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Redox potential, ligand and structural effects in rhodium(I) complexes

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Abstract

The electrochemical behaviour of the set of tetracoordinate rhodium(I) complexes $[\mathrm{Rh}(\mathrm{O}{\frown}\mathrm{O})(\mathrm{CO})\mathrm{L}]$ [$\mathrm{O}{\frown}\mathrm{O} = \mathrm{MeC(O)CHC(O)Me}$ (acac), L = CO (**1**), $\mathrm{P(NC_4H_4)_3}$ (**2**), $\mathrm{PPh(NC_4H_4)_2}$ (**3**), $\mathrm{PPh_2(NC_4H_4)}$ (**4**), $\mathrm{PPh_3}$ (**5**), $\mathrm{PCy_3}$ (**6**), $\mathrm{P(OPh)_3}$ (**7**) or $\mathrm{PPh_2(C_6H_4OMe\text{-}4)}$ (**8**); $\mathrm{O}{\frown}\mathrm{O} = \mathrm{PhC(O)CHC(O)Me}$ (bac), L = CO (**9**) or $\mathrm{PPh_3}$ (**10**); $\mathrm{O}{\frown}\mathrm{O} = \mathrm{PhC(O)CHC(O)CF_3}$(bta), L = CO (**11**) or $\mathrm{PPh_3}$ (**12**)] and of the pentacoordinate $[\mathrm{RhH(CO)L_3}]$ [L = $\mathrm{P(NC_4H_4)_3}$ (**13**), $\mathrm{PPh_3}$ (**14**), $\mathrm{P(OPh)_3}$ (**15**) or $\mathrm{P(OC_6H_4Me\text{-}4)_3}$ (**16**)] and $[\mathrm{RhHL_4}]$ [L = $\mathrm{PPh_3}$ (**17**) or $\mathrm{P(OC_6H_4Me\text{-}3)_3}$ (**18**)] was studied by cyclic voltammetry and controlled potential electrolysis, in aprotic medium, at a Pt electrode. They present a single-electron oxidation wave (I) (irreversible or quasi-reversible) that can be followed, at a higher potential, by a second and irreversible one (II). The values of first oxidation potential for the tetracoordinate complexes fit the additive Lever's electrochemical parameterisation, and the ligand electrochemical Lever E_L and Pickett P_L parameters were estimated for the *N*-pyrrolyl phosphines $\mathrm{PPh}_n(\mathrm{NC_4H_4})_{3-n}$ ($n = 0$, 1 or 2) and for the organophosphines $\mathrm{PCy_3}$ and $\mathrm{PPh_2(C_6H_4OMe\text{-}4)}$, the former behaving as weaker net electron donors (the electron donor ability decreases with the increase of the number of *N*-pyrrolyl groups) than the latter phosphines. The pentacoordinate hydride complexes **13**–**18** fit a distinct relationship which enabled the estimate of the E_L ligand parameter for the phosphites $\mathrm{P(OC_6H_4Me\text{-}3)_3}$ and $\mathrm{P(OC_6H_4Me\text{-}4)_3}$. Electrochemical metal site parameters were obtained for the square planar and the pentacoordinate Rh(I)/Rh(II) couples and, for the former, the redox potential is shown to present a much higher sensitivity to a change of a ligand than the octahedral redox couples investigated so far. Linear relationships were also observed between the oxidation potential and the P_L ligand parameter (for the series [Rh(acac)(CO)L]) or the infrared ν(CO) frequency, and a generalisation of the former type of correlation is proposed for series of square-planar 16-electron complexes $[\mathrm{M'_SL}]$ with a common 14-electron T-shaped binding metal centre $\{\mathrm{M'_S}\}$. Oxidation of **5** by $\mathrm{Ag[PF_6]}$ leads to the dimerisation of the derived Rh(II) species. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Redox potential–structure relationships; Electrochemistry; Electrochemical parameters; Ligand effects; Rhodium complexes; *N*-Pyrrolyl phosphines

1. Introduction

In spite of the relevance of rhodium complexes in homogeneous catalysis in processes involving, along the catalytic cycle [1], changes in the metal oxidation state of active species, the detailed investigation of their redox properties towards the establishment of redox potential–structure relationships has not yet been explored, although a recent work in this field has been reported by Werner et al. [2]. This contrasts with the cases of a wide variety of hexacoordinate octahedral-type complexes with other transition metals which have already been the object of systematic electrochemical studies that allowed to quantify the effects of ligands and binding metal sites on the redox potential and to propose expressions with predictive value [2–7].

In this paper we wish to report the results of a cyclic voltammetric study of sets of rhodium(I) complexes aiming to find trends in their oxidation potential and

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structural relationships and to recognise analogies of behaviour with that of octahedral-type complexes, in particular with a closed-shell electronic configuration, in order to extend to square-planar 16-electron and square-pyramid 18-electron complexes the parameterisation methods already established for the octahedral ones.

