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Preliminary communication

Electrochemical behaviour of ditertiary phosphine and diphosphazane ligand-bridged derivatives of di-iron and di-ruthenium nonacarbonyl

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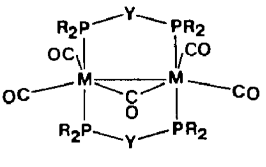
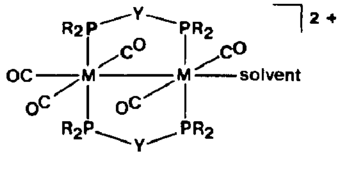
Abstract

Cyclic voltammetric studies in acetone and benzonitrile show that the oxidation of $[M_2(\mu\text{-CO})(CO)_4(\mu\text{-}R_2PYPR_2)_2]$ ($M = Fe$, $Y = CH_2$, $R = Ph$ or Me; $M = Fe$, $Y = NEt$, $R = OMe$, OPr^i or OEt; $M = Ru$, $Y = NEt$, $R = OPr^i$) generally proceeds via an EEC mechanism, whereas oxidation of $[Ru_2(\mu\text{-CO})(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ proceeds via an ECE mechanism, for which removal of the second electron is easier than the first, giving rise to an overall 2e-transfer reaction. In both mechanisms the chemical step involves solvent attack.

We are currently using ditertiary phosphine and diphosphazane ligands, in which the two phosphorus atoms are linked through a single atom, to stabilise dinuclear compounds to fragmentation [1]. Of interest here is the series of di-iron and di-ruthenium compounds $[M_2(\mu\text{-CO})(CO)_4(\mu\text{-}R_2PYPR_2)_2]$ ($M = Fe$, $Y = CH_2$, $R = Ph$ or Me; $M = Fe$, $Y = NEt$, $R = OMe$, OEt or OPr^i; $M = Ru$, $Y = NEt$, $R = OPr^i$), as well as $[Ru_2(\mu\text{-CO})(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$, all of which have structure **1** in which the two metal atoms are bridged by the two diphosphorus ligands and a carbonyl group. These compounds react readily with a wide range of electrophiles, usually to give cationic complexes, which are themselves often reactive towards a range of reagents [2]. We wished to develop the redox chemistry of the complexes **1**, in the expectation that new compounds and reactivity patterns would be uncovered,



(1)



(2)

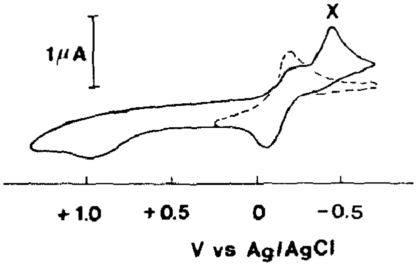


Fig. 1. CV of 1.0 mM $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ in benzonitrile (0.1 M TBAP) at Pt (298 K, 200 mVs^{-1}).

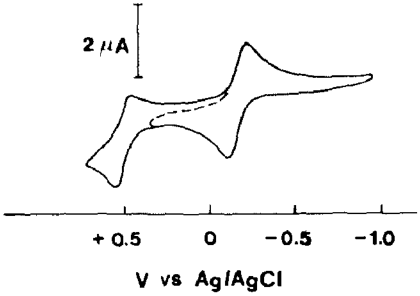


Fig. 2. CV of 1.0 mM $[Fe_2(\mu\text{-}CO)(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)_2]$ in acetone (0.1 M TBAP) at Pt (298 K, 200 mVs^{-1}).

a logical starting point being an investigation of their electrochemical behaviour using cyclic voltammetry. Being electron-rich these complexes are easily oxidised, but cannot be reduced within the solvent limit of the solvents used in this work viz. acetone and benzonitrile. Accordingly, only their oxidative electrochemistry is discussed here.

