Reduction–Oxidation Properties of Organotransition-metal Complexes. Part 2.[1] The One-electron Oxidation of Tetracarbonyl(η-cyclopentadienyl)vanadium Derivatives

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Cyclic-voltammetric studies in CH_2Cl_2 and MeCN have shown that $[V(\eta\text{-}C_5H_5)(CO)_3L]$ {1 ; L = PPh_3, $PMePh_2$, PEt_3, $P(NMe_2)_3$, $P[(OCH_2)_3CMe]$, and $P(OPh)_3$} and $[V(\eta\text{-}C_5H_5)(CO)_2(dppe)]$ (2 ; dppe = $Ph_2PCH_2CH_2PPh_2$) are oxidised at a platinum electrode to $[V(\eta\text{-}C_5H_5)(CO)_3L]^+$ (3) and $[V(\eta\text{-}C_5H_5)(CO)_2(dppe)]^+$ (4) respectively. For L = PPh_3, $PMePh_2$, PEt_3, and $P(NMe_2)_3$, and for (2), this process is reversible, but for L = $P(OPh)_3$ or $P[(OCH_2)_3CMe]$ it is irreversible at all the scan rates used. Complexes (3 ; L = PPh_3 or $PMePh_2$) and (4) may be generated in CH_2Cl_2 by treating (1) or (2) with $[p\text{-}FC_6H_4N_2][BF_4]$, and may be isolated, as their $[PF_6]^-$ salts, by treating (1 ; L = PPh_3) or (2) with $[NO][PF_6]$ in mixtures of methanol and toluene. The e.s.r. spectra of the paramagnetic cations are reported.

REVERSIBLE one-electron transfer reactions are of fundamental importance, and well recognised in organic, biological, and transition-metal co-ordination chemistry. It is surprising, therefore, that relatively few electrochemical studies of such reactions have been reported [2,3] in organotransition-metal chemistry. The detection and, in particular, the isolation of organometallic species related by reversible redox reactions are of interest for two main reasons. First, it is likely that the loss, or gain, of one electron will lead to a considerable modification in the reactivity of a complex. For example, the

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oxidised form of a redox-related couple will be more reactive towards nucleophiles than the reduced form. Secondly, studies of structural changes which occur on reversible oxidation or reduction have already yielded a great deal of information on the bonding in polynuclear organometallic species. *X*-Ray crystallographic studies on $[\{Fe(\eta\text{-}C_5H_5)(CO)(\mu\text{-}SR)\}_2]^z$ ($z = 0$, R = Ph;[4] $z = 1+$, R = Me[5]) and ^{1}H n.m.r. studies[6,7] on $[\{M(CO)_n(\mu\ PMe_2)\}_2]^z$ ($z = 0$ or $2+$, M = Fe, $n = 3$; M = Cr, Mo, or W, $n = 4$) have shown that, in each case, the highest occupied orbital in the reduced form is predominantly antibonding metal–metal in character. Further information concerning metal–metal bonding has resulted from structural studies on $[\{Mo(\eta\text{-}C_5H_5)(\mu\text{-}SMe)_2\}_2]^z$ ($z =$ 0 or $1+$),[8] $[Co_3(\eta\text{-}C_5H_5)_3S_2]^z$ ($z = 0$ or 1),[9] $[\{Fe(\eta\text{-}C_5H_5)X\}_4]^z$ (X = CO, $z = 0$[10] or $1+$;[11] X = S, $z = 0$[12] or $1+$[13]), and $[\{Co(\eta\text{-}C_5H_5)S\}_4]^z$ ($z = 0$ or $1+$[14]). Similar comparisons of suitable redox-related pairs might therefore be expected to lead to a further understanding of the bonding in simple monometallic species.

