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

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Abstract

Cyclic voltammetric studies in benzonitrile, dichloromethane and acetone show that the oxidation of the di-iron derivatives $[Fe_2(\mu\text{-}CO)(CO)_4(\mu\text{-}R_2PYPR_2)_2]$ ($Y = CH_2$, R = Me or Ph; Y = NEt, R = OMe, OEt, O^iPr or OPh) generally proceeds via an EEC mechanism, the only exception being the oxidation of the $Y = CH_2$, R = Ph derivative in acetone, which proceeds via an EE mechanism. The chemical step in the EEC mechanism involves solvent attack at an iron atom with formation of a dicationic solvento species of the type $[Fe_2(CO)_5(\text{solvent})(\mu\text{-}R_2PYPR_2)_2]^{2+}$. The electrochemical oxidation of the diruthenium tetramethoxydiphosphazane ligand-bridged derivative $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ only proceeds via an EEC mechanism in the very weakly coordinating solvent dichloromethane; in benzonitrile and acetone oxidation is via an ECE mechanism for which the potential required to remove the second electron is lower than that for the removal of the first electron giving rise to an overall 2e-transfer reaction. Again the end-product of the oxidation process is a dicationic solvento species. Electrochemical oxidation in all three solvents of the diruthenium tetraisopropoxydiphosphazane ligand-bridged derivative $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(^iPrO)_2PN(Et)P(O^iPr)_2\}_2]$ is proposed to proceed via an ECEC mechanism for which the first chemical step involves a structural rearrangement and the second solvent attack at a ruthenium atom to form the dicationic solvento species. Significantly, the separation between the potentials required to remove the first and second electrons is small, i.e., < 0.5 V. Two pathways are utilized in the electrochemical oxidation of the mixed-ligand complex $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}\{\mu\text{-}(^iPrO)_2PN(Et)P(O^iPr)_2\}]$, their nature being dependent on the choice of solvent. The ECE mechanism is adopted in all three solvents benzonitrile, acetone and dichloromethane; however, in the first solvent the second pathway is the EEC process whereas the second pathway adopted in acetone and dichloromethane is the ECEC process. Thus, the overall mechanism proposed for the electrochemical oxidation of the above derivatives of $[Fe_2(CO)_9]$ and $[Ru_2(CO)_9]$ allows for three pathways to a dicationic solvento species, the pathway adopted being dependent on the metal, the bridging ligand, in particular on its size, and on the coordinating ability of the solvent.

Introduction

We are currently using ditertiary phosphine and diphosphazane ligands, in which the two phosphorus atoms are linked through a single atom, to stabilize dinuclear

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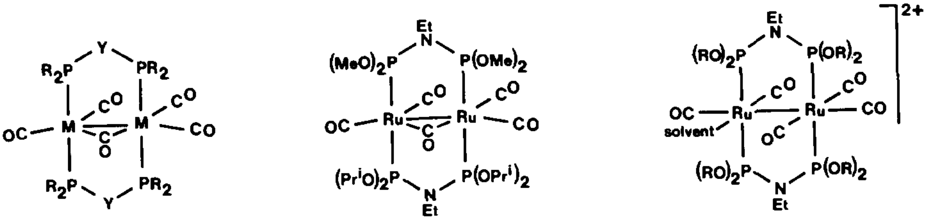

1a: M = Fe; Y = NEt; R = OPr^i
1b: M = Fe; Y = NEt; R = OMe
1c: M = Fe; Y = NEt; R = OPh
1d: M = Fe; Y = NEt; R = OEt
1e: M = Fe; Y = CH_2; R = Me
1f: M = Fe; Y = CH_2; R = Ph
2a: M = Ru; Y = NEt; R = OPr^i
2b: M = Ru; Y = NEt; R = OMe
2c: M = Ru; Y = CH_2; R = Me

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$\mathbf{4a}^{2+}$: solvent = PhCN; R = Pr^i
$\mathbf{4b}^{2+}$: solvent = PhCN; R = Me
$\mathbf{4c}^{2+}$: solvent = Me_2CO; R = Me

Scheme 1.

compounds to fragmentation. Using this approach a wide range of stable derivatives of $[Fe_2(CO)_9]$ and $[Ru_2(CO)_9]$ have been synthesized; those whose electrochemical behaviour is described in this work are listed in Scheme 1. Compounds **1a–f**, **2a** and **2b** have been synthesized by us [1], **2c** by Johnson and Gladfelter [2] while the synthesis of the mixed ligand complex **3** is first reported here. In all these compounds the two metal atoms are bridged by two bidentate diphosphorus ligands as well as by a carbonyl group, with the coordination at each metal atom being completed by a further two carbonyl ligands and the other metal atom [1]. Because of the presence of four strongly electron-donating phosphorus atoms and only five carbonyl groups these dinuclear complexes are electron-rich and, as such, should be readily oxidized. With this in mind we wished to develop their redox chemistry and, in particular, to test their ability to function as electron-donor molecules in electron-transfer reactions with electron-acceptor species. Indeed, our experience of their chemistry was that they react readily with a wide range of electrophiles, usually to give cationic complexes, which are themselves often reactive towards a range of reagents [3].

