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Five oxidation states in metal-bonded C_4 chains

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The 36-electron diruthenium buta-1,3-diynyl complexes $[Ru]C{\equiv}C{-}C{\equiv}C[Ru]$ $[Ru = Ru(PPh_3)_2Cp$ and $Ru(PMe_3)(PPh_3)Cp]$ undergo four stepwise one-electron oxidation – reduction processes by cyclic voltammetry; some of the oxidised complexes have also been prepared by chemical oxidation.

The study of compounds in which a linear, unsaturated chain of carbon atoms bridges two transition metal centres, $[ML_n]-C_x-[M'L_m]$, is a rapidly developing area in organometallic chemistry and materials science.[1] One feature of interest arises from the range of possible oxidation states and ligand environments for the metal centres, which may allow the stabilisation of unusual allotropes of carbon in the bridge. Recent reports have described the oxidations of $\{M\}_2(\mu\text{-}C_4)$ [M = Re(NO)(PPh$_3$)Cp* **1**,[2] Fe(dppe)Cp* **2**[3]] to mono- and di-cations. It is not clear to what extent this oxidation processes are governed by the nature of the metal centre and the bridging groups. The ready accessibility of Ru^{IV}, compared with Fe^{IV}, suggested that Ru species related to **2** would repay study. In this communication we report the results of electrochemical studies on the binuclear ruthenium diynyl compounds $\{Ru(PPh_3)(L)Cp\}_2(\mu\text{-}C_4)$ (L = PPh$_3$ **3**, PMe$_3$ **4**) which have given access to an unprecedented series of *five* oxidation states.

Complex **3**[4] is conveniently obtained (70% yield) from the reaction of $RuCl(PPh_3)_2Cp$ with $SiMe_3C{\equiv}CC{\equiv}CSiMe_3$ in the presence of KF. The cyclic voltammogram (CV) of **3** (Figure 1*a*) shows four waves at $E^0 = -0.23$, $+0.41$, $+1.03$ and $+1.68$ V [*versus* standard calomel electrode (SCE)]. The first three are due to reversible, diffusion-controlled, one-electron processes, whilst the fourth is an irreversible one-electron process (Figure 1*a*). Phosphine exchange of PMe$_3$ with **3** gave $\{Ru(PMe_3)(PPh_3)Cp\}_2(\mu\text{-}C_4)$ **4**.† Complex **4** also displays a four-wave CV [$E^0 = -0.26$, $+0.33$, $+0.97$ and $+1.46$ V] (Figure 1*b*). As expected, the presence of the more electron-donating PMe$_3$ ligand results in **4** being more readily oxidised than **3**. The irreversible fourth wave is also seen more clearly in the CV of **4**.

In accord with the electrochemical results, the chemical oxidation of **3** with AgPF$_6$ (1 equiv.) gave deep green $[\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C_4)][PF_6]$ (**3**·PF$_6$) in high yield.† The dark blue dication $[\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C_4)][PF_6]_2$ (**3**·[PF$_6$]$_2$)† was prepared either by oxidation of **3**·PF$_6$ with a further equiv. of AgPF$_6$, or directly from **3** with 2.5 equiv. AgPF$_6$. Complex **3**·PF$_6$ is paramagnetic, only broad resonances being found in its ^{1}H NMR spectrum. The CV of **3**·PF$_6$ is completely analogous to that of **3**.

Compounds of the type M – L – M, where the metal centres (M) are linked by a conducting bridge (L), may undergo several distinct oxidation – reduction steps. The separation of the potentials is determined by the extent of the interaction between the metals.[5] The four-peak voltammograms for both **3** and **4** are consistent with sequential formal oxidation of the metal centres from $[Ru^{II}/Ru^{II}]$ through $[Ru^{II}/Ru^{III}]$, $[Ru^{III}/Ru^{III}]$ and $[Ru^{III}/Ru^{IV}]$ to $[Ru^{IV}/Ru^{IV}]$. The stabilities of the mixed valence species are shown by the comproportionation constants, K_c,[6] as these cations can only exist if the equilibrium

$$[\{Ru^{n}\}(\mu\text{-}C_4)\{Ru^{n}\}]^{m+} + [\{Ru^{n+1}\}(\mu\text{-}C_4)\{Ru^{n+1}\}]^{(m+2)+} \rightleftharpoons [\{Ru^{n}\}(\mu\text{-}C_4)\{Ru^{n+1}\}]^{(m+1)+}$$

n, $n+1$ = formal oxidation numbers

lies well to the right. The large K_c values calculated for $\mathbf{3}^+$ (1.5×10^{11}), $\mathbf{3}^{3+}$ (1.5×10^{11}), $\mathbf{4}^+$ (2.1×10^{10}) and $\mathbf{4}^{3+}$ (2.7×10^{8})‡ are comparable with those reported for the cation $\mathbf{1}^+$ (3×10^{8})[2] and $\mathbf{2}^+$ (1.6×10^{12}),[3] and indicate the high thermodynamic stabilities of these formally mixed-valence compounds.

