements on **1** and **3** were performed in 0.1 M NBu_4PF_6 in CH_2Cl_2, potentials are quoted *vs.* the ferrocene–ferrocenium couple as an internal standard. Complex **1** undergoes two reversible one-electron reductions at $E_{1/2} = -1.304$ V (Ru_2^{5+}/Ru_2^{4+}) and -0.982 V (Ru_2^{6+}/Ru_2^{5+}) and a reversible one-electron oxidation at 0.157 V (Ru_2^{7+}/Ru_2^{6+}) *vs.* $Cp_2Fe^{0/+}$. Similar to the case of previously reported related diruthenium compounds,[8–10] four oxidation states (Ru_2^{7+}, Ru_2^{6+}, Ru_2^{5+} and Ru_2^{4+}) are in principle possible for complex **1**. For complex **3**, the two reversible one-electron reductions are observed at $E_{1/2} = -1.753$ V (Ru_2^{5+}/Ru_2^{4+}) and -0.889 V (Ru_2^{6+}/Ru_2^{5+}) *vs.* $Cp_2Fe^{0/+}$. By comparing

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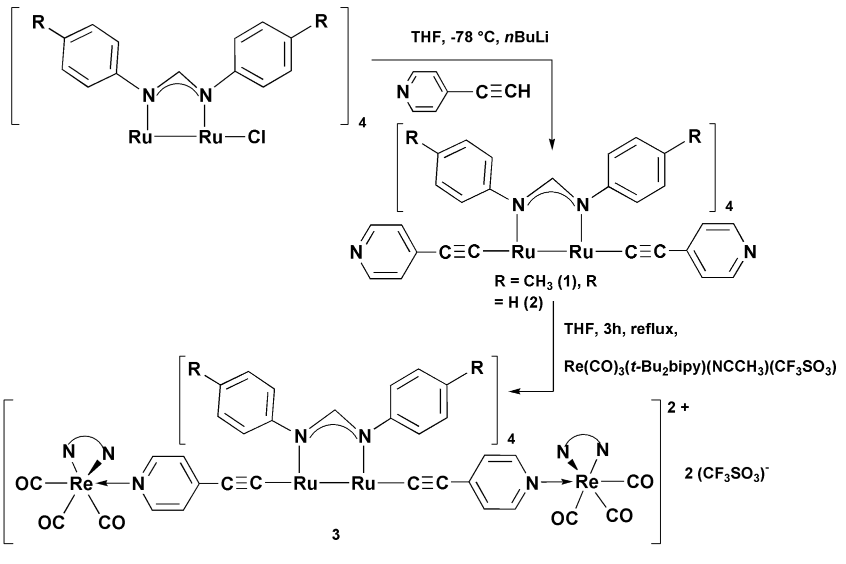
† Electronic supplementary information (ESI) available: synthesis and characterization data for **1** and **2**. See http://www.rsc.org/suppdata/dt/b1/b111068n/



3

Scheme 1

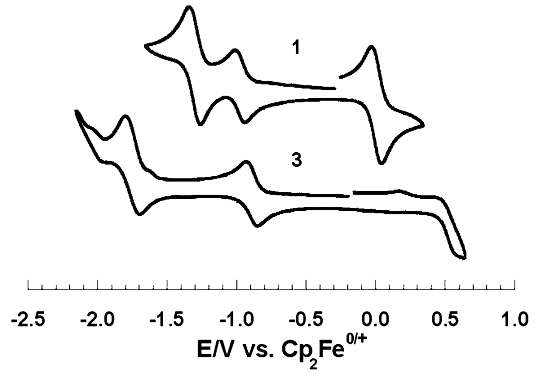


Fig. 2 Cyclic voltammograms of **1** and **3** (scan rate 250 mV s^{-1}) in CH_2Cl_2, 0.1 M NBu_4PF_6 at 298 K.

the potentials of the Ru_2^{5+}/Ru_2^{4+} couples, a shift of −0.449 V from **1** to **3** is noted, while the Ru_2^{6+}/Ru_2^{5+} couple is shifted only 0.093 V. The latter shift can be attributed to the influence of the two cations coordinated to the axial ligands whose presence make a one electron reduction of the Ru_2^{6+} core slightly easier. However, the pronounced shift of the Ru_2^{5+}/Ru_2^{4+} is clearly caused by another factor. This shift reflects an increased stabilization of the higher oxidation state of the Ru_2-core. The enlarged gap between the Ru_2^{6+}/Ru_2^{5+} and Ru_2^{5+}/Ru_2^{4+} couples in complex **3** (0.863 V) compared to complex **1** (0.322 V) can be very likely attributed to a pronounced delocalisation of electrons in the tetranuclear complex **3** which stabilizes the Ru_2^{5+} state.