Our investigation of their redox chemistry began with a study of the oxidation of **1a–f**, **2a** and **2b** in benzonitrile and acetone using electrochemical methods such as rotating disc electrode (RDE) voltammetry and cyclic voltammetry. The preliminary results of this investigation have been communicated [4]. The chemical significance of the electrochemical work is that it showed that oxidation of the diruthenium complexes **2a** and **2b** in particular, occurs at low positive potentials with ready formation of dicationic solvento species of the type $\mathbf{4a}^{2+}$, $\mathbf{4b}^{2+}$ and $\mathbf{4c}^{2+}$ (see Scheme 1). Because of the general lability of solvento ligands, the latter are potentially excellent precursors for the synthesis of a wide range of dinuclear derivatives of ruthenium and, accordingly, the oxidation of **2a** and **2b** was subsequently attempted using chemical oxidants such as silver salts in aprotic weakly coordinating solvents. As reported by us [5] salts of the type **4a–4c**,$(SbF_6)_2$ are indeed easily synthesized in good yields and the acetone ligand, in particular, is readily replaced by a variety of neutral and anionic nucleophiles to form new substituted products.

The electrochemical work also showed that the mechanism of oxidation of compounds **1a–f**, **2a** and **2b** depends on the metal, the bridging ligand and the solvent. Of particular interest was the ECE mechanism [6] proposed for the two-electron oxidation of **2b**, especially as the chemical step is unusual in that it involves solvent coordination to the metal [7*] rather than a geometric isomerisation [8] or ligand loss [9] for example. In fact there is current interest in the intimate mechanism of two-electron transfer reactions [10] and in the electrochemistry of di- and polynuclear compounds in general [11]. We wished to obtain a better understanding of the mechanism of the electrochemical oxidation of these derivatives of $[Fe_2(CO)_9]$ and $[Ru_2(CO)_9]$ and thus the electrochemical study has been extended to compounds **2c** and **3** and to measurements in the very weakly coordinating solvent, dichloromethane. Full details of all the electrochemical work are reported here as well as a proposed overall mechanism for the electrochemical oxidation of compounds **1a–f**, **2a-2c** and **3**.

Results and discussion

The syntheses of compounds **1a–f**, **2a**, **2b** [1] and **4a–c**,$(SbF_6)_2$ [5] have been previously reported by us, while the synthesis of **2c** has been described by Johnson and Gladfelter [2]. Compound **3** is new, and has been synthesized according to equations 1 and 2 using procedures similar to those described in ref. 1.

$$[Ru_3(CO)_{12}] + (^iPrO)_2PN(Et)P(O^iPr)_2 \xrightarrow{h\nu} [Ru_3(CO)_{10}\{\mu\text{-}(^iPrO)_2PN(Et)P(O^iPr)_2\}] + 2CO \qquad (1)$$

$$[Ru_3(CO)_{10}\{\mu\text{-}(^iPrO)_2PN(Et)P(O^iPr)_2\}] + 2(MeO)_2PN(Et)P(OMe)_2 \xrightarrow{h\nu} \mathbf{3} + [Ru(CO)_3\{(MeO)_2PN(Et)P(OMe)_2\}] + 2CO \qquad (2)$$

Table 1 lists all the essential electrochemical data for the above compounds.

Electrochemistry of the di-iron compounds 1a–f

Figure 1 illustrates the cyclic voltammogram (CV) of **1a** in benzonitrile. With the exception of **1f** (see below) this CV is typical of the CV's of the other di-iron complexes, recorded not only in benzonitrile, but also in acetone and dichloromethane. The initial anodic wave is reversible (i_{pc}/i_{pa} 1.0) and corresponds to a one-electron oxidation as judged by comparison with ferrocene as an internal calibrant [12]. The low $E_{1/2}$ values and reversibility of this wave (Table 1) establish that these complexes are easily oxidized with the formation of a monocation which is stable on the timescale of the experiment. Also the trend in $E_{1/2}$ values for the primary oxidation wave is the expected one of a shift to more cathodic values as the donor capacity of the bidentate bridging ligand is increased (Table 1). When the initial 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 [13] for the electrochemical oxidation of the di-iron complexes **1a–e**.

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

Table 1. Electrochemical data [a] for compounds **1a–f**, **2a–c**, **3** and **4a–c**,$(SbF_6)_2$