2. Results and discussion

The cyclic voltammograms of the following rhodium(I) complexes were run in 0.2 mol dm^{-3} $[NBu_4][BF_4]/CH_2Cl_2$ (or NCMe), at a Pt-disc electrode: the tetracoordinate square-planar diketonato compounds [Rh(O⌒O)(CO)L] [O⌒O = MeC(O)CHC(O)Me (acac), L = CO (**1**), $P(NC_4H_4)_3$ (**2**), $PPh(NC_4H_4)_2$ (**3**), $PPh_2(NC_4H_4)$ (**4**), PPh_3 (**5**), PCy_3 (**6**), $P(OPh)_3$ (**7**) or $PPh_2(C_6H_4OMe\text{-}4)$ (**8**); O⌒O = PhC(O)CHC(O)Me (bac), L = CO (**9**) or PPh_3 (**10**); O⌒O = $PhC(O)CHC(O)CF_3$ (bta), L = CO (**11**) or PPh_3 (**12**)], and the pentacoordinate hydrides $[RhH(CO)L_3]$ [L = $P(NC_4H_4)_3$ (**13**), PPh_3 (**14**), $P(OPh)_3$ (**15**) or $P(OC_6H_4Me\text{-}4)_3$ (**16**)] and $[RhHL_4]$ [L = PPh_3 (**17**) or $P(OC_6H_4Me\text{-}3)_3$ (**18**)]. They exhibit, at 200 mV s^{-1} (Tables 1 and 2), with the exception of **11**, an irre-

Table 1
Cyclic voltammetric data for the rhodium(I) complexes [Rh(OO)(CO)L] (**1**–**12**) and estimated E_L and P_L ligand parameters for L ligands[a]

Complex	O⌒O	L	${}^{I}E^{ox}_{p/2}$	${}^{II}E^{ox}_{p}$	$E^{red}_{p/2}$	E_L (L)	P_L (L)
1[b]	acac	CO	2.14	2.77			
2[c]		$P(NC_4H_4)_3$	1.65			0.69	−0.05
3[d]		$PPh(NC_4H_4)_2$	1.47	1.94		0.60	−0.16
4[e]		$PPh_2(NC_4H_4)$	1.33	1.85		0.53	−0.24
5		PPh_3	1.29				
6		PCy_3	1.21	1.78		0.45	−0.41
7[f]		$P(OPh)_3$	1.48				
8		$PPh_2(C_6H_4OMe\text{-}4)$	1.06	1.57		0.40	−0.39
9	bac	CO	2.44		−1.31		
10[g]		PPh_3	1.29		−1.62		
11	bta	CO			−0.85[h]		
12[i]		PPh_3	1.42		−1.25[j]		

[a] Potentials ($E_{p/2}$ = half-peak potential, E_p = peak potential, for irreversible waves) in V ± 0.02 versus NHE measured at a scan rate of 0.2 V s^{-1}, in 0.2 mol dm^{-3} $[NBu_4][BF_4]/CH_2Cl_2$ (or NCMe for compounds **1**, **9** and **11**); E_L(L) (V versus NHE) estimated from Eq. (2) (Fig. 1(a)) and the known values of E_L for the other ligands; P_L(L) (V) estimated from the corresponding E_L(L) value (Eq. (4)).

[b] Two other irreversible oxidation waves (not always resolved), with lower and irreproducible peak currents, are observed, but only in the first anodic scan, at E^{ox}_p ca. 1.2 and 1.5 V versus NHE, without appearing in subsequent multiple CV scans, conceivably being associated with adsorption effects.

[c] On scan reversal, following the oxidation waves, a reduction one is detected at $E^{red}_p = -0.86$ V.

[d] On scan reversal, following the oxidation waves, a reduction one is detected at $E^{red}_p = -1.15$ V.

[e] On scan reversal, following the oxidation waves, a reduction one is detected at $E^{red}_p = -1.18$ V.

[f] On scan reversal, following the oxidation wave, a reduction one is detected at $E^{red}_p = -1.40$ V.

[g] On scan reversal, following the reduction wave, an oxidation one is detected at $E^{ox}_p = 1.12$ V.

[h] A second irreversible wave is observed at $E^{red}_{p/2} = -1.27$ V.

[i] On scan reversal, following the reduction wave, an oxidation one is detected at $E^{ox}_p = 1.00$ V.

[j] Reversible wave ($E^{red}_{1/2}$).

Table 2
Cyclic voltammetric data for the rhodium(I) pentacoordinate complexes $[RhH(CO)L_3]$ (**13**–**16**) and $[RhHL_4]$ (**17**–**18**), and estimated E_L and P_L ligand parameters for L ligands[a]

Complex	L	${}^{I}E^{ox}_{p/2}$ (${}^{I}E^{ox}_{1/2}$)	${}^{II}E^{ox}_{p}$	E_L (L)	P_L (L)
13	$P(NC_4H_4)_3$	1.37			
14	PPh_3	(0.34)	0.81		
15	$P(OPh)_3$	0.99			
16	$P(OC_6H_4Me\text{-}4)_3$	0.81	1.08	0.50	−0.28
17	PPh_3	0.20			
18	$P(OC_6H_4Me\text{-}3)_3$	(0.55)	1.08	0.54	−0.23

[a] Potentials ($E_{p/2}$ = half-peak potential, $E_{1/2}$ = half-wave peak potential, E_p = peak potential) in V ± 0.02 versus NHE measured at a scan rate of 0.2 V s^{-1}, in 0.2 mol dm^{-3} $[NBu_4][BF_4]/CH_2Cl_2$; E_L(L) (V versus NHE) estimated from Eq. (3) (Fig. 1(b)) and the known values of E_L for the other ligands; P_L(L) (V) estimated from the corresponding E_L(L) value (Eq. (4)).

