Reduction–Oxidation Properties of Organotransition-metal Complexes. Part 10.[1] Formation and Reactivity of the Paramagnetic Cyclobutadiene-iron and -ruthenium Derivatives $[M(CO)_{3-n}L_n(C_4Ph_4)]^+$ (n = 1—3, L = phosphorus donor)

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The tetraphenylcyclobutadiene complexes $[M(CO)_{3-n}L_n(\eta^4\text{-}C_4Ph_4)]$ [1: M = Fe, n = 1, L = PPh_3 or $P(OMe)_3$; M = Fe, n = 2, L = $P(OMe)_3$; M = Ru, n = 2 or 3, L = $P(OMe)_3$] undergo reversible one-electron oxidation, at the platinum electrode in CH_2Cl_2, to give the paramagnetic radical cations $[M(CO)_{3-n}L_n(C_4Ph_4)]^+$ (2). Chemical oxidation of (1) with $Ag[BF_4]$ or $[N(C_6H_4Br\text{-}p)_3][PF_6]$ in CH_2Cl_2 affords salts of [2: M = Fe, n = 1, L = PPh_3; M = Fe, n = 2, L = $P(OMe)_3$]. Complexes (2) are implicated as intermediates in the formation of $[Fe(CO)(NO)\{P(OMe)_3\}(\eta^4\text{-}C_4Ph_4)]^+$ from $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$ and $Ag[NO_3]$, of $[Fe(CO)\{P(OMe)_3\}(\eta^2\text{-tcne})(\eta^4\text{-}C_4Ph_4)]$ (3) from tetracyanoethylene (tcne) and $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$, and of $[MX(CO)_{3-n}L_n(\eta^4\text{-}C_4Ph_4)]^+$ [4; X = Cl, Br, or I] from (1) and halogens, X_2. The reaction of polyhalide salts of $[RuX(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]^+$ (4; X = Cl or Br) with PPh_3 leads to cleavage of the metal–ring bond and formation of halogenotetraphenylcyclobutenyl radicals, C_4Ph_4X.

As part of an extensive study of the redox properties of organotransition-metal complexes we have shown that $[Mn(CO)_{3-n}L_n(\eta^5\text{-}C_5R_5)]$ [2] (n = 1 or 2, L = phosphine or phosphite, R = H or Me) and $[Cr(CO)_2L(\eta^6\text{-}C_6Me_6)]$ (L = phosphine, phosphite,[3] or acetylene [4]) undergo chemical and electrochemical one-electron oxidation to stable radical cations. The isoelectronic complexes of iron, $[Fe(CO)_{3-n}L_n(\eta^4\text{-diene})]$, are also oxidised [5] but the fate of the resulting radical cation is largely dependent on the nature of the diene ligand. Formation of $[Fe(CO)_3(C_8H_8)]^+$ from the neutral η^4-cyclo-octatetraene complex results [6] in rapid dimerisation at the co-ordinated polyene to give $[Fe_2(CO)_6(\eta^5{:}\eta'^5\text{-}C_{16}H_{16})]^{2+}$, and $[Fe(CO)_3(C_7H_8)]^+$, formed from the η^4-cycloheptatriene compound, undergoes [5] hydrogen-radical addition to give the cycloheptadienyl complex $[Fe(CO)_3(\eta^5\text{-}C_7H_9)]^+$.

We now give details of our studies [5] with the cyclobutadiene derivatives $[M(CO)_{3-n}L_n(\eta^4\text{-}C_4Ph_4)]$ [1: M = Fe, n = 1, L = PPh_3 or $P(OMe)_3$; M = Fe, n = 2, L = $P(OMe)_3$; M = Ru, n = 2 or 3, L = $P(OMe)_3$] including the isolation of salts of the paramagnetic radical cations $[M(CO)_{3-n}L_n(C_4Ph_4)]^+$ (2) and the involvement of such radicals in the reactions of (1) with $Ag[NO_3]$, with tetracyanoethylene (tcne), and with halogens.