Compound	Solvent	Redox step	n [b]	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)	i_{pc}/i_{pa}
1a	PhCN	1. Ox.	1	−0.09	−0.18	−0.14	1.0
		2. Ox.	1	0.9			irrev
		X [c]	2		−0.48		irrev
	Me_2CO	1. Ox.	1	0.06	−0.06	0.00	1.0
		2. Ox.	1	0.8			irrev
		X [c]	2		−0.25		irrev
1b	PhCN	1. Ox.	1	0.10	0.00	0.05	1.0
		2. Ox.	1	1.1			irrev
		X [c]	2		−0.36		irrev
	CH_2Cl_2	1. Ox.	1	0.09	−0.05	0.02	1.0
		2. Ox.	1	0.9			irrev
		X [c]	2		−0.43		irrev
	Me_2CO	1. Ox.	1	0.20	0.11	0.16	1.0
		2. Ox.	1	0.8			irrev
		X [c]	2		−0.08		irrev
1c	PhCN	1. Ox.	1	0.23	0.02	0.13	1.0
		2. Ox.	1	1.2			irrev
		X [c]	2		−0.26		irrev
	Me_2CO	1. Ox.	1	0.28	0.19	0.24	1.0
		2. Ox.	1	0.9			irrev
		X [c]	2		−0.06		irrev
1d	PhCN	1. Ox.	1	0.06	−0.12	−0.03	1.0
		2. Ox.	1	1.0			irrev
		X [c]	2		−0.46		irrev
	Me_2CO	1. Ox.	1	0.26	0.06	0.11	1.0
		2. Ox.	1	0.9			irrev
		X [c]	2		−0.14		irrev
1e	PhCN	1. Ox.	1	−0.35	−0.45	−0.40	1.0
		2. Ox.	1	0.29			irrev
		X [c]			not observed		
1f	PhCN	1. Ox.	1	−0.11	−0.32	−0.21	1.0
		2. Ox.	1	0.47			irrev
		X [c]	2		−1.04		irrev
	CH_2Cl_2	1. Ox.	1	−0.15	−0.28	−0.21	1.0
		2. Ox.	1	0.54	0.35	0.45	0.8
		X [c]	2		−0.85		irrev
	Me_2CO	1. Ox.	1	−0.11	−0.18	−0.14	1.0
		2. Ox.	1	0.56	0.46	0.51	1.0
2a	PhCN	1. Ox.	1	−0.08	−0.17	−0.13	1.0
		2. Ox.	1	0.24			irrev
		X [c]	2		−1.27		irrev
	CH_2Cl_2	1. Ox.	1	−0.12	−0.21	−0.16	1.0
		2. Ox.	1	0.24			irrev
		X [c]	2		−1.42		irrev
	Me_2CO	1. Ox.	1	0.03	−0.07	−0.02	1.0
		2. Ox.	1	0.17			irrev
		X [c,d]	2		−0.91		irrev
			2		−1.42		irrev
2b	PhCN	1. Ox.	2	0.10			irrev
		X [c]	2		−1.16		irrev
	CH_2Cl_2	1. Ox.	1	0.07	−0.02	0.02	1.0
		2. Ox.	1	0.9			irrev
		X [c]	2		−1.25		irrev
	Me_2CO	1. Ox.	2	0.18			irrev
		X [c,d]	2		−0.80		irrev
			2		−1.05		irrev

Table 1

Compound	Solvent	Redox step	n [b]	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)	i_{pc}/i_{pa}
2c	PhCN	1. Ox.	2	−0.23			irrev
		X [c]	2		−1.15		irrev
3	PhCN	1. Ox.	1	0.06	−0.04	−0.01	0.8
		2. Ox.	1	0.6			irrev
		X [c]	2		−1.11		irrev
	CH_2Cl_2	1. Ox.	1	0.02	−0.10	−0.04	0.8
		2. Ox.	1	0.12			irrev
		X [c]	2		−1.21		irrev
	Me_2CO	1. Ox.	1	0.10	0.02	0.06	0.8
		2. Ox.	1	0.41			irrev
		X [c,d]	2		−0.85		irrev
					−1.10		irrev
4a,$(SbF_6)_2$	PhCN	1. Red.	2		−1.25		irrev
		Y [e]	1	−0.10			
			1	0.22			irrev
4b,$(SbF_6)_2$	PhCN	1. Red.	2		−1.15		irrev
		Y [e]	2	0.11			irrev
4c,$(SbF_6)_2$	Me_2CO	1. Red. [d]	2		−0.85		irrev
			2		−1.10		irrev
		Y [e]	2	0.17			irrev

[a] Scan rate 200 mV s^{-1}; solvents 0.1 M in TBAP, ~10^{-3} M in compd; T 298 K; all potentials quoted vs pseudo-Ag/AgCl reference electrode (see Experimental Section). [b] Number of electrons transferred. Where possible estimated by comparison of limiting currents from RDE voltammograms. [c] Reverse scan wave due to the reduction of the dicationic solvento species (see text). [d] Two reverse scan waves are observed; one due to the reduction of the dicationic acetone species, the other due to the reduction of a dicationic aquo complex which is also present because of the difficulty of removing water entirely from acetone [5]. [e] Reverse scan wave due to the oxidation of the neutral parent complex (see text).

As noted, the electrochemical oxidation of **1f**, which contains the bis(diphenylphosphino)methane (dppm) ligand, does not follow the pattern described above for **1a–e**; rather the CV's are found to be solvent dependent. When the CV is recorded in benzonitrile, a relatively strongly coordinating solvent, the oxidation does, indeed, proceed via an EEC mechanism (Table 1). However, in acetone, two reversible one-electron oxidation waves are observed (Fig. 2, Table 1) indicating an overall EE process. The CV recorded in dichloromethane appears to be intermediate between those in benzonitrile and acetone, in that the second oxidation wave has an

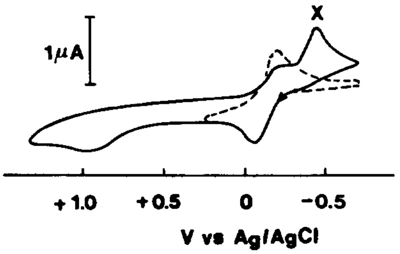


Fig. 1. CV of 1.0 mM $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(^iPrO)_2PN(Et)P(O^iPr)_2\}_2]$ (**1a**) in benzonitrile (0.1 M TBAP) at Pt (298 K, 200 mV s^{-1}).