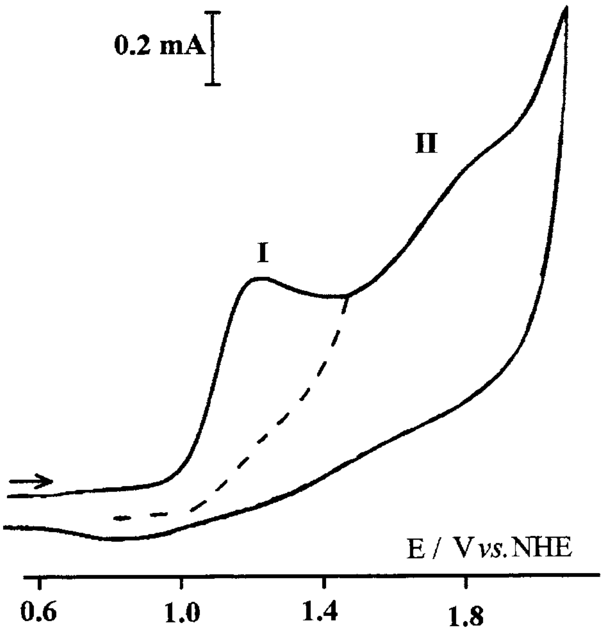

Fig. 1. Cyclic voltammogram of the tetracoordinate complex **6** (1.1 mmol dm^{-3} in CH_2Cl_2 with 0.2 mol dm^{-3} $[NBu_4][BF_4]$) at a platinum disc ($d = 0.5$ mm) working electrode and at a scan rate of 0.2 V s^{-1}.

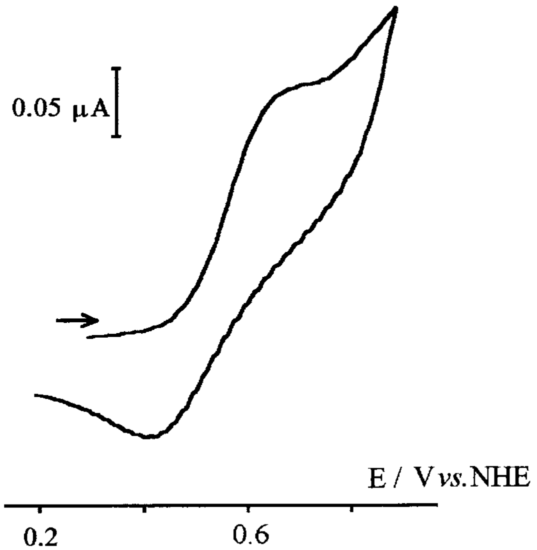

Fig. 2. Cyclic voltammogram of the hydride complex **18** (0.8 mmol dm^{-3} in CH_2Cl_2 with 0.2 mol dm^{-3} $[NBu_4][BF_4]$) at a platinum disc ($d = 0.5$ mm) working electrode and at a scan rate of 0.2 V s^{-1}.

versible (Fig. 1 for **6**), quasi-reversible (Fig. 2 for **18**) or fully reversible (complex **14**) oxidation wave (I) at ${}^{I}E^{ox}_{p/2}$ (or ${}^{I}E^{ox}_{1/2}$) in the 0.20–2.44 V versus NHE range, which in some cases is followed, at a higher potential (${}^{II}E^{ox}_{p}$ in the range 0.57–2.77 V) by a second irreversible one (wave II). Increasing the scan rate results, in the cases of the hydride complexes, in an increase (or appearance of some degree) of reversibility, as shown in Fig. 3 for **13**. However, for the tetracoordinate complexes, the reversibility was not achieved even by fast scanning at least until 500 V s^{-1} (the use of faster scan rates was prevented by the loss of definition of the wave) at microelectrodes and lowering the temperature up to −40°C.

The electrode process at wave I is believed to involve a single electron, i.e. the Rh(I) → Rh(II) oxidation, as known to occur for the related complexes $[RhCl(L)(PPr^i_3)_2]$ [L = CPh_2 (**1′**); C=CPh_2 (**2′**); C=C=CPh_2 (**3′**); CO (**4′**); and C_2H_4 (**5′**)] [2] and $[RhH(CO)(PPh_3)_3]$ (**14**) [8]. This was confirmed in some cases by anodic controlled potential electrolysis (e.g. for the bac and bta complexes **9**, **10** and **12**) and by chronoamperometry (for those complexes and for other members of both tetracoordinate and pentacoordinate series), but in many of the acac complexes the strong electrode passivation associated with the electrode process prevented the determination of the number of electrons by controlled potential electrolysis or by other techniques such as steady state cyclic voltammetry coupled to chronoamperometry [9]. The oxidation waves of the dicarbonyl complexes **1** and **9** were detected only in NCMe, a solvent which allows a wider anodic potential window to be studied, relative to CH_2Cl_2, but for **11**, with the expected highest oxidation potential, no anodic wave was found before the onset of the solvent–electrolyte discharge potential. For **1**, two other irreversible oxidation waves (not always resolved), with irreproducible and lower peak currents, were observed at lower potentials (E^{ox}_{p} ca. 1.2 and 1.5 V) than that of wave I (${}^{I}E^{ox}_{p/2} = 2.14$ V) but only in the first anodic scan; in contrast to wave I, they do not appear in subsequent multiple cyclic voltammetric scans and conceivably are associated with adsorption effects.

The bac (**9** and **10**) and bta (**11** and **12**) complexes present an irreversible (or partially reversible for **12**, at a scan rate of 0.2 V s^{-1}) reduction wave at $E^{red}_{p/2}$ in the −0.85 to −1.31 V range, but the accurate determination of the number of electrons exchanged in the cathodic process was not possible due to the electrode passivation.