Results and discussion

Figure 1 illustrates cyclic voltammograms (CV's) of $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (**1a**) measured in benzonitrile. The initial anodic wave is reversible (ΔE_p 110 mV; i_p^c/i_p^a 1.0), and corresponds to a one-electron oxidation as judged by comparison with ferrocene as a calibrant [3]. The low E_p^a value of −0.08 V [4*] establishes that the complex is easily oxidised. When the scan is extended to more positive potentials, a second, broad and irreversible wave is observed; moreover, on the reverse scan a new cathodic wave appears (X, Fig. 1). These data indicate an EEC mechanism for the electrochemical oxidation of **1a** in benzonitrile. The same mechanism is observed for the electrochemical oxidation of **1a** in acetone, and for the other diphosphazane ligand-bridged di-iron compounds in acetone and benzonitrile. However, an exception is provided by the CV of $[Fe_2(\mu\text{-}CO)(CO)_4(\mu\text{-}dppm)_2]$ (**1b**) (dppm = $Ph_2PCH_2PPh_2$) in acetone (Fig. 2). Two reversible one-electron oxidation waves are observed with no evidence for an extra cathodic wave on the reverse scan, thus indicating an EE mechanism and that the $[Fe_2(\mu\text{-}$

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* This and other references marked with asterisks denote notes in the reference list.

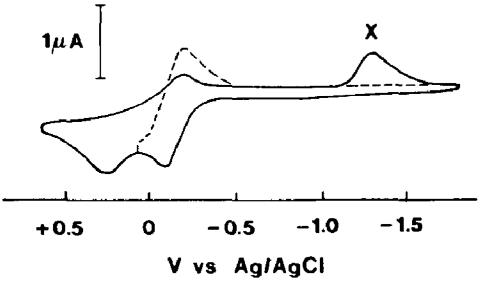


Fig. 3. CV of 1.0 mM $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ in benzonitrile (0.1 M TBAP) at Pt (298 K, 200 mVs^{-1}).

$CO)(CO)_4(\mu\text{-}dppm)_2]^{2+}$ dication is stable, at least on the time scale of the cyclic voltammetric experiment. Interestingly, the dppm complex exhibits the typical EEC mechanism in benzonitrile as does the $Me_2PCH_2PMe_2$ complex in both acetone and benzonitrile. Clearly the unusual stability of $[Fe_2(\mu\text{-}CO)(CO)_4(\mu\text{-}dppm)_2]^{2+}$ is solvent dependent because, although it is stable in acetone, it reacts further in benzonitrile. A further implication is that the chemical step in the EEC process observed for the other di-iron complexes involves the solvent (see Scheme 2 and discusion below).

Figure 3 shows the CV of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]$ (**1c**) measured in benzonitrile; a similar CV is obtained in acetone. The initial anodic wave is probably best described as quasi-reversible (ΔE_p 140 mV; i_p^c/i_p^a 1.0) and, provided the anodic scan is not carried too far beyond this peak (E_p^a −0.05 V), no additional cathodic wave is observed on the reverse scan. When the positive scan is extended, a second broad and irreversible oxidation wave is observed and, moreover, a new cathodic wave (X, Fig. 3) is observed on the reverse scan. An overall EEC mechanism is indicated as for nearly all the di-iron complexes, but with the difference that the separation between the peaks corresponding to the removal of the first and second electrons is much smaller, cf. 0.17 V for **1c**, and 1.04 V for **1a**.

The CV of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ (**1d**) in benzonitrile is illustrated in Fig. 4. A similar CV is observed in acetone. In contrast to the CV of **1c** only one broad and irreversible wave is observed on the positive scan. Moreover, its peak height (i_p^a 3.8 μA) is approximately double that observed for the primary

