SUPPLEMENTARY INFORMATION

Bimetallic complexes based on carboxylate and xanthate ligands: Synthesis and electrochemical investigations.

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Additional electrochemical data

The response for $[Ru(S_2COMe)(dppm)_2]^+$ shows some electrochemical reversibility but the reduction peak is complex and broad and appears to consist of two overlapping peaks (Figure S1c). In contrast, the response for the binuclear complex **6** is entirely irreversible and sigmoidal, indicative of further chemical reaction of the complex following the oxidation. The oxidation current for the binuclear complex was found to be more than three times that of the (presumed one electron) peak for the mononuclear complex, which may indicate some electrocatalytic process involving the decomposition of the oxidised complex **6**. That the oxidation process is not a simple diffusion-controlled electron transfer process is further illustrated in Figure S1d, where the oxidation peak current, i_p^{ox} is plotted against square root of scan rate. The mononuclear complex shows the linear response anticipated for an electrochemically reversible, diffusion-controlled system, despite some evidence of structural rearrangement in the CV at slow scan rates. The response for complex **6** is, in contrast, non-linear, exhibiting an especially notable deviation from linearity at slow scans, where larger currents than predicted are observed.

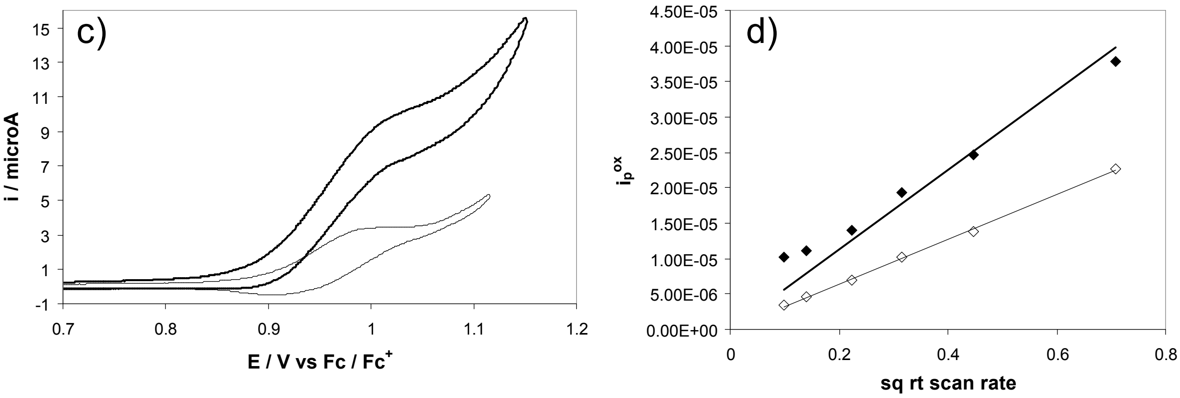

Figure S1. c) CV of 0.64 mM complex **6** (thick black) and 0.64 mM mononuclear $[Ru(S_2COMe)(dppm)_2]^+$ (thin black) cycling to 1.15 V vs. Fc/Fc^+ only, scan rate 10 mVs^{-1} glassy carbon electrode. (d) Plot of oxidation peak height, i_p^{ox}, vs. square root scan rate for complex **6** (black diamonds) and mononuclear $[Ru(S_2COMe)(dppm)_2]^+$ (open diamonds). Lines show best linear fit of data through the origin.

The CVs of $[\{(dppm)_2Ru\}_2(S_2COCH_2C_6H_4CH_2OCS_2)]^{2+}$ (**6**) and $[\{(dppm)_2Ru\}_2(O_2CC_6H_4CH_2OCS_2)]^{2+}$ (**12**) were also compared (Figure S2). The potential of the quasireversible Ru(II/III) couple is identical for the two complexes, despite the latter having the carboxylate-xanthate linker, which is shorter, more conjugated and has different donor combinations at either end.