RESULTS AND DISCUSSION

The complexes (1), used in the electrochemical and chemical studies described below, were prepared as yellow crystalline solids by treating $[M(CO)_3(\eta^4\text{-}C_4Ph_4)]$ (M = Fe or Ru) with the phosphorus ligand, L, in tetrahydrofuran (thf) under u.v. irradiation. The complex $[Fe(CO)_2(PPh_3)(\eta^4\text{-}C_4Ph_4)]$ has been described previously; [7] the new compounds have been fully characterised by elemental analysis and i.r. and n.m.r. spectroscopy (Table 1). In that the sequential replacement, by phosphorus donors, of the carbonyl ligands of a mononuclear polycarbonyl becomes progressively more difficult, usually precluding full substitution, the ready synthesis of $[Ru\{P(OMe)_3\}_3(\eta^4\text{-}C_4Ph_4)]$ from $[Ru(CO)_3(\eta^4\text{-}C_4Ph_4)]$ and $P(OMe)_3$ is noteworthy.

Electrochemical Studies.—Each of the complexes (1) undergoes one-electron oxidation to the radical cation (2) in CH_2Cl_2 at the platinum-wire electrode. Although the electrochemical study was hampered by the slow de-

TABLE 1

Analytical, i.r., and hydrogen-1 n.m.r. data for tetraphenylcyclobutadiene complexes of iron and ruthenium

Complex	Analysis [a] (%) C	H	$\tilde{\nu}$(CO)/cm^{-1} [b]	τ [c] Phenyl protons	Methyl protons
$[Fe(CO)_2(PPh_3)(\eta^4\text{-}C_4Ph_4)]$	78.5 (78.9)	4.9 (4.8)	1 965, 1 913		
$[Fe(CO)_2\{P(OMe)_3\}(\eta^4\text{-}C_4Ph_4)]$	66.5 (66.9)	5.0 (4.9)	1 979, 1 923	2.73 (20 H, m)	6.66 [9 H, d, J(PH) 6]
$[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$	61.1 (61.1)	5.6 (5.5)	1 903	2.80 (20 H, m)	6.72 [18 H, t, J(PH) 6]
$[Fe(CO)\{P(OMe)_3\}_2(C_4Ph_4)][BF_4]$ [d]	50.3 (50.2)	4.8 (4.7)	1 983		
$[Fe(CO)\{P(OMe)_3\}(\eta^2\text{-tcne})(\eta^4\text{-}C_4Ph_4)]$ [e]	63.9 (63.9)	4.3 (4.1)	1 981 [f]	2.72 (20 H, m)	6.52 [9 H, d, J(PH) 12]
$[Ru(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$	56.9 (57.3)	5.4 (5.2)	1 921	2.78 (20 H, m)	6.68 [18 H, t, J(PH) 6]
$[Ru\{P(OMe)_3\}_3(\eta^4\text{-}C_4Ph_4)]$	54.0 (53.6)	6.0 (5.7)		2.80 (20 H, m)	6.62 (27 H, m)
$[RuI(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)][I_3]$	33.5 (33.8)	3.2 (3.1)	2 001 [g]		
$[RuI\{P(OMe)_3\}_3(\eta^4\text{-}C_4Ph_4)][I_3]$	33.5 (33.2)	3.6 (3.5)		2.70 (20 H, m)	6.32 (27 H, m)

[a] Calculated values are given in parentheses. [b] In CH_2Cl_2. [c] In $CDCl_3$; J values in Hz. [d] Crystallises with one molecule of CH_2Cl_2. [e] Crystallises with ½ molecule of CH_2Cl_2. Found: Cl, 2.8; N, 7.8. Requires Cl, 3.3; N, 7.8%. [f] ν(CN) at 2 215w and 2 195s cm^{-1}. [g] In Nujol.

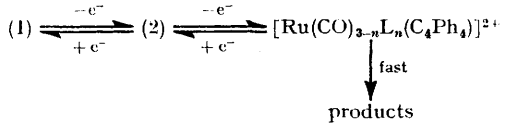
composition of (1) in CH_2Cl_2, even in the absence of air, rapid measurements on freshly prepared solutions enabled the full reversibility of the electron-transfer process to be verified. Thus the values of $(E_p)_{ox} - (E_p)_{red}$, of the half peak widths $(E_p)_{ox} - (E_{p/2})_{ox}$ and $(E_p)_{red} - (E_{p/2})_{red}$, and of $(i_p)_{ox}/(i_p)_{red}$ are generally in agreement with the expected [8] 60, 57, −57 mV, and 1.0 respectively. The poorest agreement was found for the most readily oxidised, fully substituted complex, $[Ru\{P(OMe)_3\}_3(\eta^4\text{-}C_4Ph_4)]$. In addition, the electrochemical data for the isolable, redox-related pair $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$ and $[Fe(CO)\{P(OMe)_3\}_2(C_4Ph_4)]^+$ are identical within experimental error.