As most mononuclear organotransition-metal complexes obey the 18-electron rule their reversible one-electron reduction to stable monoanions, which would have 19-electron configurations, is less likely than their oxidation to monocations. A concentration on the search for reversibly oxidised species would therefore seem desirable. In 1966 Dessy *et al.*[15,16] subjected 130 organotransition-metal complexes to detailed electrochemical study. Although many electron-transfer processes were detected, most were found to be irreversible, and the use of mercury as an electrode effectively prohibited the study of oxidation reactions occurring at potentials higher than the relatively low potential at which mercury itself is oxidised. Since then, although a number of reversible one-electron oxidations of organotransition-metal complexes has been detected either chemically or electrochemically,[2,3] no further systematic study appears to have been initiated. As it is likely that such a study will reveal much of interest concerning the bonding in, and reactivity of, organotransition-metal complexes, we are investigating by electrochemical and chemical methods the redox properties of a wide variety of organometallic compounds. We now report on the one-electron oxidation of $[V(\eta\text{-}C_5H_5)(CO)_4]$ derivatives, the isolation and characterisation of the resulting paramagnetic monocations, and comment on the relative reactivities of the oxidised and reduced forms of the redox-related pairs.

RESULTS AND DISCUSSION

The yellow to red complexes $[V(\eta\text{-}C_5H_5)(CO)_3L]$ (1) (Table 1) are best prepared by u.v. irradiation of toluene solutions of $[V(\eta\text{-}C_5H_5)(CO)_4]$ in the presence of the ligand L. Although an excess of the ligand may be used, no disubstituted species were observed. In contrast, however, the dicarbonyl $[V(\eta\text{-}C_5H_5)(CO)_2(dppe)]$ (2) was prepared by the thermal reaction of the tetracarbonyl with 1,2-bis(diphenylphosphino)ethane (dppe) in refluxing methylcyclohexane.

In either CH_2Cl_2 or MeCN, all the complexes prepared underwent electrochemical oxidation (Table 2). Cyclic-voltammetric studies, at scan rates of 0.2, 0.1, and 0.05 V s^{-1}, using a stationary platinum-wire electrode, have shown that, by comparison with the known[17] reversible process $[Ni\{S_2C_2(CN)_2\}_2]^{2-} \rightleftharpoons [Ni\{S_2C_2(CN)_2\}_2]^{-}$, the oxidations involve the transfer of one electron. For [1; L = PPh_3 or $P(NMe_2)_3$] and (2) the redox process was reversible * at all scan rates used, whereas for (1; L = PEt_3 or $PMePh_2$) it was reversible except at the lowest scan rate of 0.05 V s^{-1} when it is chemically irreversible. The phosphite complexes {1; L= $P(OPh)_3$ or $P[(OCH_2)_3CMe]$} underwent chemically irreversible one-electron oxidations at all the scan rates used; no reverse peak was observed.

The potentials at which {3; L = $P(OPh)_3$ or $P[(OCH_2)_3CMe]$} are generated are considerably higher than those for the phosphine analogues (Table 2). It is likely, therefore, that the chemical irreversibility of the oxidation of the phosphite complexes results from (3; L = phosphite) being a stronger oxidising agent than (3; L = phosphine). Chemical reaction of the phosphite cation, probably with the solvent, is therefore more rapid, preventing detection of the electrochemical reduction. The chemical irreversibility of the oxidation of (1; L = PEt_3 or $PMePh_2$) at the lowest scan rate used cannot be so readily explained. Since the potentials at which these species are oxidised are lower than that for (1; L = PPh_3) but higher than that for [1; L = $P(NMe_2)_3$], both of which are reversibly oxidised at all the scan rates, the cations (3; L = PEt_3 or $PMePh_2$) are unlikely to be functioning in the same way as the phosphite cations.

The potential, E_p, at which oxidation of (1; L = phosphine) occurs was dependent, as expected, on the donor–acceptor properties of L, and varied in CH_2Cl_2

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* Particularly good agreement between the values of $(E_p)_c - (E_p)_a$ for the oxidations of $[Ni\{S_2C_2(CN)_2\}_2]^{2-}$ and of (1) and (2) is found in MeCN.