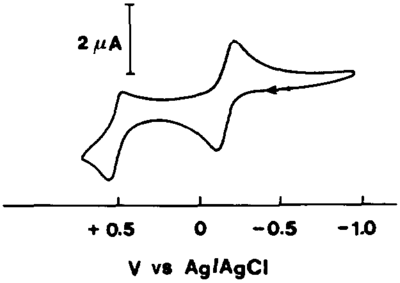


Fig. 2. CV of 1.0 mM [$Fe_2(\mu\text{-}CO)(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)_2$] (**1f**) in acetone (0.1 M TBAP) at Pt (298 K, 200 mV s^{-1}).

i_{pc}/i_{pa} value of 0.8, indicating a wave which is neither fully reversible nor fully irreversible. Clearly the solvent plays a role in determining the stability of **1f**$^{2+}$ and, in particular, the dication does not appear to be stable in the presence of coordinating solvents such as benzonitrile. A further implication is that the chemical step in the EEC process observed for **1f** in benzonitrile and for the other di-iron complexes in a range of solvents, involves solvent attack at the metal atom centre. Further details of the proposed mechanism are discussed below.

Electrochemistry of the diruthenium compounds 2a–c and 3

Figure 3 shows the CV of **2a** measured in benzonitrile; similar CV's are obtained in acetone and dichloromethane (Table 1). The initial anodic wave is reversible (i_{pc}/i_{pa} 1.0) and, provided the anodic scan is not carried too far beyond this peak ($E_{pa} = -0.08$ 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. In our earlier communication we suggested that the electrochemical oxidation of **2a** proceeded via an EEC mechanism as for nearly all the di-iron complexes. This would appear to be an oversimplification in view of the unexpectedly small differences between the E_{pa} values for the first and second oxidation waves (0.32, 0.36 and 0.14 V in PhCN, CH_2Cl_2 and Me_2CO, respectively) compared to gaps of greater than 0.5 V for the di-iron complexes (Table 1). This problem is examined further in the discussion, below, of the mechanism of the electrochemical oxidation of the diruthenium complexes. However, it has been possible to confirm, at least in

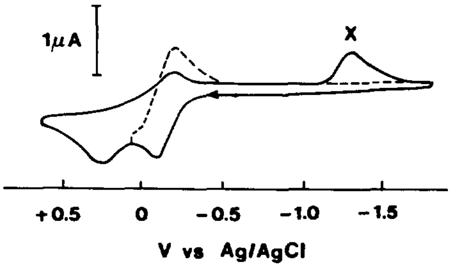


Fig. 3. CV of 1.0 mM [$Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(^iPrO)_2PN(Et)P(O^iPr)_2\}_2$] (**2a**) in benzonitrile (0.1 M TBAP) at Pt (298 K, 200 mV s^{-1}).

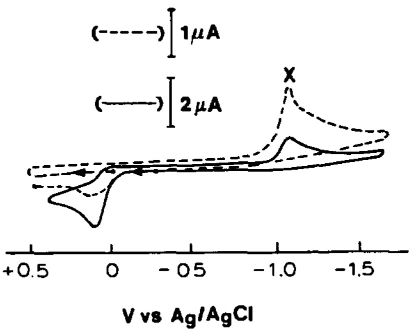


Fig. 4. CV's of 1.0 mM [$Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2$] (**2b**) (———) and [$Ru_2(CO)_5(PhCN)\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2$]$(SbF_6)_2$ (**4b**,$(SbF_6)_2$) (----) in benzonitrile (0.1 M TBAP) at Pt (298 K, 200 mV s^{-1}).

benzonitrile, that the species formed following the removal of the second electron and which is subsequently reduced at X on the reverse scan (Fig. 3), is the dicationic solvento species $\mathbf{4a}^{2+}$. This was confirmed by synthesis of an authentic sample of **4a**,$(SbF_6)_2$ [5] and measurement of its CV in benzonitrile. As shown by the potential data in Table 1, the reduction of $\mathbf{4a}^{2+}$ coincides with peak X in the CV of the parent compound and, furthermore, on reversal of the scan two anodic waves are obtained which correspond to the oxidation of the parent complex, **2a**.

The CV of the tetramethoxydiphosphazane ligand derivative **2b** in benzonitrile is illustrated in Fig. 4. In contrast to the CV's of **2a** only one broad and irreversible wave is observed on the positive scan. Moreover, its peak height (i_{pa} 3.8 μA at 200 min s^{-1}) is approximately double that observed for the primary oxidation wave in the CV of the di-iron tetramethoxydiphosphazane ligand derivative **1b** (i_{pa} 2.0 μA at 200 mV s^{-1}). 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 **2b**, an ECE mechanism is indicated where $E_1^\circ > E_2^\circ$ (the subscripts 1 and 2 denote the removal of the first and second electrons) giving rise to an overall 2e-transfer reaction [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 noted in an earlier communication [4], the chemical step involves solvent coordination to a ruthenium atom in the radical cation with a concomitant rearrangement of the ligands in the coordination spheres of the two ruthenium atoms to form the dicationic solvento species $\mathbf{4b}^{2+}$. This was confirmed by synthesis of an authentic sample of **4b**,$(SbF_6)_2$, by addition of a twice-molar amount of $AgSbF_6$ to **2b** in benzonitrile [5], and the measurement of its CV in benzonitrile. As shown in Fig. 4, reduction of $\mathbf{4b}^{2+}$ occurs on the initial cathodic scan at a potential ($E_{pc} = -1.15$ V) which coincides with that of the additional cathodic wave (X) observed in the CV of **2b** (Fig. 4). In addition, reduction of $\mathbf{4b}^{2+}$ leads to the formation of **2b** as evidenced by an anodic wave on the reverse (positive) scan at an E_{pa} value (0.11 V) corresponding to the oxidation of **2b** (Fig. 4). The CV of **2b** recorded in acetone shows the same form as the CV recorded in benzonitrile (see Table 1) and an ECE mechanism therefore appears to operate in this solvent as well. Certainly, the CV of an authentic sample of **4c**,$(SbF_6)_2$, measured in acetone, shows waves at the positions expected from the CV of **2b** itself in acetone and predicted on

