Facile electronic communication between bimetallic termini bridged by elemental carbon chains

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Rich electrochemistry and strong electronic couplings across the carbon bridges are revealed for compounds composed of two tetra(μ-*N*,*N*′-2-anilinopyridinate)diruthenium(II,III) termini bridged by either butadiynediyl (1) or ethynediyl (2) ligands.

The proposal of constructing molecular wires from linear arrays of covalently-linked metal-complexes (M) and elemental carbon chain (C_m) has been inspired by the pioneering work of Nast[1] and Hagihara.[2] Extensive electronic delocalization along the $-(\mathrm{M}-\mathrm{C}_m)_\infty-$ backbone holds the promise for new generation electronic and optoelectronic materials.[3] Much of the work during this decade has focused on the $\mathrm{M-C}_m\mathrm{-M}$ type molecular compounds.[4,5] The degree of delocalization between two equivalent termini M is gauged by the comproportionation constant K_{com} for the following equilibrium:

$$[\mathrm{M}-\mathrm{C}_m-\mathrm{M}]+[\mathrm{M}-\mathrm{C}_m-\mathrm{M}]^{2+} \overset{K_{\mathrm{com}}}{\rightleftharpoons} 2[\mathrm{M}-\mathrm{C}_m-\mathrm{M}]^{+} \qquad (1)$$

K_{com} ($= \exp\{F[E_{1/2}(2+/1+)-E_{1/2}(1+/0)]/RT\}$) can be computed from the electrode potentials $E_{1/2}(2+/1+)$ and $E_{1/2}(1+/0)$.[6] Significant delocalization along the C_m-bridge (K_{com} *ca.* 10^8–10^{12}) has been achieved with termini of CpFe(P–P),[7] CpRe(P)(NO),[8] CpRu(P)$_2$[9] and Mn(P–P)$_2$I[10] (P and P–P are mono- and bi-dentate phosphines, respectively), all mononuclear transition metal complexes. We report the first examples of capping elemental carbon chains (C_2 and C_4) with a bimetallic terminus, $[\mathrm{Ru_2}(\mu\text{-ap})_4]^+$ (ap = 2-anilinopyridinate), which is the valence-averaged (not mix-valence!) diruthenium species with a 2.5 Ru–Ru bond order.[11,12]

It has been established that the mono-capped complexes [Ru$_2$](C≡CR) (**3**) with R as Ph, H (**3a**), SiMe$_3$ (**3a**) and CH$_2$OCH$_3$ (**3c**) can be obtained from the transmetalation reaction between [Ru$_2$]Cl and LiC≡CR.[12,13] Similarly, treating [Ru$_2$]Cl with either 0.5 equiv. of LiC≡CC≡CLi or 1 equiv. of LiC≡CLi yields **1** and **2**, respectively.† Formulation of (C≡C)$_n$-bridged dimers was established by both the elemental analysis and FAB-mass spectrometry.† Further confirmation of (C≡C)$_n$-bridging structural motif is provided by an X-ray diffraction study of molecule **1**.‡ Asymmetric unit of the crystal **1** contains the halves of two independent molecules, and each is related to the other half *via* a crystallographic inversion center. Metric parameters of the two independent molecules are very similar, and the structural plot of one of them is presented in Fig. 1, where a linear array formed by the bridging C$_4$-chain and two [Ru$_2$] termini is clear.

$$[\mathrm{Ru_2}]\!-\!\left(\!\equiv\!\right)_n\!-\![\mathrm{Ru_2}] \qquad \mathbf{1}\ n = 2;\ \mathbf{2}\ n = 1$$

$$[\mathrm{Ru_2}]\!-\!\!\equiv\!\!-\mathrm{R} \qquad \mathbf{3}\ [\mathrm{Ru_2}] = [\mathrm{Ru_2(ap)_4}]^+$$