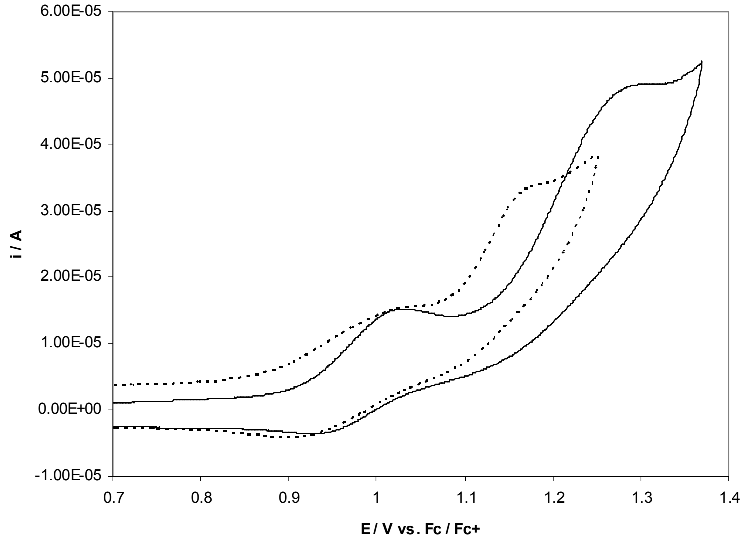

Figure S2: CVs of 0.64 mM of complexes **6** (full line) and **12** (broken line) in 0.1 M $TBAClO_4$ in DCM at 50 mV s^{-1}, Pt electrode, A = 0.03141 cm^2.

Figure S3c shows the CV at 10 mVs^{-1} for **2** and shows that this complex is much more stable towards oxidation than that with the dppm ligands, showing no evidence of decomposition or irreversible chemical reaction even at slow scan rates. Figure S3d shows a plot of i_p^{ox} *vs.* square root of scan rate for both bi- and mononuclear complexes, where both complexes exhibit model behaviour for reversible, diffusion controlled electron transfer processes.

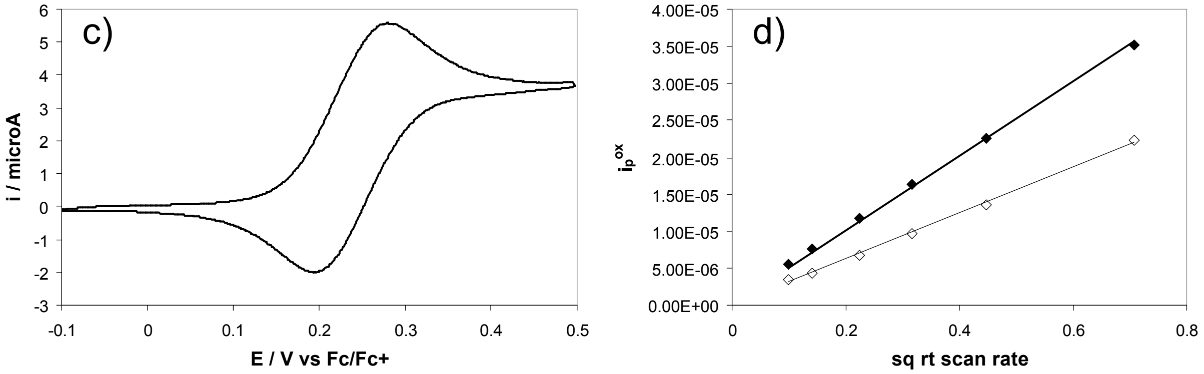

Figure S3: (c) CV of 0.64 mM complex **2** cycling to 0.5 V vs. Fc/Fc$^+$ only, scan rate 10 mVs^{-1} glassy carbon electrode. (d) Plot of oxidation peak height, i_p^{ox}, vs. square root scan rate for complex **2** (black diamonds) and mononuclear [Ru(CH=CHC$_6$H$_4$Me-4)(S$_2$COMe)(CO)(PPh$_3$)$_2$] (open diamonds). Lines show best linear fit of data through the origin.

The CVs of [{Ru(CH=CHC$_6$H$_4$Me-4)(CO)(PPh$_3$)$_2$}$_2$(S$_2$COCH$_2$C$_6$H$_4$CH$_2$OCS$_2$)] (**2**) and [{Ru(CH=CHC$_6$H$_4$Me-4)(CO)(PPh$_3$)$_2$}$_2${O$_2$CC$_6$H$_4$CH$_2$OCS$_2$}] (**10**) were also compared. In a similar way (Figure S4) to the comparison of the CV of complexes **6** and **12** discussed above, E^0 of the Ru(II/III) couple was identical for complexes **2** and **10**, despite the latter having the shorter, more conjugated carboxylate-xanthate linker. It therefore must be the co-ligands that dominate the electrochemical behaviour of these species rather than the dixanthate or carboxylate-xanthate linker.