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from 0.15 [L = $P(NMe_2)_3$] to 0.25 V (L = PPh_3). On replacement of a second carbonyl ligand by a phosphorus donor the potential is lowered substantially so that in CH_2Cl_2 E_p for (2) is −0.29 V. Such low values for E_p suggest that chemical oxidation of (1) and (2) to paramagnetic monocations should be readily achieved. Although the reactions between (1) or (2) with either silver(I) salts or I_2 in CH_2Cl_2 resulted only in decomposition, the use of [NO][PF_6] or [p-$FC_6H_4N_2$][BF_4] as the oxidising agent caused rapid generation of [$V(\eta$-$C_5H_5)(CO)_2$(dppe)]$^+$ (4) from (2). The oxidation of (1; L = PPh_3 or $PMePh_2$) to [$V(\eta$-$C_5H_5)(CO)_3L$]$^+$ (3) in CH_2Cl_2 could, however, only be brought about with the diazonium salt. In each case the monocation was characterised by e.s.r. studies (see below) and by the observation of a shift in the carbonyl bands of between 100 and 170 cm^{-1} to higher frequency (Table 1). It is somewhat surprising that oxidation of [1; L = $P(NMe_2)_3$], which has the lowest E_p value of the tricarbonyls, could not be achieved, decomposition occurring with any of the oxidising agents used. It is possible that $[NO]^+$ or [p-$FC_6H_4N_2$]$^+$ might react with this complex such that preferential attack at the nitrogen of the phosphorus ligand, rather than at the metal, occurs. Although neither (3) nor (4) could be isolated from CH_2Cl_2 because of decomposition of the generated cations, addition of [NO][PF_6] to (1; L = PPh_3) or (2) in mixtures of toluene and methanol rapidly afforded precipitates of the corresponding cations (3) and (4). These species are very unstable, decomposing in the solid state in air in less than 30 min. They have, however, been characterised by elemental analysis (Table 1).

TABLE 1

I.r., analytical, and m.p. data for [$V(\eta$-$C_5H_5)(CO)_{4-n}L$]^z

						Analyses [a] (%)		ν(CO) [b]/cm^{-1}	
n	L	z	Colour	Yield (%)	M.p. (θ_c/°C)	C	H	CH_2Cl_2	n-hexane
1	PPh_3	0	Red	80	181	67.7 (67.5)	4.8 (4.4)	1 953s, 1 849vs, br	1 960s, 1 882m, 1 865vs
1	PPh_3	1+ [c]	Golden-yellow	82	Decomp. >66	51.7 (51.4)	3.7 (3.3)	2 065, 2 015	
1	$PMePh_2$	0	Red	29	Decomp. 130—135	62.5 (63.0)	4.8 (4.5)	1 951, 1 843	1 959s, 1 884m, 1 881m,[d] 1 861s, 1 853ms
1	$P(NMe_2)_3$	0	Orange	50	Decomp. 120—125	46.1 (46.3)	6.6 (6.4)	1 946, 1 846	1 955, 1 875, 1 857
1	$P[(OCH_2)_3CMe]$	0	Yellow	24	Decomp. >106	45.0 (44.9)	4.1 (4.1)	1 973, 1 871	1 980, 1 906, 1 890
1	$P(OPh)_3$	0	Orange	36	113	61.3 (61.2)	4.1 (4.0)	1 972, 1 875	1 978, 1 906, 1 885
2	dppe	0	Dark red	48	Decomp. 115	67.5 (69.5)	5.3 (5.1)	1 862s, 1 783s	
2	dppe	1+ [c]	Yellow-brown	54	Decomp. >180	55.5 (55.4)	4.9 (4.1)	2 000, 1 945	

[a] Calculated values are given in parentheses. [b] s = Strong, vs = very strong, m = medium, br = broad. The relative intensities of the carbonyl bands were similar for all of the complexes listed, and are therefore not repeated in the Table. [c] Isolated as the $[PF_6]^-$ salt. [d] Multiplicity of bands due to occurrence of rotamers.