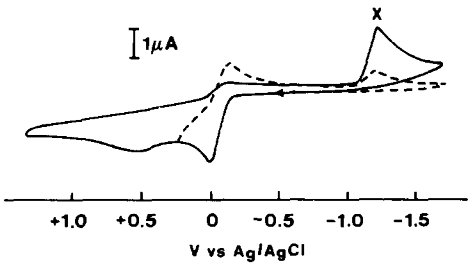


Fig. 5. CV of 1.0 m*M* $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}({}^iPrO)_2PN(Et)P(O{}^iPr)_2\}\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}]$ (3) in benzonitrile (0.1 *M* TBAP) at Pt (298 K, 200 mV s^{-1}).

the basis that the chemical step following the oxidation of **2b** involves solvent attack at a ruthenium atom centre (Table 1). On the other hand, the CV of **2b** recorded in dichloromethane exhibits the same form as the CV's of most of the di-iron complexes (Table 1), i.e., a reversible primary oxidation wave is followed by an irreversible one with the appearance of a peak X on the reverse scan. Unlike benzonitrile and acetone, dichloromethane is essentially a non-coordinating solvent which probably accounts for the stability of the radical cation **2b**$\cdot^+$ in dichloromethane. Nevertheless, the end-product of the EEC process for the electrochemical oxidation of **2b** in dichloromethane is probably also a dicationic solvento species as found in benzonitrile and acetone.

Interestingly, the electrochemical oxidation in benzonitrile of the extremely electron-rich bis(dimethylphosphino)methane (dmpm) complex, **2c**, also proceeds via an ECE mechanism as evidenced by the data given in Table 1. Clearly, the radical cation **2c**$\cdot^+$ is rapidly attacked by the benzonitrile solvent in the chemical step, as found for the radical cation of the tetramethoxydiphosphazane ligand complex **2b**.