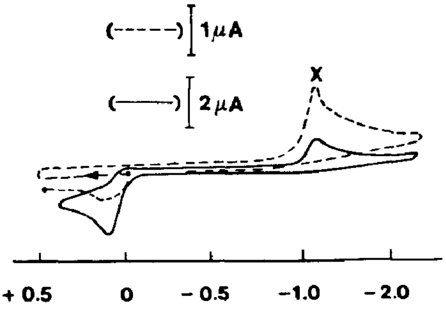
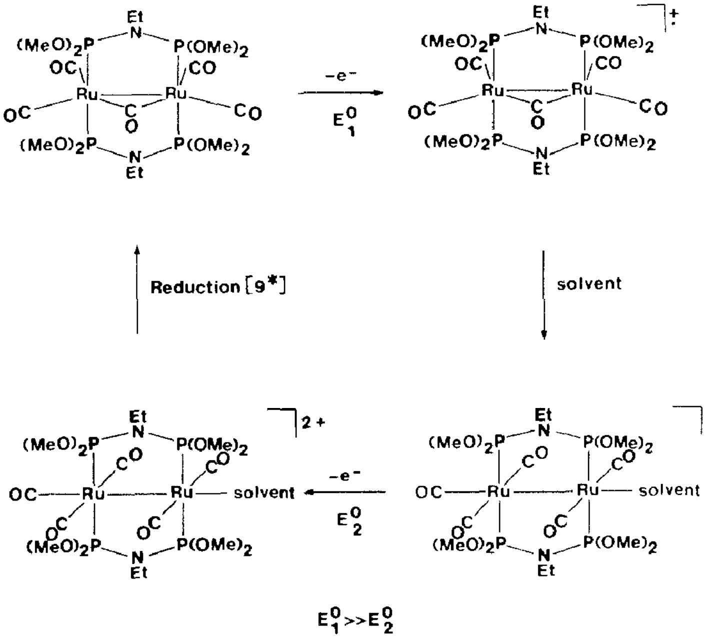
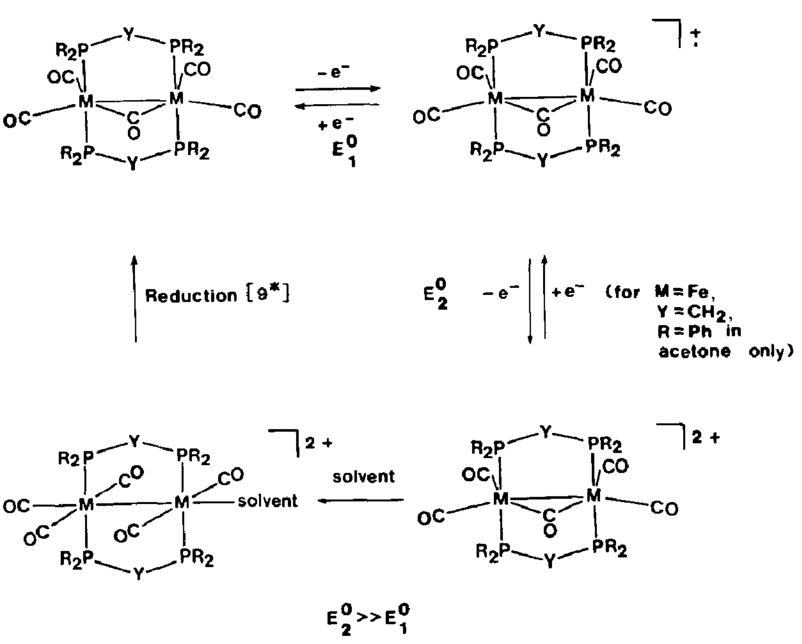


Fig. 4. CV's of 1.0 mM $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ (———) and $[Ru_2(CO)_5(C_6H_5CN)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2](SbF_6)_2$ (- - - - -) in benzonitrile (0.1 M TBAP) at Pt (298 K, 200 mVs^{-1}).

oxidation wave in the CV of $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$, the iron analogue of **1d** (i_p^a 2.0 μA). Also significant is the appearance of a broad cathodic wave (X, Fig. 4) on the reverse scan. In view of the enhanced peak current for the oxidation wave in the CV of **1d**, an ECE mechanism is indicated where $E_1^0 \gg E_2^0$ (the subscripts 1 and 2 denote the removal of the first and second electrons) giving rise to an overall 2e-transfer reaction [5,6*]. The implication is that the chemical step which follows the removal of the first electron allows the second electron to be removed more easily. As already noted, the stability of the species formed in the oxidation of the di-iron complexes is dependent on the choice of solvent and, for this reason, we suspected that the chemical step in the ECE process might involve solvent coordination to a Ru atom in the radical cation with a concomitant rearrangement of the ligands in the coordination spheres of the two Ru atoms. If this is indeed the case, removal of a second electron could be facilitated and, following its removal the dicationic solvento species $[Ru_2(CO)_5(solvent)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^{2+}$ should be formed. To test this hypothesis, the CV of an authentic sample of $[Ru_2(CO)_5(C_6H_5CN)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2](SbF_6)_2$, synthesised by addition of a twice-molar amount of $AgSbF_6$ to **1d** in benzonitrile, was recorded in benzonitrile (Fig. 4). Reduction of $[Ru_2(CO)_5(C_6H_5CN)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]^{2+}$ (**2d**) occurs on the initial cathodic scan at a potential ($E_p^c = -1.15$ V) which coincides with that of the additional cathodic wave (X) observed in the CV of **1d** (Fig. 4). In addition, reduction of **2d** leads to the formation of **1d** as evidenced by an anodic wave on the reverse (positive) scan at an E_p^a value (0.11 V) corresponding to the oxidation of **1d** (Fig. 4). These observations support our contention that the chemical step in the ECE mechanism for the oxidation of **1d**, involves solvent coordination to a Ru atom in the radical cation [7*]. The proposed reaction pathway is summarised in Scheme 1 [8*].