The oxidation potential of the first anodic process of the complexes reflects the relative electron donor–acceptor abilities of the ligands as measured by the electrochemical E_L ligand parameter proposed by Lever [3] for which the empirical linear correlation (Eq. (1)) was shown to be followed by many redox couples. The redox potential of the complex (E) is expressed in V versus NHE, ΣE_L is the sum of the E_L values for all the ligands (additive effects), whereas S_M and I_M depend upon the metal and redox couple, the spin state and stereochemistry.

$$E = S_M \times (\Sigma E_L) + I_M \qquad (1)$$

In fact, for our tetracoordinate complexes with ligands with known [3a] E_L values (**1**, **5**, **7**, **9**, **10** and **12**),

$^{I}E^{ox}_{p/2}$ varies linearly with ΣE_L as shown by the plot of Fig. 4(a) which also comprises the data reported by Werner et al. [2] for the Rh(I) complexes [RhCl(L)(PPr$^i_3$)$_2$] [L = CPh_2 (**1′**), C=CPh_2 (**2′**), C=C=CPh_2 (**3′**), CO (**4′**) and C_2H_4 (**5′**)]. This relationship is expressed by Eq. (2) ($r = 0.98$) which allows the estimate of S_M and I_M (compare with Eq. (1)) for the square-planar Rh(I)/Rh(II) redox couples: $S_M = 1.93$ and $I_M = -1.29$ V versus NHE. These values agree with those previously proposed (1.83 and −1.22 V, respectively) [2] on the basis of the data for the fewer chloro-rhodium(I) complexes shown above (**1′**–**5′**).

$$E^{ox}_{p/2} = 1.93 \times \Sigma E_L - 1.29 \qquad (2)$$

The value determined for S_M, 1.93, is quite high, being normally well above those reported (in the 0.38–1.61 range) [3] for the hexacoordinate redox couples studied so far. This indicates that the oxidation potential (thus the energy of the HOMO) of the square planar Rh(I)/Rh(II) redox centres exhibits a much

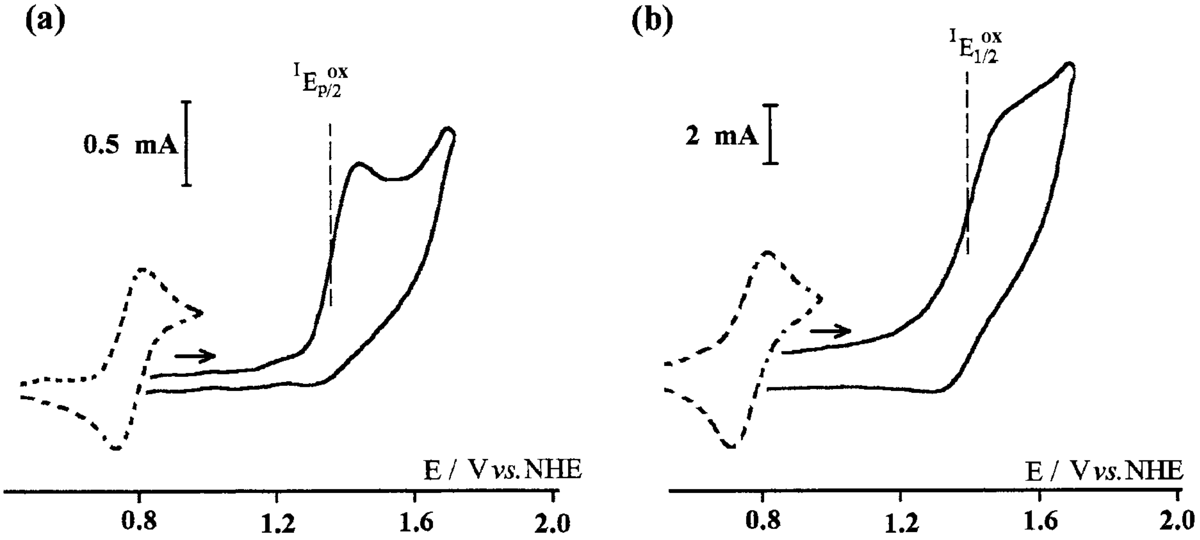

Fig. 3. Cyclic voltammograms of the hydride complex **13** (1.3 mmol dm^{-3} in CH_2Cl_2 with 0.2 mol dm^{-3} [NBu_4][BF_4]) at a platinum disc ($d = 0.5$ mm) working electrode at scan rates of 0.2 V s^{-1} (a) and 8.0 V s^{-1} (b). The reversible wave for ferrocene is also shown in dashed line for comparative purposes.