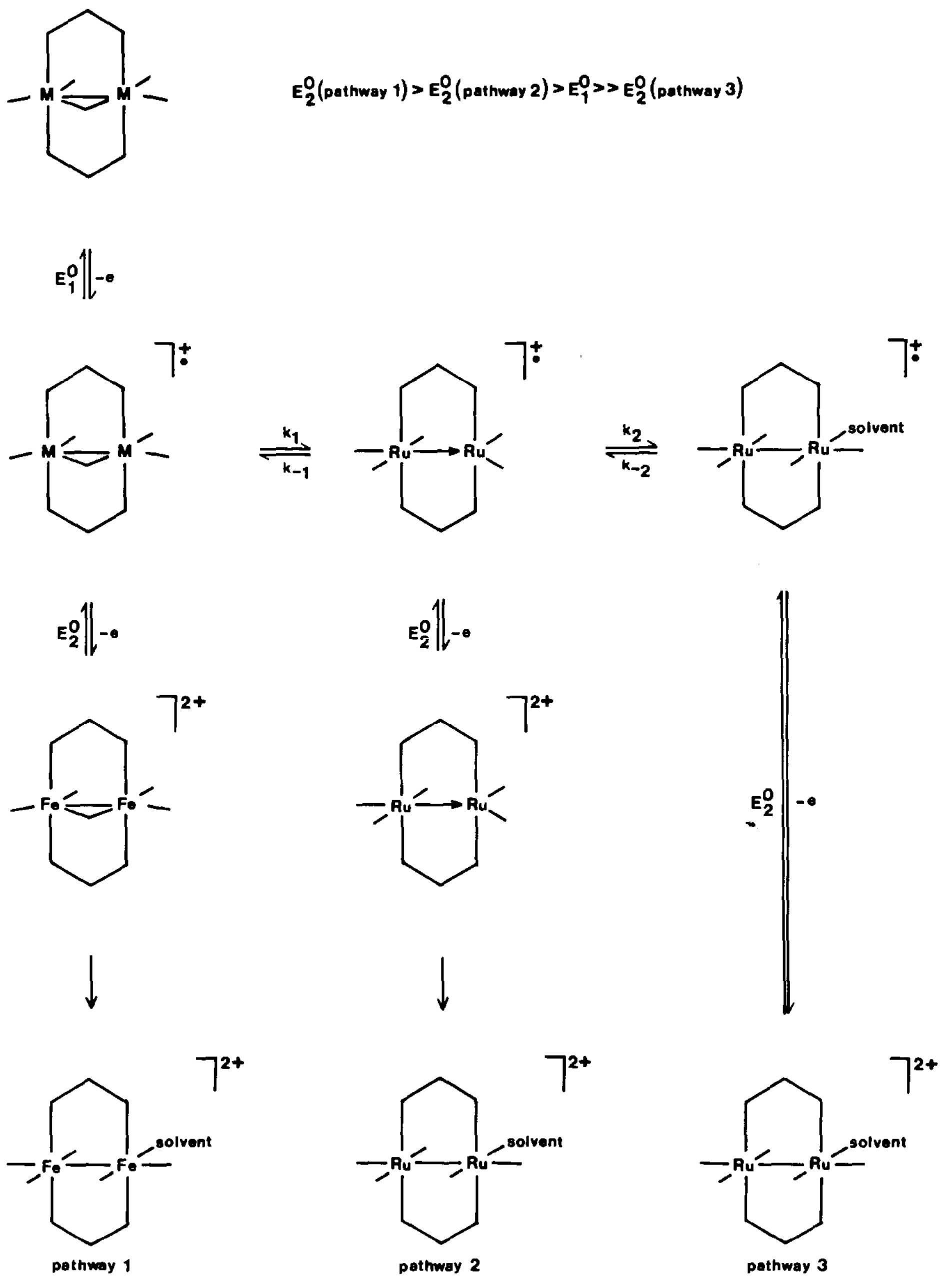
Compounds **2b** and **2c** have in common that the bridging bidentate ligands are relatively small in size, at least compared to the tetraisopropoxydiphosphazane ligand of **2a**. In order to test the hypothesis that the steric bulk of the bridging diphosphorus ligand plays a crucial role in determining the extent of attack by the solvent at a ruthenium atom centre in the radical cation, the mixed ligand complex, **3**, which contains both the bulky tetraisopropoxydiphosphazane and the less bulky tetramethoxydiphosphazane ligands, was prepared and its CV recorded in a range of solvents. Figure 5 shows the CV of **3** in benzonitrile. The form of the CV is very similar to that observed for the majority of the di-iron complexes but, significantly, the primary oxidation wave has an i_{pc}/i_{pa} value of 0.8; thus it is not fully reversible the implication being that the radical cation **3**$\cdot^+$ is not wholly stable on the time-scale of the experiment. Consistent with this interpretation is the observation that, when the scan is carried just past the primary oxidation peak and reversed, the familiar peak, X due to the reduction of a dicationic solvento species, is observed as a small wave (Fig. 5). It would appear that **3**$\cdot^+$ is attacked by the benzonitrile but relatively slowly. Extending the scan past the primary oxidation wave by slightly more than 0.5 V reveals a second broad and irreversible oxidation wave as well as a significant enhancement in the height of peak X. Thus the CV of **3** recorded in benzonitrile displays features of both the EEC mechanism observed for the di-iron complexes and the ECE mechanism observed for the diruthenium complex, **2b** (*vide supra*). In contrast, the CV's of **3** recorded in acetone and dichloromethane are similar in appearance to the CV's of **2a** in respect of the small separation between the first and second oxidation waves (0.31 and 0.10 V respectively, see Table 1). However, the primary oxidation wave is not fully reversible exhibiting an i_{pc}/i_{pa} value of ~ 0.8 which indicates that the radical cation $\mathbf{3}^{\bullet +}$ is attacked to some extent by acetone and dichloromethane as well. Thus the CV's of **3** in these solvents also display features of the ECE mechanism but, in addition, features of the mechanism utilized in the oxidation of **2a** (discussed below) are shown.

Finally, with regard to the electrochemistry of the diruthenium complexes **2a**–**c** and **3** it is noteworthy that the ease of oxidation follows the trend expected on the basis of the electron donating ability of the bridging bidentate ligand. As evidenced by the potential data given in Table 1 the order of ease of oxidation in a particular solvent is **2b** < **3** < **2a** < **2c**.

Mechanism of the electrochemical oxidation of 1a–f, 2a–c and 3

Scheme 2 gives the proposed overall mechanism of the electrochemical oxidation of the di-iron and diruthenium complexes discussed in this work. The essential feature of Scheme 2 is that, following the primary oxidation step, there are three possible pathways to the inevitable end-product of the oxidation process viz. a dicationic solvento species of general formula $[M_2(CO)_5(\text{solvent})\{\mu\text{-}(L\text{–}L)\}_2]^{2+}$ (M = Fe or Ru; L–L = bridging diphosphorus ligand). The form of the CV depends on which pathway is utilized and, more specifically, on the potential required to remove the second electron. As will now be discussed, the pathway taken by a particular complex appears to be determined by the extent to which the metal atom centre in the radical cation is open to attack by a solvent molecule.

With regard to the di-iron complexes **1a**–**f** pathway 1 is utilized. Here the radical cation initially formed does not react with the solvent and is further oxidized to the dication at a potential which is considerably more anodic than the primary oxidation potential. Indeed, the observed potential differences of ⩾ 0.5 V between the first and second oxidation waves (Table 1), are typical of the separations between successive one-electron redox steps which do not have a structural reorganization or some chemical step between them, i.e. coulombic and solvation effects alone determine the potentials [14]. Once the dication is formed, the solvent immediately coordinates to the iron atom, with a concomitant rearrangement of the carbonyl groups to form a dicationic solvento species, probably with the same structure as the diruthenium analogues, $\mathbf{4a}^{2+}$ etc. [15*]. The high reactivity of the dication towards the solvent is presumably because it is a 32e species, which would be expected to react readily with a 2e-donor solvent molecule. An exception is provided by the dication of the dppm complex, $\mathbf{1f}^{2+}$, which resists attack by the weakly coordinating solvents, acetone and dichloromethane, as evidenced by a second oxidation wave which is reversible in acetone and nearly reversible in dichloromethane (Table 1). We suggest that the inertness of $\mathbf{1f}^{2+}$ in particular to solvent attack, is due to the presence of the bulky phenyl groups of the dppm ligand, which effectively block attack by the solvent molecule at the iron atom centre. Clearly, the coordinating ability of the solvent is also a factor since $\mathbf{1f}^{2+}$ is rapidly attacked by the more strongly coordinating solvent, benzonitrile, as evidenced by a second oxidation wave which is irreversible in this solvent.