Compared with [Ru$_2$](C≡CSiMe$_3$) (**3b**),[13] the ‘half’ molecule of **1**, the coordination geometry of the 2-anilionopyridinates around the Ru$_2$ core in **1** is essentially unchanged as evidenced by the averaged Ru(II)–N and Ru(III)–N bond lengths 2.050 and 2.095 Å in **1**, and 2.046 and 2.096 Å in **3b**. Room temperature effective magnetic moments of **1** and **2** are respectively 4.2 and 3.8 μ_B per [Ru$_2$], indicating a $S = 3/2$ ground state that has been observed for many Ru$_2$(II,III) compounds including **3** and [Ru$_2$]Cl.[11–13] Hence, the termini of both **1** and **2** are globally isoelectronic with **3** and [Ru$_2$]Cl. Some small but notable differences, however, do exist between **1** and **3b**: the Ru–Ru (2.331(2) Å) and $\mathrm{C}_\alpha{\equiv}\mathrm{C}_\beta$ (1.258(16) Å) distances in **1** are elongated from that of **3b** (2.3162(5) and 1.207(6) Å), while the Ru–C$_\alpha$ distance is shortened (2.047(14) Å in **1** and 2.077(4) Å in **3b**). The C_β–$\mathrm{C}_\beta{}'$ (≡C–C≡) distance, 1.33(2) Å, is identical to that found for the highly delocalized [Mn(dmpe)$_2$I]$_2$(μ-C$_4$),[10] but shorter than 1.367[9] Å found for *trans*-[Pt(PPh$_3$)$_2$Cl]$_2$(μ-C$_8$), a molecule lacking delocalization.[14] Although barely significant, all these changes are consistent with the strengthening of the Ru–C π interaction and concurrent weakening of the π(C≡C) bond. The valence structure of the [Ru$_2$]$_2$(μ-C$_4$) backbone may contain a significant contribution of cumulenic resonance structure **B** in addition to the predominant resonance structure **A** depicting the localized carbon–carbon triple bonds.

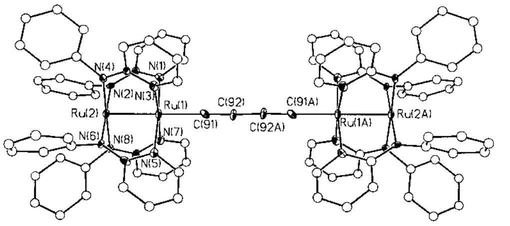

Fig. 1 ORTEP of **1** at 20% probability level. Selected bond lengths and angles: Ru(1)–C(91), 2.047(14) Å; C(91)–C(92), 1.258(16) Å; C(92)–C(92A), 1.33(2) Å; Ru(1)–Ru(2), 2.3311(15) Å; Ru(2)–Ru(1)–C(91), 179.5(4)°; Ru(1)–C(91)–C(92), 177.8(12)°; C(91)–C(92)–C(92A), 176.1(19)°.

$$\underset{\mathbf{A}}{\mathrm{Ru_2}\!-\!\left(\mathrm{C{\equiv}C}\right)_n\!-\!\mathrm{Ru_2}} \longleftrightarrow \underset{\mathbf{B}}{\mathrm{Ru_2}{=}\left(\mathrm{C{=}C}\right)_n{=}\mathrm{Ru_2}}$$

Cyclic voltammograms (CV) of **3** indicate two quasireversible redox processes (CV for **3a** shown in Fig. 2): an oxidation (**3a**$^+$/**3a**) around 462 mV and a reduction (**3a**/**3a**$^-$) around −873 mV and an irreversible couple at more positive potential (*ca.* 1300 mV). Upon a change from simple axial coordination of C≡CR to (C≡C)$_n$-bridge, both **1** and **2** undergo four quasireversible and one irreversible one-electron redox processes between −1600 and +1200 mV (Fig. 2). Therefore, there are six accessible oxidation states in both molecules **1** and **2**, surpassing the record of five established for [CpRu(P)$_2$]$_2$(μ-C$_4$).[9]