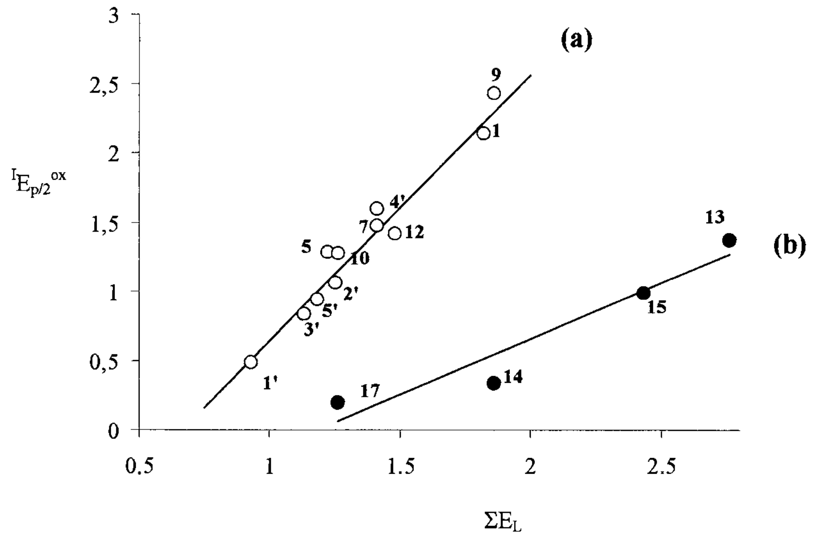

Fig. 4. Plot of $^{I}E^{ox}_{p/2}$ (V versus NHE) versus ΣE_L (V versus NHE): (a) for the tetracoordinate complexes [Rh(O⌒O)(CO)(L)] [O⌒O = acac, L = CO (**1**), PPh_3 (**5**), $P(OPh)_3$ (**7**). O⌒O = bac, L = CO (**9**) and PPh_3 (**10**). O⌒O = bta, L = PPh_3 (**12**)] (this study) and [RhCl(L)(PPr$^i_3$)$_2$] [L = CPh_2 (**1′**), C = CPh_2 (**2′**), C = C = CPh_2 (**3′**), CO (**4′**) and C_2H_4 (**5′**)] [2]; (b) for the pentacoordinate hydride complexes [RhH(CO)L_3] [L = $P(NC_4H_4)_3$ (**13**), PPh_3 (**14**), $P(OPh)_3$ (**15**)] and [RhHL_4] [L = PPh_3 (**17**)]. E_L(L) values (V versus NHE) taken from the literature for L = H (−0.30) [3a], acac (−0.08) [3a], bac (−0.06) [3a], bta (0.05) [3a], CO (0.99) [3a], PPh_3 (0.39) [3a], $P(OPh)_3$ (0.58) [3a], C_2H_4 (0.76) [3a], CPh_2 (0.51) [2], C=CPh_2 (0.83) [2] and C=C=CPh_2 (0.71) [2].

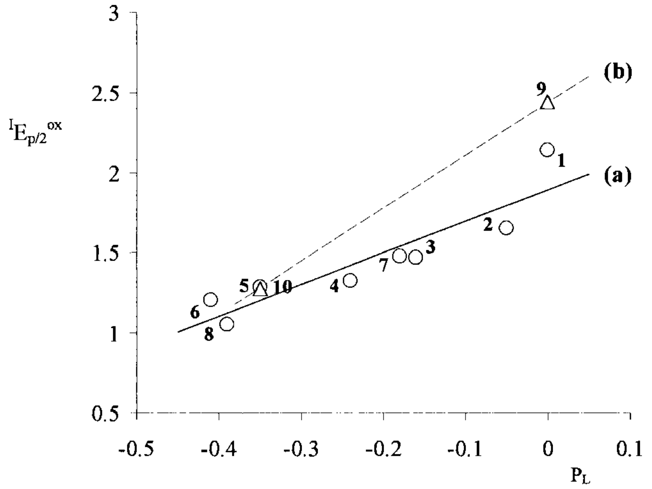

Fig. 5. Plots of ${}^{I}E^{ox}_{p/2}$ (V versus NHE) versus P_L (V): (a) For [Rh(acac)(CO)L] [L = CO (**1**), $P(NC_4H_4)_3$ (**2**), $PPh(NC_4H_4)_2$ (**3**), $PPh_2(NC_4H_4)$ (**4**), PPh_3 (**5**), PCy_3 (**6**), $P(OPh)_3$ (**7**) or $PPh_2(C_6H_4OMe\text{-}4)$ (**8**)] (○). (b) For [Rh(bac)(CO)L] [L = CO (**9**) or PPh_3 (**10**)] (△).

higher sensitivity, in comparison with the octahedral metal centres, to a change of the ligands. Hence, the ligand effects on the redox potential are more pronounced at the Rh(I) square planar sites than at the octahedral centres. However, further study on a variety of square-planar transition metal complexes is required before the generality of such a relative behaviour can be proposed.

The hydride pentacoordinate complexes $[RhH(CO)L_3]$ (**13**–**16**) and $[RhHL_4]$ (**17** and **18**) do not fit the above linear relationship for the square planar complexes, since S_M and I_M are dependent on the stereochemistry. A distinct linear correlation (Fig. 4(b)) is followed by the pentacoordinate Rh(I)/Rh(II) redox couples (Eq. (3), $r = 0.96$), which enabled the estimate of the corresponding S_M and I_M.

$$E^{ox}_{p/2} = 0.80 \times \Sigma E_L - 0.95 \qquad (3)$$

From the application of Eq. (2) to the complexes **2**–**4**, **6** and **8**, and of Eq. (3) to **16** and **18**, and taking into account their measured ${}^{I}E^{ox}_{p/2}$ (or ${}^{I}E^{ox}_{1/2}$) values and the known [3a] E_L values for the acac (−0.08 V), PPh_3 (0.39 V), $P(OPh)_3$ (0.58 V) and CO (0.99 V) ligands, it was possible to estimate the previously unknown E_L values for the following *N*-pyrrolyl phosphines, organophosphines and phosphites (Tables 1 and 2), ordered according to their net electron donor ability: $P(NC_4H_4)_3$ ($E_L = 0.69$ V) < $PPh(NC_4H_4)_2$ ($E_L = 0.60$ V) < $PPh_2(NC_4H_4)$ ($E_L = 0.53$ V) ≈ $P(OC_6H_4Me\text{-}3)_3$ ($E_L = 0.54$ V) < $P(OC_6H_4Me\text{-}4)_3$ ($E_L = 0.50$ V) < PCy_3 ($E_L = 0.45$ V) < $PPh_2(C_6H_4OMe\text{-}4)$ ($E_L = 0.40$ V). Hence, the *N*-pyrrolyl phosphines generally behave as weaker net electron donors than the organo-phosphines or the phosphites, and the electron donor ability of the former decreases with the increase of the number of *N*-pyrrolyl groups.