Scheme 2.

As noted above, the electrochemical oxidation of the diruthenium complex **2a** proceeds in all solvents in two one-electron steps, the first reversible, the second irreversible (Fig. 3) with a small separation between the two waves (Table 1). Because of this small difference it would appear that the radical cation $\mathbf{2a}^{\bullet +}$ undergoes some chemical transformation which makes it easier to oxidize than otherwise would be expected. In addition, the chemical step must be a reversible one (i_{pc}/i_{pa} 1.0). We propose (see Scheme 2) that the radical cation rearranges rapidly and reversibly (k_1 and k_{-1} very large) to give an intermediate in which all the carbonyls are terminally bonded but which does not have the solvent formally coordinated. This intermediate is then oxidized in the second electron-transfer to give the dication, which is immediately and irreversibly attacked by the solvent to form the dicationic solvento species **4a**$^{2+}$ (solvent = PhCN, Me_2CO or CH_2Cl_2) i.e., the electrochemical oxidation of **2a** proceeds via pathway 2 and an ECEC mechanism for which the first chemical step involves a structural rearrangement and the second solvent attack. The proposed intermediate is distinguished by the presence of five terminal carbonyls and no bridging carbonyls as opposed to four terminal carbonyls and one bridging carbonyl in the radical cation **2**$^{\bullet +}$ and, for this reason, is expected to be more electron-rich than **2a**$^{\bullet +}$ and therefore more easily oxidized. This accounts for the fact that, in the electrochemical oxidation of **2a**, the potential required to remove the second electron (E_2°) is not much greater than the potential required to remove the first electron (E_1°). Of course the all terminal carbonyl intermediate proposed in Scheme 2 would be expected to be susceptible to solvent attack because it is a 33e species with a vacant coordination site. Scheme 2 allows for such a solvolysis reaction which is reversible; whether or not this occurs will depend on the magnitude of k_2. As far as the electrochemical oxidation of **2a** is concerned, k_2 appears to be small since there is no evidence for irreversibility in the primary oxidation wave nor for the formation of a solvento species in any of the chosen solvents, at least not following the primary oxidation. We suggest that it is because of steric bulk of the tetraisopropoxydiphosphazane ligand in **2a** that solvent attack at a ruthenium atom of the radical cation is hindered.

A somewhat different situation is encountered with the diruthenium complexes **2b** and **2c**. Here the bridging ligands are smaller and less sterically demanding and, for this reason, the radical cations formed by these two complexes might be expected to be highly reactive towards the solvent (k_1 and k_2 large). Should this be the case, the solvento cation which forms, being a 35e species and therefore destabilized relative to **2b**$^{\bullet +}$ and **2c**$^{\bullet +}$, must be oxidized at a potential (E_2°) cathodic to the potential required for the removal of the first electron (E_1°). An irreversible 2e-transfer with the formation of a dicationic solvento species is predicted. As noted above, this is indeed observed for the electrochemical oxidation of **2b** in benzonitrile and acetone and **2c** in benzonitrile, and they are therefore proposed to be oxidized via pathway 3 and an ECE mechanism in these solvents. On the other hand, the oxidation of **2b** in dichloromethane proceeds via an EEC mechanism (*vide supra*), the implication being that the radical cation **2b**$^{\bullet +}$ is stable in this solvent, presumably because dichloromethane is very weakly coordinating if it coordinates at all.

With regard to the mixed ligand complex **3**, more than one pathway of Scheme 2 appears to be utilized probably reflecting the presence of both a large and a small diphosphazane ligand in the complex. As described above, the primary oxidation wave is not fully reversible with i_{pc}/i_{pa} values of 0.8 for all three solvents benzonitrile, acetone and dichloromethane (Table 1). Moreover, reversal of the positive scan after the primary oxidation wave and before the onset of the second oxidation wave reveals the familiar peak (X) due to the reduction of the dicationic solvento species (Fig. 5). Thus, it is apparent that pathway 3 is utilized in all three solvents, but not exclusively, because the primary oxidation wave is followed by a second, broad and irreversible oxidation wave when the positive scan is extended. In the case of the coordinating solvent benzonitrile, the rate constant for solvent attack, k_2 (see Scheme 2) would be expected to be relatively large but, in view of the peak separations between the first and second oxidation waves being quite large in benzonitrile (> 0.5 V) it would appear that k_1 (see Scheme 2) is relatively small in this solvent. Thus, pathway 1, rather than pathway 2 (for which $E_1^\circ - E_2^\circ$ is expected to be small, *vide supra*) is utilized in addition to pathway 3. In the case of the weakly coordinating solvents, acetone and dichloromethane, k_2 is expected to be small but, evidently k_1 is large since pathway 2 rather than pathway 1 is also utilized, as evidenced by the small separations between the two oxidation waves (Table 1).