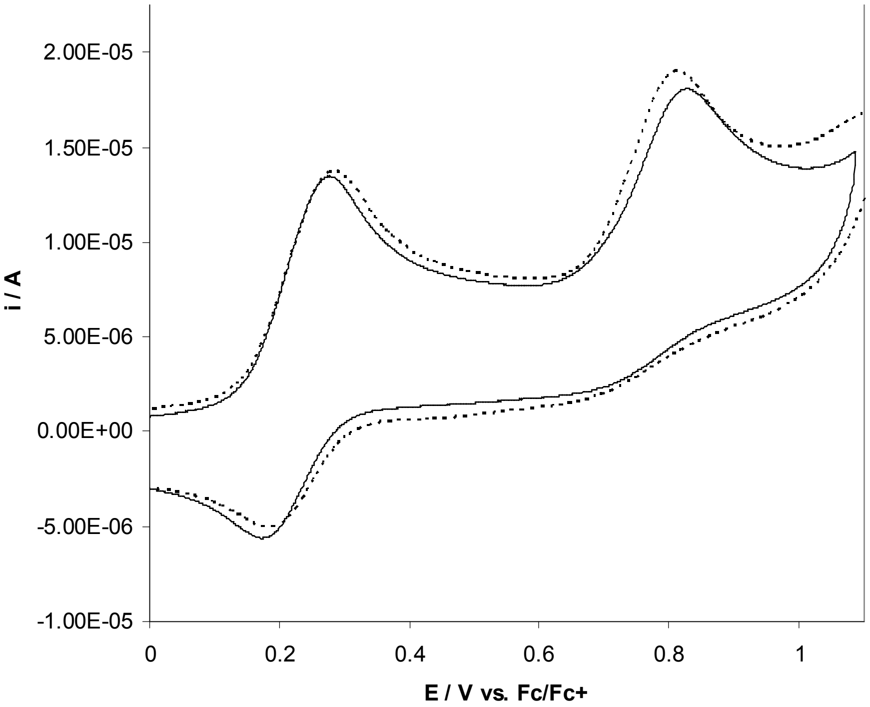

Figure S4: CVs of 0.64 mM of complexes **2** (full line) and **10** (broken line) in 0.1 M $TBAClO_4$ in DCM at 50 mV s^{-1}, Pt electrode, A = 0.03141 cm^2.

A CV of the osmium analogue, $[\{Os(CH{=}CHC_6H_4Me\text{-}4)(CO)(PPh_3)_2\}_2(S_2COCH_2C_6H_4CH_2OCS_2)]$ (**5**) was also obtained (Figure S5), however, the behaviour appeared to be very similar to that of the ruthenium version apart from the characteristically lower value of 0.1 V for the Os(II/III) couple. The other noteworthy feature is the greater irreversibility of the ligand-based electrochemical behaviour above 0.5 V compared to that found for the ruthenium vinyl complex.

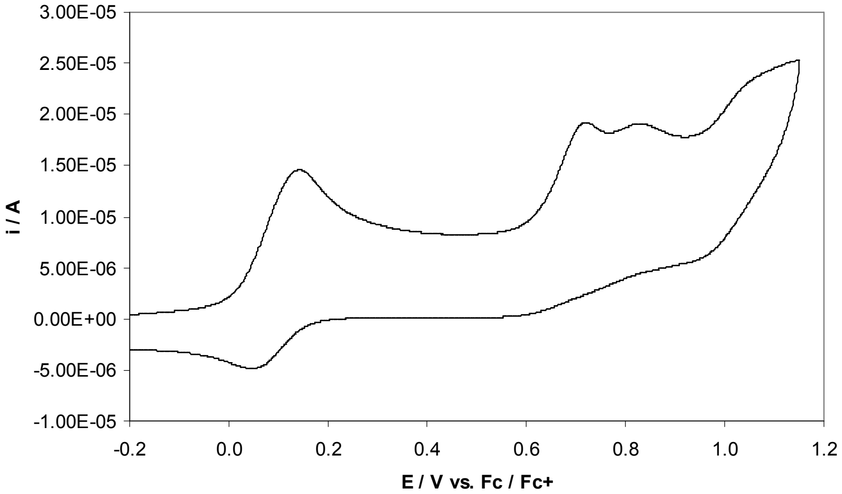

Figure S5: CV of 0.64 mM of complex **5** in 0.1 M $TBAClO_4$ in DCM at 50 mV s^{-1}, Pt electrode, A = 0.03141 cm^2.