Scheme 1



Scheme 2

As noted above, unstable dications of the type $[M_2(\mu\text{-CO})(CO)_4\{\mu\text{-}R_2PYPR_2\}_2]^{2+}$ are formed after removal of the second electron in the EEC mechanism for the electrochemical oxidation of **1a**, **1c** and the other di-iron complexes (except **1b** in acetone). Presumably these, being 34e-species, would be expected to bind a 2e-donor, in this case a solvent molecule, with a concomitant rearrangement of the ligands to form complexes of type **2**; Scheme 2 summarises the proposed reaction pathway. Assuming that the species reduced at X in the CV's of **1a** (Fig. 1), **1c** (Fig. 3) and the other di-iron complexes is indeed a dication of type **2**, the expectation is, by analogy with the CV of **2d**, that it will be reduced on the cathodic scan to reform a type **1** complex, which should then be re-oxidised on the positive scan. This is the case since, when repetitive scans are applied to **1a**, **1c** etc., the successive CV's essentially superimpose on each other with only a small diminuition in peak heights; in fact a steady-state condition is reached after 3–4 cycles. This observation also lends support to the reaction pathway proposed in Scheme 2.

In conclusion, it can be stated that the electron-rich complexes studied in this work are all easily oxidised, but that their electrochemical behaviour following the primary oxidation step is dependent on the choice of metal, ligand and of solvent.

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3 R.R. Gagne, C.A. Koral, and G.C. Lisensky, Inorg. Chem., 19 (1980) 2854.

4 Ferrocene was used as an internal standard [3]. E^0 values for [ferrocene]$^{+/0}$ vs. our pseudo Ag/AgCl reference electrodes were: 0.44 V in benzonitrile (ΔE_p 75 mV); 0.52 V in acetone (ΔE_p 60 mV). No compensation for iR drop losses was applied.

5 R.S. Nicholson and I. Shain, Anal. Chem., 37 (1965) 178; J.M. Saveant, Electrochim. Acta, 12 (1967) 753.

6 For other examples of ECE mechanisms see (a) J.G. Gaudiello, T.C. Wright, R.A. Jones and A.J. Bard, J. Am. Chem. Soc., 107 (1985) 888; (b) K. Hinkelmann, F. Mahlendorf, J. Heinze, H.-T. Schacht, J.S. Field and H. Vahrenkamp, Angew. Chem. Int. Ed. Engl., 26 (1987) 352; (c) D.A. Lacombe, J.E. Anderson and K.M. Kadish, Inorg. Chem., 25 (1986) 2074; (d) K.M. Kadish, D.A. Lacombe and J.E. Anderson, ibid., 25 (1986) 2246.

7 Oxidation of $[\mathrm{Os_4H_3(CO)_{12}}]^-$ in acetonitrile is also followed by a chemical step which involves solvent attack at a metal atom; see B.F.G. Johnson, J. Lewis, W.J.H. Nelson, J. Puga, P.R. Raithby, M. Schröder, and K.H. Whitmire, J. Chem. Soc., Chem. Commun., (1982) 610.

8 Scheme 1 ignores the fact that the following disproportionation reaction is favoured on thermodynamic grounds if $E_1^0 \gg E_2^0$:

$$[\mathrm{Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2}]^{+\cdot} + [\mathrm{Ru_2(CO)_5(solvent)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2}]^{+\cdot} \underset{k_b}{\overset{k_f}{\rightleftarrows}}$$
$$[\mathrm{Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2}] + [\mathrm{Ru_2(CO)_5(solvent)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2}]^{2+}$$

At present we have no means of establishing its contribution to the overall reaction pathway.

9 Studies are in progress to elucidate the nature of this reduction step. Significantly, two well-defined peaks are observed for the reduction of $[\mathrm{Ru_2(CO)_5(Me_2CO)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2}]^{2+}$ in acetone.