TABLE 2

Cyclic-voltammetry data [a] for the process [$V(\eta$-$C_5H_5)(CO)_{4-n}L$] $\rightleftharpoons$ [$V(\eta$-$C_5H_5)(CO)_{4-n}L$]$^+$

		In CH_2Cl_2 [b]				In MeCN [c]			
n	L	E_p/V	$(E_p)_c - (E_p)_a$/mV	$(i_p)_c$/µA	$(i_p)_a$/µA	E_p/V	$(E_p)_c - (E_p)_a$/mV	$(i_p)_c$/µA	$(i_p)_a$/µA
1	PPh_3	0.25	160	4.8	5.2	0.24	120	5.9	5.7
1	$PMePh_2$	0.24	160	4.8	4.8	0.20	120	4.3	3.9
1	PEt_3	0.18	160	4.5	4.9	0.16	130	5.6	4.3
1	$P(NMe_2)_3$	0.15	180	3.6	4.1	0.12	120	4.3	4.3
1	$P[(OCH_2)_3CMe]$	0.50 [d]		5.6		0.36 [d]		3.2	
1	$P(OPh)_3$	0.42 [d]		4.8		0.39 [d]		3.5	
2	dppe	−0.29	140	3.2	3.5	−0.30	120	2.8	2.7

[a] Results obtained using a scan rate of 0.1 V s^{-1}. [b] For $[Ni\{S_2C_2(CN)_2\}_2]^{2-} \rightleftharpoons [Ni\{S_2C_2(CN)_2\}_2]^{1-}$: $(E_p)_c - (E_p)_a$ = 140 mV, $(i_p)_c$ = 3.2 µA, and $(i_p)_a$ = 3.5 µA. [c] For $[Ni\{S_2C_2(CN)_2\}_2]^{2-} \rightleftharpoons [Ni\{S_2C_2(CN)_2\}_2]^{1-}$: $(E_n)_c - (E_p)_a$ = 120 mV, $(i_p)_c$ = 4.6 µA, and $(i_p)_a$ = 4.6 µA. [d] $(E_p)_c$ value. All the potentials are referred to a calomel electrode, 1 mol dm^{-3} in LiCl, at 20 °C.

The observation of the e.s.r. spectra of the cations confirms their paramagnetic nature and strongly suggests that they each contain only one unpaired electron. The complexes are, however, too unstable for bulk-susceptibility measurements to be carried out. The monophosphine complexes, (3; L = PPh_3 or $PMePh_2$), each showed 16-line spectra centred at $\langle g \rangle$ values of 2.00 and 1.99 respectively. The eight-line spectra expected for coupling with the ^{52}V nucleus ($I = \frac{7}{2}$) were further split by coupling with ^{31}P ($I = \frac{1}{2}$). For L = PPh_3, $\langle A_V \rangle$ = 51.9 G and $\langle A_P \rangle$ = 24.4 G, and for L = $PMePh_2$, $\langle A_V \rangle$ = 63.6 G and $\langle A_P \rangle$ = 22.8 G.* The e.s.r. spectrum of (4) was centred at $\langle g \rangle$ = 1.98 and consisted of eight 1 : 2 : 1 triplets arising from coupling with one vanadium nucleus, $\langle A_V \rangle$ = 78.9 G, and two equivalent phosphorus nuclei, $\langle A_P \rangle$ = 25.1 G. No further splittings, which might have suggested

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* 1 G = 10^{-4} T.

further delocalisation on to the cyclopentadienyl rings or the phosphorus-ligand substituents, could be detected.

The isolation of (3; L = PPh_3) has allowed a brief study to be made of its reactivity relative to that of (1; L = PPh_3). Although the neutral complex does not react with halide ion, addition of $[N(PPh_3)_2]Cl$ to a CH_2Cl_2 solution of the cation caused immediate evolution of CO and disappearance of the carbonyl bands from the i.r. spectrum of the reaction mixture. Although no product could be isolated, it is clear that the reactivity of (3), relative to (1), towards chloride ion is considerably enhanced. Further studies are in hand by which we hope to show that activation of organotransition-metal complexes towards nucleophilic attack can be brought about by prior, reversible, one electron-oxidation.