The large ΔE^0 values observed in the CV's of **3** and **4** (between 0.49 and 0.65 V) show that there are strong electronic interactions between the ruthenium centres in a

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† All isolated complexes had satisfactory analyses. Selected spectroscopic data follow.

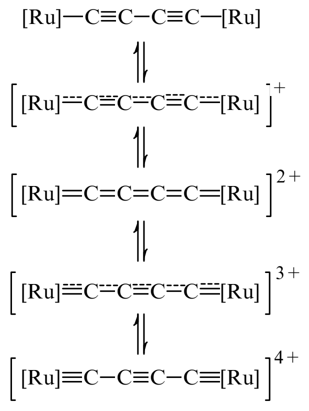
3: ν_{max}/cm^{-1} (Nujol) ν(CC) 1970 m. ^{1}H NMR: δ(CDCl$_3$) 4.17 (s, 5H, Cp), 7.03 – 7.64 (m, 30H, PPh$_3$). *m*/*z* (ES): 1430, M$^+$; 715, M^{2+}; 692, $[Ru(PPh_3)_2(C_5H_5)]^+$.

3·PF$_6$: ν_{max}/cm^{-1} (Nujol) ν(CC) 1861 s. ^{1}H NMR: δ(CDCl$_3$) 5.0 (br, Cp), 7.11, 7.31 (br, PPh$_3$). *m*/*z* (ES): 1430, M$^+$; 715, M^{2+}; 692, $[Ru(PPh_3)_2(C_5H_5)]^+$.

3·[PF$_6$]$_2$: ν_{max}/cm^{-1} (Nujol) ν(CC) 1766 s. ^{1}H NMR: δ(CDCl$_3$) 5.03 (s, 5H, Cp), 7.07 – 7.70 (m, 30H, PPh$_3$). *m*/*z* (ES): 715, M^{2+}.

4: ν_{max}/cm^{-1} (Nujol) ν(CC) 1974 m. ^{1}H NMR: δ(CDCl$_3$) 1.17 (s, 9H, Me), 4.42 (s, 5H, Cp), 7.14 – 7.70 (m, 15H, PPh$_3$). *m*/*z* (ES): 1058, M$^+$; 796, $[M-PPh_3]^+$; 505, $[Ru(PMe_3)(PPh_3)Cp]^+$; 429, $[Ru(PPh_3)Cp]^+$.

‡ $\ln K_c = \Delta E(F/RT)$; $\Delta E = |E_1^{\circ} - E_2^{\circ}|$ or $|E_3^{\circ} - E_4^{\circ}|$. See ref. 3.



[Ru] = $Ru(PPh_3)_2Cp$ (**3**) or $Ru(PMe_3)(PPh_3)Cp$ (**4**)

Scheme 1

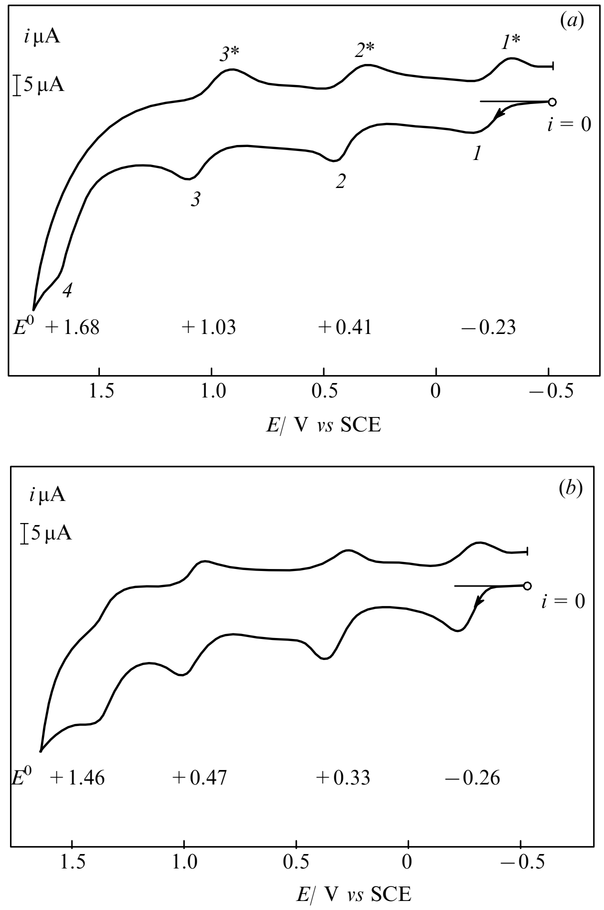


Figure 1 (*a*) CV of complex **3**. (*b*) CV of complex **4**. Conditions: glassy carbon electrode, CH_2Cl_2, 0.1 M $[NBu_4][BF_4]$, 200 mV s^{-1}, *vs* SCE. $E^{\ominus} = (E_{\text{p.a.}} + E_{\text{p.c.}})/2$.