Based on the established electrochemistry of **3**,[13] the quasireversible redox couples in both **1** and **2** can be unambiguously assigned as:

$$[\mathrm{Ru_2}]_2^{2-} \overset{\mathrm{I}}{\rightleftharpoons} [\mathrm{Ru_2}]_2^{-} \overset{\mathrm{II}}{\rightleftharpoons} [\mathrm{Ru_2}]_2 \overset{\mathrm{III}}{\rightleftharpoons} [\mathrm{Ru_2}]_2^{+} \overset{\mathrm{IV}}{\rightleftharpoons} [\mathrm{Ru_2}]_2^{2+}$$

Redox couples I and II correspond to the one electron reduction couple in **3**, and III and IV correspond to the oxidation couple in **3**. $\Delta E_{1/2}$(II/I) and $\Delta E_{1/2}$(IV/III), the differences in electrode

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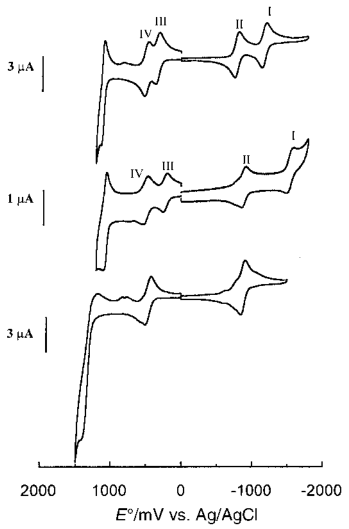

Fig. 2 Cyclic voltammograms of compounds **1**, **2** and **3a** recorded at a scan rate of 100 mV/s in 0.20 M $(Bu^n)_4NPF_6$ solution (THF, N_2-degassed) on a BAS CV-100W voltammetric analyzer with a glassy carbon working electrode, a Pt-wire auxiliary electrodes, and a Ag/AgCl reference electrode.

potentials, are respectively 389 and 157 mV in **1**, and 667 and 285 mV in **2**, which are undoubtedly the result of strong electronic coupling between two $[Ru_2]$ termini mediated by the $(C\equiv C)_n$-bridges. Corresponding comproportionation constants K_{com}(red) and K_{com}(ox) are 3.8×10^6 and 506 for **1**, and 1.9×10^{11} and 6.6×10^4 for **2**, and K_{com}(red) for **2** is comparable to the largest K_{com} determined for other $(C\equiv C)_n$-bridged complexes with CpFe(P–P) (1.6×10^{12}),[7] CpRe(P)(NO) (1.1×10^9),[8] $CpRu(P)_2$ (1.5×10^{11}),[9] and $Mn(P\text{–}P)_2I$ (5.4×10^{10})[10] termini. Distance-dependence of the coupling is evident: K_{com} of C_4-bridged **1** is several orders of magnitude smaller than that of C_2-bridged **2**. Furthermore, K_{com}(red) is much larger than K_{com}(ox) in the same molecule, indicating that the Ru–C π-bonding is much stronger in the reduced form than in the oxidized form. Both linear and square arrays of bimetallic units covalently linked by dicarboxylates have been reported recently,[15] and K_{com} as high as 1.3×10^{12} was determined for $[W_2(O_2C^tBu)_3]_2(\mu\text{-oxalate})$.

Effect of electronic delocalization over the C_m-bridge is also evident from the UV–VIS–NIR spectra (Fig. 3). The 'half' molecule **3a** absorbs strongly at 465 (**A**) and 745 nm (**B**), which may be respectively attributed to σ(Ru–C) to $\delta^*(Ru_2)$ and $\pi(Ru_2)$ to π*(Ru–N) transitions in analogy to the case of $Ru_2(O_2CR)_4Cl$.[16] Upon establishing the C_m bridge, each band is 'split' into two intensified bands (A1 and A2; B1 and B2), and the emergence of bands A2 and B2 accounts for the color change from the dark green for all $Ru_2(ap)_4(C\equiv CR)$ species[12,13] to the dark blue and red–purple colors for **1** and **2**, respectively. Clearly, the strong electronic coupling across the C_m bridge results in a significant orbital mixing between two $[Ru_2]$ termini. The energy splitting of either the ground state or the excited state due to the mixing is sufficiently large that each of transitions **A** and **B** evolves into two bands.