EXPERIMENTAL

The preparation, purification, and reactions of the complexes described, as well as the electrochemical studies, were carried out under an atmosphere of dry nitrogen. The complex $[V(\eta\text{-}C_5H_5)(CO)_4]$,[18] and $[p\text{-}FC_6H_4N_2][BF_4]$,[19] were prepared by published methods; $[NO][PF_6]$ was purchased from Ozark Mahoning Co., Tulsa, Oklahoma. Solvents were dried by standard methods and were deoxygenated before use.

Infrared spectra were recorded on a Perkin-Elmer PE 257 spectrophotometer using the ×10 expansion facility, and calibrated using the 1 601-cm^{-1} absorption of polystyrene. *X*-Band e.s.r. spectra, calibrated against a solid sample of the diphenylpicrylhydrazyl radical, were recorded on a Varian Associates 4502/15 spectrometer. Cyclic voltammetry was carried out at 20 °C using platinum-wire auxiliary and working electrodes and a calomel electrode (1 mol dm^{-3} in LiCl) as reference. Solutions were 10^{-3} mol dm^{-3} in complex and either 0.05 (CH_2Cl_2) or 0.1 mol dm^{-3} (MeCN) in $[NEt_4][ClO_4]$ as supporting electrolyte. Criteria for reversibility are based on the assumption that data for the complex under study should be similar to that found for the reversible one-electron oxidation of $[Ni\{S_2C_2(CN)_2\}_2]^{2-}$. Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol. Melting points are uncorrected.

Tricarbonyl(η-cyclopentadienyl)triphenylphosphinevanadium, $[V(\eta\text{-}C_5H_5)(CO)_3(PPh_3)]$.—A solution of $[V(\eta\text{-}C_5H_5)(CO)_4]$ (0.5 g, 2.2 mmol) and PPh_3 (0.6 g, 2.3 mmol) in toluene (75 cm^3) was irradiated until all the tetracarbonyl had reacted (22 h). The solvent was then removed and the residue was recrystallised from hot ethanol to yield the product as a red crystalline solid (yield 0.82 g, 80%). The monosubstituted complexes in Table 1 may all be made by the same method; the $P(NMe_2)_3$ derivative was recrystallised from hot hexane. The complexes are all yellow to red solids which, apart from $[V(\eta\text{-}C_5H_5)(CO)_3\{P(OPh)_3\}]$ and $[V(\eta\text{-}C_5H_5)(CO)_3(PEt_3)]$, are stable in air. They are only moderately soluble in hexane but readily so in more polar solvents such as CH_2Cl_2 to give air-sensitive yellow to red solutions.

[1,2-Bis(diphenylphosphino)ethane]dicarbonyl(η-cyclopentadienyl)vanadium, $[V(\eta\text{-}C_5H_5)(CO)_2(dppe)]$.—The complex $[V(\eta\text{-}C_5H_5)(CO)_4]$ (0.5 g, 2.2 mmol) and dppe (1 g, 2.5 mmol) were heated under reflux in methylcyclohexane (50 cm^3) for 24 h. On cooling the dark red solution yielded a brown-red precipitate which was recrystallised twice from diethyl ether–hexane to give the complex as a dark red solid (yield 0.6 g, 48%). The complex is unstable in air. It is insoluble in hexane but soluble in polar solvents such as CH_2Cl_2 to give very air-sensitive red solutions.

Tricarbonyl(η-cyclopentadienyl)triphenylphosphinevanadium Hexafluorophosphate, $[V(\eta\text{-}C_5H_5)(CO)_3(PPh_3)][PF_6]$.—To a stirred solution of $[V(\eta\text{-}C_5H_5)(CO)_3(PPh_3)]$ (0.1 g, 0.22 mmol) in a mixture of methanol (1.5 cm^3) and toluene (7.5 cm^3) was added $[NO][PF_6]$ (0.04 g, 0.22 mmol). After 3 min, addition of diethyl ether (10 cm^3) completed precipitation of the complex as golden-yellow crystals (yield 0.11 g, 82%). The complex is unstable in light, and *in vacuo*, decomposing in *ca.* 30 min. When stored at 10 °C in the absence of light it appears to be stable for 1 or 2 d. It is soluble in polar solvents such as acetone or CH_2Cl_2 to give very air-sensitive yellow solutions.

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