Conclusions

The available data appear to be consistent with the mechanism proposed in Scheme 2 for the electrochemical oxidation of the tetrasubstituted derivatives of $[Fe_2(CO)_9]$ and $[Ru_2(CO)_9]$ described in this work. The pathway adopted is dependent on the metal, the bridging diphosphorus ligand, in particular on its size, and on the coordinating ability of the solvent. The fact that a ruthenium atom is somewhat larger (covalent radius 1.26 Å [16]) than an iron atom (covalent radius 1.20 Å [16]) implies that there is less steric crowding in the diruthenium as opposed to the di-iron complexes. It is probably for this reason that the electrochemistry of the di-iron complexes is uncomplicated by the attack of solvent at the iron atom centre in the radical cation. In contrast, the ruthenium atom centre in the radical cation is more accessible to solvent attack which has as a result that more than one pathway is available for the electrochemical oxidation of the diruthenium complexes [17*].

Experimental

Compounds **1a–f**, **2a–b** [1] and **4a–c**,$(SbF_6)_2$ [5], were synthesized according to the published procedures. Compound **2c** was provided by Johnson and Gladfelter [2]. Prior to each measurement, the purity of all samples was checked by recording their IR spectra in solution with a Perkin-Elmer 457 spectrometer.

Synthesis of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}({}^iPrO)_2PN(Et)P(O^iPr)_2\}\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}]$, *3*

A mixture of $[Ru_3(CO)_{10}\{\mu\text{-}({}^iPrO)_2PN(Et)P(O^iPr)_2\}]$ [1] (0.200 g, 0.216 mmol) and $(MeO)_2PN(Et)P(OMe)_2$ (0.148 g, 0.433 mmol) in ether (150 ml) was irradiated with ultraviolet light for 30 min. After removal of the solvent under reduced pressure, the orange oily residue was dissolved in warm methanol (5 ml, 40°C) and kept at −25°C for 15 h. Yellow crystals of the title compound precipitated from solution. Yield: 0.100 g, 50%. Anal. Found: C, 32.7; H, 5.6; N, 3.1. $C_{25}H_{50}N_2O_{13}P_4Ru_2$ calc.: C, 32.9; H, 5.5;N, 3.1%. IR: ν(CO) (C_6H_{12}); 1955s, 1947s, 1917s, 1986vs, 1718s cm^{-1}. ^1H NMR $(C_6D_6$, 22°C): δ 1.14–1.52 (m, 30H); 3.10–3.20 (m, 2H); 3.40–3.45 (m, 10H); 4.01–4.07 (m, 4H); 4.60–4.70 (m, 2H); 5.40–5.55 (m, 2H). ^{31}P NMR $(C_6D_6$, 34°C): δ 156.5 (centre of AA′BB′ pattern).

Electrochemical procedures

The electrochemical techniques employed were direct current rotating disc electrode (RDE) and cyclic voltammetry. A PAR 175 universal programmer, a PAR 173 potentiostat fitted with a PAR 176 current follower and connected to a HP 7045A X-Y recorder, were used for the RDE and cyclic voltammetric measurements. All measurements were made under an argon atmosphere in benzonitrile, dichloromethane or acetone. The solvents were purified by refluxing over P_2O_5, followed by at least two fractional distillations through a 1 m glass-helice vacuum-jacketed column (at 10 mmHg for benzonitrile and at atmospheric pressure for dichloromethane and acetone). The acetone was stored over Type 4A molecular sieve while the dichloromethane was stored and used only in the dark. The supporting electrolyte for all solvents was Bu_4NClO_4 (TBAP) present in 0.1 *M* concentration; the salt was purified by repeated crystallizations from ethanol/water mixtures and dried at 80°C and 10^{-2} mmHg. The purity of the solvent system was checked by running a blank voltammogram before each measurement. Compound concentrations were always 0.001 ± 0.0001 *M*.

All the experiments employed a conventional three-electrode configuration, with a platinum spiral wire auxiliary electrode [18*] and a reference electrode comprising a AgCl-coated Ag wire [18*] both dipped in a 0.1 *M* solution of Bu_4NClO_4 in the relevant solvent and separated from the electrolyte solution by a fine frit. All potentials are quoted relative to the Ag/AgCl reference electrode against which the $[\text{ferrocene}]^{+/0}$ couple has the following $E_{1/2}$ values:

0.44 V in benzonitrile ($\Delta E_p = 75$ mV at 100 mV s^{-1});
0.44 V in dichloromethane ($\Delta E_p = 80$ mV at 100 mV s^{-1});
0.52 V in acetone ($\Delta E_p = 60$ mV at 100 mV s^{-1}).

Ferrocene was usually added to the solution under investigation at the end of each experiment as an internal standard to check on the stability of the reference electrode. In cases where this was not possible, e.g. when oxidation waves from the sample interfered with that of the $[\text{ferrocene}]^{+/0}$ couple, ferrocene was run immediately before, or after, the experiment under identical conditions. No compensation for IR drop losses was made and thus the above peak-to-peak separations (ΔE_p values) were taken as the diffusion-controlled parameter for the particular solvent. The working electrode was a platinum disc electrode (0.013 cm^2) [18*] which was rotated at 500 rpm for the RDE voltammograms. Its surface was polished with 2–6 μm diamond paste until no scratches were observed at tenfold magnification. Before being inserted into the solution, the electrode was rinsed with acetone and distilled water and dried in a warm dry air stream. Measurements were made at 25 ± 2°C, temperature control being achieved by careful operation of an air-conditioning unit in a closed laboratory.

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