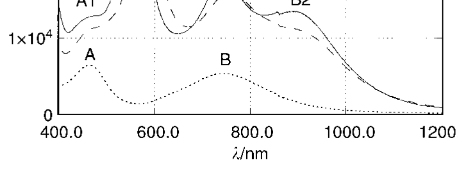

Fig. 3 UV–VIS spectra of compounds **1** (dash), **2** (solid) and **3a** (dot) recorded in THF.

The unprecedented number of accessible oxidation states in a C_m-bridged complex discovered for **1** and **2** clearly demonstrates the advantage of using bimetallic units as terminal electron reservoirs in constructing molecular conductors. The presence of multiple reversible redox couples in **1** and **2** may furthermore allow access to both the anionic (*e.g.* $\mathbf{1}^-$ and $\mathbf{1}^{2-}$) and cationic derivatives ($\mathbf{1}^+$ and $\mathbf{1}^{2+}$). Isolations of these derivatives and the analogs with longer C_m bridges are being explored in our laboratory.

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Notes and references

† **1** and **2** were obtained by treating $Ru_2(ap)_4Cl$ with either LiCCCCLi (0.6 equiv.) or LiCCLi (1 equiv.) in THF at room temperature for 12 h under argon. After the mixture was washed with brine, the solvent was removed from the organic layer to yield a purple solid. Residual starting material was removed *via* rinsing with CH_2Cl_2 till the washings became colorless. Recrystallization in THF yield dark purple microcrystalline solids (53% for **1** and 42% for **2**). Compound **1**: Anal. for $C_{92}H_{72}N_{16}Ru_4$, Found (calcd.): C, 61.24 (61.18); H, 4.06 (4.02); N, 12.37(12.41); MS-FAB (*m/z*, based on ^{101}Ru): 1808 [M^+]. UV–VIS in THF λ, nm (ε/M^{-1} cm^{-1}): 467(sh), 578(31 900), 757(16 100), 910(sh). CV data ($E_{1/2}$(mV)/ΔE_p(mV)/i_{pa}/i_{pc})): I, −1173/61/0.94; II, −784/64/1.10; III, 334/59/1.65; IV, 491/63/0.66; third oxidation, 1115/71/4.72. Compound **2**: Anal. for $C_{90}H_{72}N_{16}Ru_4$, Found (calcd.): C, 60.64 (60.66); H, 4.05 (4.07); N, 12.35 (12.58). MS-FAB (*m/z*, based on ^{101}Ru): 1784 [M^+]. UV–VIS in THF λ, nm (ε/M^{-1} cm^{-1}): 465(sh), 558(33 000), 743(17 900), 892(13 500). Cyclic voltammetry data ($E_{1/2}$(mV)/ΔE_p(mV)/(i_{pa}/i_{pc})): I, −1555/75/1.97; II, −888/57/1.142; III, 223/58/1.22; IV, 508/78/1.45; third oxidation, 1079/63/5.40.

‡ *Crystal data* for $\mathbf{1}\cdot 8H_2O$: $C_{92}H_{88}N_{16}O_8Ru_4$, M = 1933.94, triclinic, $P\bar{1}$, a = 10.0838(17), b = 20.023(3), c = 22.504(4) Å, α = 95.518(3), β = 95.250(3), γ = 93.827(4)°, U = 4490.7(13) Å^3, Z = 2, μ(MoKα) = 0.723 mm^{-1}, T = 300 K, 19970 reflections measured, 12401 unique (R_{int} = 0.0696), final $R1$ = 0.075, $wR2$ = 0.159. CCDC 182/1662. See http://www.rsc.org/suppdata/cc/b0/b002777o/ for crystallographic files in .cif fomat.

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