From the linear expression (Eq. (4)) experimentally observed [3a] (for a considerable number of ligands except CO [3a] and other strong π-electron acceptors such as carbynes [6a]) between the electrochemical ligand parameters E_L and P_L, the latter defined by Pickett [4] as the difference $E^{ox}[Cr(CO)_5L] - E^{ox}[Cr(CO)_6]$ and considered as a measure of the net electron σ-donor minus π-acceptor ability of the ligand L (the lower this character the higher P_L), it was also possible to estimate the still unknown P_L values for the above phosphines or phosphites (Table 1): $P(NC_4H_4)_3$ ($P_L = -0.05$ V), $PPh(NC_4H_4)_2$ ($P_L = -0.16$ V), $P(OC_6H_4Me\text{-}3)_3$ ($P_L = -0.23$ V), $PPh_2(NC_4H_4)$ ($P_L = -0.24$ V), $P(OC_6H_4Me\text{-}4)_3$ ($P_L = -0.28$ V), PCy_3 ($P_L = -0.41$ V) and $PPh_2(C_6H_4OMe\text{-}4)$ ($P_L = -0.39$ V).

$$P_L = 1.17 \times E_L - 0.86 \qquad (4)$$

The oxidation potential of our set of acac complexes [Rh(acac)(CO)L] (**1**–**8**), with the common {Rh(acac)(CO)} metal centre, also correlates linearly with the P_L ligand parameter (Fig. 5(a), Eq. (5)) ($r = 0.91$) and this corresponds to the expression (Eq. (6)) proposed by Pickett [4] that relates the oxidation potential of the members of a series of 18-electron octahedral complexes $[M_sL]$ (with a common 16-electron $\{M_S\}$ site) with P_L for the variable L ligand. E_S is a measure of the electron-richness of the metal site and is expressed by the oxidation potential of the carbonyl complex $[M_S(CO)]$ (the higher E_S, the lower the electron-richness is), and β is a measure of the polarisability of the metal site.

$$E^{ox}_{p/2} = 1.89 + 1.96 \times P_L \qquad (5)$$

$$E^{ox}[M_SL] = E_S + \beta \times P_L \qquad (6)$$

By this analogy, 1.89 V versus NHE and 1.96 (Eq. (5)) represent the values of E_S and β, respectively, for the 14-electron {Rh(acac)(CO)} metal site, and both of them are rather high in comparison with nearly all the 16-electron $\{M_S\}$ centres whose E_S and β parameters have been reported [4,5]. Hence, the T-shaped 14-electron Rh(I) centre has a lower electron-richness and higher polarisability (in agreement with the high S_M value discussed above) than the latter metal sites.

These results suggest that, by analogy with the 18-electron octahedral complexes, the oxidation potential of 16-electron square planar complexes $[M'_SL]$ with a common 14-electron T-shaped metal centre $\{M'_S\}$ can be given by the general expression (Eq. (7)) in which the electron-richness of the site, $E_S\{M'_S\}$, is given by the oxidation potential of its carbonyl complex (Eq. (8)).

$$E^{ox}[M'_SL] = E_S\{M'_S\} + \beta\{M'_S\} \times P_L \qquad (7)$$

$$E_S\{M'_S\} = E^{ox}[M'_S(CO)] \qquad (8)$$

By applying Eq. (7) to any two complexes of the series, $[M'_SL]$ and $[M'_SL']$, and by taking into consideration the definition of P_L (see above), one can derive the expression (Eq. (9)) which indicates that the shift of the oxidation potential of the square-planar 16-electron complex resulting from the replacement of a ligand (L′) by another one (L) is proportional to the shift (equal to $P_L(L) - P_L(L')$, Eq. (10)) that occurs in the pentacarbonyl chromium series upon the replacement of L′ by L. One can anticipate that the generality of this proposal can present some limitations since we are comparing a series of non-isoelectronic complexes, but the current unavailability of redox potential data prevents the use of a series of square-planar 16-electron complexes as a reference for the definition of P_L instead of the pentacarbonylchromium one. Nevertheless, the approach proposed herein has the advantage of using the same definition of the P_L parameter and thus benefiting from the knowledge of its values for a wide variety of ligands [4,5] and allowing the direct estimate of others without requiring further relationships for conversion between the two types of structures.

$$E^{ox}[M'_SL] - E^{ox}[M'_SL']$$

$$= \beta\{M'_S\} \times \{E^{ox}[Cr(CO)_5L] - E^{ox}[Cr(CO)_5L']\} \quad (9)$$

$$E^{ox}[Cr(CO)_5L] - E^{ox}[Cr(CO)_5L'] = P_L(L) - P_L(L') \quad (10)$$

For the bac series of complexes, with the common {Rh(bac)(CO)} metal site, only two members are available (**9** and **10**) and therefore the obtained values of E_S (2.44 V) and β (3.31) for that site considering the plot of $^{I}E^{ox}_{p/2}$ versus P_L (Fig. 5(b)) should be considered only as rather preliminary ones. Another possible limitation of the current work concerns the use, for the irreversible process, of an oxidation potential which is not that of a reversible one. However, we believe that, in our systems, $E^{ox}_{p/2}$ does not differ appreciably from the thermodynamic potential (given by $E^{ox}_{1/2}$) in view of the following arguments: (i) for the hydride complexes, $E^{ox}_{p/2}$ measured for the irreversible wave at 200 mV s^{-1} is identical (within ± 0.05 V, i.e. the radius of the circles that represent the various complexes in the plots of Figs. 4 and 5) to $E^{ox}_{1/2}$ measured for the quasi-reversible wave observed at high scan rate (see Fig. 3); (ii) the measured $E^{ox}_{p/2}$ values are in accord with $E^{ox}_{1/2}$ for the fully reversible wave of **14** (see Fig. 4(b)); (iii) for the tetracoordinate complexes, the measured $E^{ox}_{p/2}$ values correlate well (Fig. 4(a)) with the $E^{ox}_{1/2}$ values quoted by Werner [2] for the reversible waves of the related complexes **1′**–**5′**, observed at high scan rates; (iv) the use of $E^{ox}_{p/2}$ for irreversible processes, instead of the inaccessible $E^{ox}_{1/2}$, has also been successfully applied to other complexes which also exhibit irreversible oxidation waves [6a,b,f,j]. Nevertheless, the proposed correlations and estimates of E_L (or P_L) values should be taken cautiously.