The structure of complex **3** was confirmed by X-ray crystallography,§ and an ORTEP style illustration of the molecule is shown in Fig. 3. The asymmetric unit consists of one half of **3** related to the other half *via* a crystallographic two-fold axis. The Ru–Ru distance [2.5666(4) Å] indicates a comparatively weak bonding interaction between two ruthenium centres and is slightly longer than that in $Ru_2(dpf)_4(C{\equiv}CPh)_2$ [2.556(1) Å][9] and $Ru_2[(p\text{-}ClC_6H_4)NCHN(p\text{-}ClC_6H_4)]_4(C{\equiv}CPh)_2$ [2.5554(12) Å].[8] The strong axial interaction from the pyridylacetylide ions results in the energy of the σ(Ru–Ru) orbital being above that of the π* orbital and thus giving a ground-state electronic configuration of $\pi^4\delta^2\pi^{*4}$.[4,11] This may be the reason for the Ru–Ru single bonds in these complexes and their diamagnetic behaviour. The Ru–C, C≡C and Re–N distances are 1.961(4), 1.204(6) and 2.207(3) Å, respectively. The axial pyridylacetylides are bent away from the Ru–Ru vector to yield a Ru–Ru–C angle of 161.12(10)°. Two inequivalent Ru–N bonds and Ru–Ru–N angles are observed, implying structural distortion of the bridging ligand.

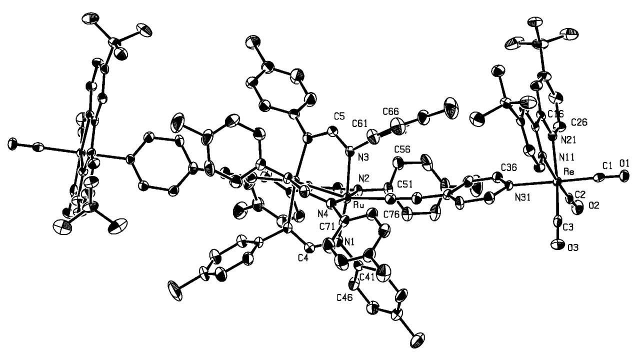


Fig. 3 PLATON drawing of complex **3** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. For selected bond distances and angles see text.

In conclusion, complexes of the type described here allow, in principle, the combination of different mono- and bi-metallic building blocks for the construction of molecular rods and wires. Both mono- and bi-metallic subunits can be straightforwardly attached to the axial coordination sites of the Ru_2(III,III) core units described here. Electrochemical examinations indicate electronic delocalisation within tetranuclear subunits. Work to combine different bimetallic subunits in one molecular chain is currently under way in our laboratory.

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Notes and references

‡ A solution of compound **1** (130.0 mg, 0.10 mmol) and $Re(CO)_3(t\text{-}Bu_2bipy)(MeCN)(CF_3SO_3)$[12] (145.0 mg, 0.20 mmol) in THF (20 ml) was refluxed in the dark for 3 h. The reaction mixture was then cooled to room temperature and the residue was dissolved in CH_2Cl_2 and chromatographed on neutral Al_2O_3, eluting with CH_2Cl_2–MeOH (100 : 1) to yield the dark brown solid **3** (160.5 mg, 60%). Single crystals suitable for structure determination were obtained by slowly diffusing Et_2O into a CH_2Cl_2 solution of the complex. IR (KBr, cm^{-1}) 2092, 2067, 2029, 1917, 1601, 1262, 638. δ_H (CD_2Cl_2, 400 MHz) 1.51 [s, 36H, $C(CH_3)_3$], 2.06 (s, 24H, CH_3), 6.59 (d, 16H, form), 6.81 (d, 16H, form), 6.85 (d, 4H, py), 7.64 (d, 4H, py), 7.69 (m, 4H, *t*-Bu_2bipy), 8.09 (d, 4H, *t*-Bu_2bipy), 8.78 (s, 4H, NCHN), 8.86 (d, 4H, *t*-Bu_2bipy). δ_C ($CDCl_3$, 100.6 MHz) 20.8, 30.2, 36.3, 119.6, 120.3, 123.4–128.9 (m), 135.2, 149.7, 152.0, 152.7, 152.9, 156.0, 166.6, 168.8, 169.0. Anal. calc. for

$C_{118}H_{116}N_{14}F_6O_{12}S_2Re_2Ru_2$: C, 52.98, H; 4.37; N, 7.33. Found C, 53.16; H, 4.60; N, 7.20%.

§ Crystal data for **3**: $C_{122}H_{126}F_6N_{14}O_{13}Re_2Ru_2S_2$, M = 2749.08, monoclinic, space group $C2/c$, a = 48.4644(4), b = 11.4260(1), c = 23.0519(2) Å, β = 108.2667(7)°, V = 12121.8(2) Å^3; Z = 4; ρ_{calc} = 1.506 g cm^{-3}, F_{000} = 5536, μ(Mo-Kα) = 2.344 mm^{-1}, T = 123(1) K. 86734 data were collected on a Nonius KappaCCD device at the window of a rotating anode. Of a total of 49714 reflections integrated, 10698 were independent (R_{int} = 0.043). The structure was solved by direct methods and refined by full-matrix least squares on F^2. Final $R1$ = 0.0292 [$I > 2\sigma(I)$] and $wR2$ = 0.0634 (all data). A solvent molecule, diethyl ether, is disordered (50 : 50) over two positions.

CCDC reference number 173272. See http://www.rsc.org/suppdata/dt/b1/b111068n/ for crystallographic data in CIF or other electronic format.

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