range of oxidation states.[§] In $\mathbf{1}^+$ and $\mathbf{2}^+$ the odd electron is completely delocalised between the metal centres on the IR time-scale. However, while the four-carbon bridge in $\mathbf{2}{\cdot}[PF_6]_2$ appears to retain diacetylide character,[3] that in the structurally-characterised rhenium analogue $\mathbf{1}{\cdot}[PF_6]_2$ is best described as a cumulenic chain of carbon atoms linking the two Re centres.[7]

The nature of the C_4 bridge in **3**, $\mathbf{3}^+$ and $\mathbf{3}^{2+}$ is conveniently probed by IR spectroscopy. The presence of the diynyl bridge in **3** has been confirmed by an X-ray study[4] and gives rise to a single $\nu(C{\equiv}C)$ absorption at 1970 cm^{-1}. The cations in $\mathbf{3}{\cdot}PF_6$ and $\mathbf{3}{\cdot}[PF_6]_2$ have strong ν(CC) absorptions at 1861 cm^{-1} and 1766 cm^{-1}, respectively. These values are consistent with a gradual decrease in bond order along the carbon chain as **3** is oxidised. The carbon chain in $\mathbf{3}{\cdot}[PF_6]$ closely resembles that observed in $\mathbf{1}{\cdot}[PF_6]$ [ν(CC), 1870 cm^{-1}][2] and $\mathbf{2}{\cdot}PF_6$ [ν(CC), 1973, 1880 cm^{-1}],[3] with the odd electron fully delocalised over the six-atom $Ru{-}C_4{-}Ru$ chain. The IR evidence suggests that in $\mathbf{3}{\cdot}[PF_6]_2$ the chain has cumulenic character, more in keeping with the situation found in $\mathbf{1}{\cdot}[PF_6]_2$ than in $\mathbf{1}{\cdot}[PF_6]_2$.

Preliminary calculations show that the two HOMOs in **3** have $Ru{-}C_4$ π-anti-bonding character and are somewhat separated from the other occupied orbitals.[8] The variation in bond order along the $Ru{-}C_4{-}Ru$ chain which occurs as **3** is oxidized can be formally represented by the structures in Scheme 1. These show the conversion of the neutral diyndiyl complex **3** through the dicarbenic $\mathbf{3}^{2+}$ into dicarbynic $\mathbf{3}^{4+}$. We noted that similar electronic arrangements to the latter two, although not their interconversions, have been found in the C_2 derivatives $(silox)_3Ta{=}C{=}C{=}Ta(silox)_3$ (silox = $OSiBu^t_3$)[9] and $(Bu^tO)_3W{\equiv}C{-}C{\equiv}W(OBu^t)_3$.[10] Evidently, the electron distribution along a C_n chain linking two metal centres may be controlled by suitable combinations of ligands and oxidation states.

In conclusion, the binuclear ruthenium diynyl complexes **3** and **4** behave as electron-rich systems capable of losing up to four electrons from the $Ru{-}C_4{-}Ru$ system, giving rise to a novel series of five oxidation states. These include (a) the formal mixed valence Ru^{II}/Ru^{III} and Ru^{III}/Ru^{IV} cations, which on the basis of the electrochemical evidence are not only thermodynamically stable species, but also contains a highly delocalised unpaired electron, and (b) the highly electron-deficient species $[\{Ru^{IV}\}(\mu\text{-}C_4)\{Ru^{IV}\}]^{4+}$ cation. Three of the $Ru(PPh_3)_2Cp$ series have been prepared by chemical oxidation and isolated. Experiments to obtain the remaining examples, which should contain other curious electronic arrangements in the carbon bridge, and studies of related C_n complexes will be described elsewhere.

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[§] The value $E_p^{3/4}$ was used to calculate $|E_3^{\ominus} - E_4^{\ominus}|$ for the irreversible peaks 4 (Figure 1*a*,*b*). This assumes that any subsequent chemical reactions of the tetracation do not have a significant influence on the electrode potentials.