Other relationships were recognised between the oxidation potential and the infrared ν(CO) frequency (Fig. 6) for the tetracoordinated complexes **1**–**12** and the pentacoordinated **13**–**16**, the former parameter increasing roughly linearly with the latter. This can be accounted for by considering that a decrease in the π-electron acceptance of the carbonyl ligands to their π*-CO orbitals [increase of ν(CO)] corresponds to a lowering of the π-electron release ability of the binding

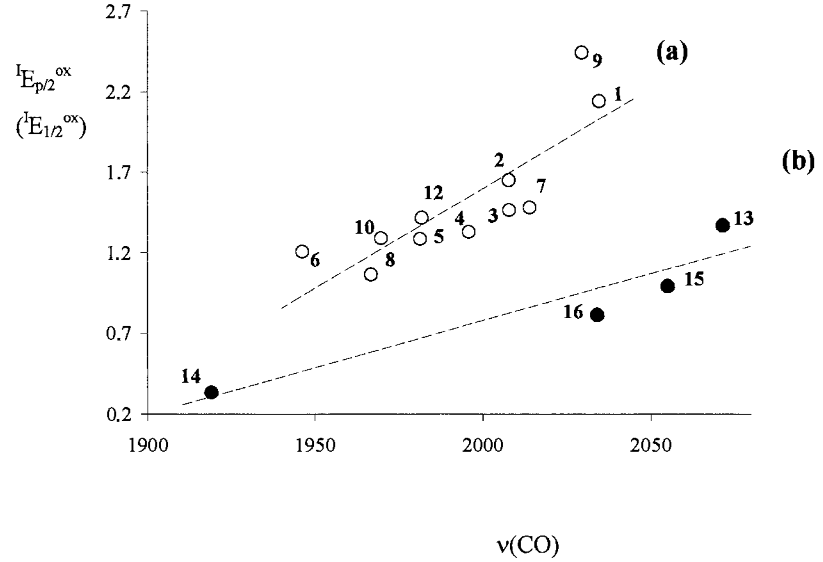

Fig. 6. Plot of $^{I}E^{ox}_{p/2}$ (or $^{I}E^{ox}_{1/2}$; in V versus NHE) versus ν(CO) (cm^{-1}): (a) for the tetracoordinated complexes **1**–**12** [$^{I}E^{ox}_{p/2} = 0.0124 \times \nu(CO) - 23.3$; $r = 0.83$]; (b) for the pentacoordinated hydride complexes **13**–**16** [$^{I}E^{ox} = 0.0058 \times \nu(CO) - 10.8$; $r = 0.93$]. For the dicarbonyl complexes, the average of the two observed ν(CO) values was taken.

metal centre resulting from a decrease of net electron donor ability of the co-ligands (L and/or the diketonates) (increase of E_L or P_L which was shown above to lead to an enhancement of the oxidation potential). Correlations between the redox potential and the infrared stretching frequencies of unsaturated ligands have been reported [6c,10] for octahedral transition metal complexes.

Finally it is noteworthy to mention that in order to identify the chemical reaction induced by the oxidation of rhodium(I) in our complexes, we have investigated the reaction of [Rh(acac)(CO)(PPh_3)] (**5**), in CH_2Cl_2, with Ag[PF_6] (in a stoichiometric amount) as an oxidising agent. Elemental analysis and the FAB-MS spectrum, in 3-nitrobenzyl alcohol (NOBA) matrix, of the isolated product are consistent with the dinuclear formulation $[Rh_2(acac)_2(CO)_2(PPh_3)_2][PF_6]_2$. In fact, both the ionic aggregate of the molecular ion with PF_6^-, $[Rh_2(acac)_2(CO)_2(PPh_3)_2 \cdot PF_6]^+$ (*m*/*z* 1129), and the dinuclear ion $[Rh_2(acac)_2(CO)_2(PPh_3)_2]^+$ (*m*/*z* 984) are detected. The formation of monocationic aggregates of the type $[ML_n^{2+} + Y^-]^+$ is a known behaviour [12] for $[ML_n^{2+}][Y^-]_2$ type salts and was also observed [13], e.g. in the FAB-MS spectra of *trans*-$[Fe(NCR)_2(Et_2PCH_2CH_2PEt_2)_2][BF_4]_2$. Possible fragmentation patterns of the above dirhodium species, upon stepwise loss of CO, formation of mononuclear ions with further loss of CO, acac or PPh_3 fragments have been recognised, as well as oxygenation of some of the fragment ions by the NOBA matrix. Examples of detected ions are as follows (in the oxygenated ones, the position of the O atom was not located): $[Rh_2(acac)_2(CO)(PPh_3)_2 \cdot O]^{+\bullet}$ (*m*/*z* 972), $[Rh(CO)(PPh_3)_2]^+$ (*m*/*z* 655), $[Rh(PPh_3)_2]^+$ (*m*/*z* 627), $[Rh(PPh_3)(PPh_2) \cdot O]^{+\bullet}$ (*m*/*z* 564), $[Rh(acac)(PPh_3) \cdot O_2]^{+\bullet}$ (*m*/*z* 496), $[Rh(acac)(PPh_3) \cdot O]^{+\bullet}$ (*m*/*z* 480), $[Rh(acac)(PPh_3)]^{+\bullet}$ (*m*/*z* 463), $[Rh(PPh_3)]^+$ (*m*/*z* 365) and $[Rh(PPh_2)]^{+\bullet}$ (*m*/*z* 288). The spectrum is quite different from that of the starting complex **5**, in which no dinuclear species was detected apart from simple dirhodium carbonyls, thus ruling out the hypothesis of formation of the dinuclear species in the FAB conditions of the mass spectrometer. Hence, oxidation of rhodium(I) to rhodium(II) results in dimerisation with conceivable formation of a metal–metal bond in accord with the diamagnetism of the complex and with the known [11] tendency of Rh(II) to form a Rh–Rh bond. The observed dimerisation resulting from the oxidation of the metal can account for the irreversibility of the anodic wave in the cyclic voltammogram of the starting complex.

3. Final comments

This study indicates that 16-electron square-planar and 18-electron square-pyramid transition metal d^8 complexes can exhibit redox potential–structure relationships, as well as correlations of the redox potential with other molecular properties (e.g. infrared spectroscopic ones), that are similar to those already established for closed-shell octahedral-type complexes, in particular with d^6 transition metals. Hence, the extension to the former types of structures of the redox potential parameterisation, and quantification of ligand and metal centre effects, already established for the octahedral one, constitute a promising but still unexplored subject which deserves further investigation.

In addition, oxidation of the Rh(I) complexes to Rh(II) can result in dimerization and the possibility of its application as a convenient preparative method for complexes with Rh(II)–Rh(II) bonds is expected to be developed in a systematic way.

4. Experimental

The complexes **1** [14a], **2** [14b], **3** [14b], **4** [14b], **9** [14a], **10** [14c], **11** [14a], **12** [14c], **13** [14b], **14** [14d], **15** [14e], **16** [14e], **17** [14d] and **18** [14f] were prepared according to published procedures. Complexes **5**–**8** were obtained by a similar procedure to that for **2** using stoichiometric amounts of $[Rh(acac)(CO)_2]$ and the suitable phosphine. All products gave satisfactory elemental analyses and IR spectra. The electrochemical experiments were performed on an EG&G PAR 273 potentiostat/galvanostat connected to a PC computer through a GPIB interface (National Instruments PC-2A) or on an EG&G PAR 173 potentiostat/galvanostat and an EG&G PARC 175 Universal programmer. Cyclic voltammetry was undertaken in a two-compartment three-electrode cell, at a platinum-disc working electrode ($d = 0.5$ mm), probed by a Luggin capillary connected to a silver-wire pseudo-reference electrode; a platinum auxiliary electrode was employed. Controlled potential electrolysis was carried out in a two-compartment three-electrode cell with platinum gauze working and counter electrodes in compartments separated by a glass frit; a Luggin capillary, probing the working electrode, was connected to a silver wire pseudo reference electrode. The experiments were performed in an inert atmosphere (N_2) at room temperature, the potentials were measured in 0.2 mol dm^{-3} $[NBu_4][BF_4]/CH_2Cl_2$ (or NCMe) in the presence of ferrocene as the internal standard, and the redox potential values are quoted relative to the normal hydrogen electrode (NHE) by using the $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ couple [$E_{1/2}^{ox} =$ 0.77 or 0.66 V vs. NHE, in 0.2 mol dm^{-3} $[NBu_4][BF_4]/CH_2Cl_2$ or NCMe, respectively, values obtained by converting to the NHE (by adding + 0.24 V [15]) those we have measured relatively to the SCE]. The criterion used for quasi-reversibility was that of Matsuda and Ayabe [16]. The controlled potential electrolysis experiments were monitored regularly by cyclic voltammetry, thus assuring that no significant potential drift occurred along the electrolyses. Due strong working electrode passivation, the electrolyses had to be interrupted frequently for cleaning of this electrode.

The fast-atom bombardment (FAB) mass spectrometric measurements were performed on a Trio 2000 spectrometer. Positive-ion FAB mass spectra were obtained by bombarding 3-nitrobenzyl alcohol (NOBA) matrices of the samples with 8 keV xenon atoms. Mass calibration for data system acquisition was achieved using CsI.

The oxidation of [Rh(acac)(CO)(PPh$_3$)] (**5**) by Ag[PF$_6$] was performed as follows: a CH_2Cl_2 solution (5.0 cm^3) of complex **5** (0.050 g, 0.10 mmol) was treated with Ag[PF$_6$] (0.025 g, 0.10 mmol) and the system left stirred for 30 min. During that time the solution colour changed from yellow to red and a fine powder of metallic silver was formed. The solution was filtered, evaporated to dryness and the solid washed with hexane and dried in vacuo. IR (KBr pellet): $\nu(CO) = 1992$ cm^{-1}. The complex is diamagnetic at 4–300 K and the FAB-MS spectrum (see text) is consistent with the dinuclear formulation [Rh$_2$(acac)$_2$(CO)$_2$(PPh$_3$)$_2$][PF$_6$]$_2$. Anal. Calcd. for $C_{24}H_{22}F_6OPRh$: C, 45.3; H, 3.5. Found: C, 45.1; H, 3.7%.

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