Although $[Fe(CO)_2(PPh_3)(\eta^4\text{-}C_4Ph_4)]$ is said [9] to undergo electrochemically irreversible one-electron reduction at the dropping-mercury electrode (at −2.69 V *vs.* Ag–Ag$[ClO_4]$, in 1,2-dimethoxyethane), we have observed no other redox processes for (1; M = Fe) in the range ±1.5 V (*vs.* a calomel electrode, 1 mol dm^{-3} in LiCl), other than that detailed above.

The bonding in $[Fe(CO)_3(\eta^4\text{-}C_4H_4)]$ involves [10] the tricarbonyliron group acting as a donor to cyclobutadiene resulting, in effect, in an aromatic 6π system. Reduction of $[Fe(CO)_3(\eta^4\text{-}C_4H_4)]$ might, therefore, result in the loss of aromaticity and be expected to be unfavourable. With other $[Fe(CO)_3(\eta^4\text{-diene})]$ complexes no such loss is involved and, particularly where additional electron density can be delocalised on the organic fragment, reduction is possible. Thus it is noteworthy that $[Fe(CO)_3(C_4H_4)]^-$ has not been detected [11] in the negative-ion mass spectrum of $[Fe(CO)_3(\eta^4\text{-}C_4H_4)]$, although related anions are formed from $[Fe(CO)_3(\eta^4\text{-diene})]$ ('diene' = butadiene,[11] cycloheptatriene,[12] *etc.*), and ^{60}Co γ-irradiation, at 77 K, of solid $[Fe(CO)_2(PPh_3)(\eta^4\text{-}C_6H_8)]$ (C_6H_8 = cyclohexadiene) also results [13] in electron capture. In the last case the e.s.r. spectrum of the radical anion shows some evidence for unpaired electron density on the hydrocarbon ligand.

By contrast to (1; M = Fe) each of the ruthenium analogues (1; M = Ru) undergoes a second irreversible oxidation process at a potential *ca.* 0.4—0.5 V more positive than the first. On the first cyclic voltammetric scan the peak currents for the two oxidation steps are similar but on the second and subsequent sweeps the height of the first peak is diminished. The tentative proposal shown in Scheme 1 accounts for this behaviour.

The potential, E_p, at which (1) is oxidised to (2) is dependent on M, L, and *n* (Table 2). Thus $[Ru(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$ is less readily oxidised, by *ca.* 0.2 V, than the iron analogue, and $[Fe(CO)_2(PPh_3)(\eta^4\text{-}C_4Ph_4)]$ is more readily oxidised, by *ca.* 0.2 V, than $[Fe(CO)_2\{P(OMe)_3\}(\eta^4\text{-}C_4Ph_4)]$. The effect of *n*, however, is most marked in that for each carbonyl being replaced by $P(OMe)_3$, E_p is lowered by *ca.* 0.4 V.



SCHEME 1

For the series of complexes $[Mn(CO)_{6-n}(CNMe)_n]^+$ and $[Cr(CO)_{6-n}(CNMe)_n]$ there is a linear relationship between *n* and the potential [14] at which one-electron oxidation, to $[Mn(CO)_{6-n}(CNMe)_n]^{2+}$ and $[Cr(CO)_{6-n}(CNMe)_n]^+$, occurs. Such a relationship for (1; M = Fe) would suggest the E_p value of $[Fe(CO)_3(\eta^4\text{-}C_4Ph_4)]$ to be *ca.* 1.2—1.3 V. At a scan rate of 100 mV s^{-1} the cyclic voltammogram of the tricarbonyl shows an irreversible oxidation wave $[(E_p)_{ox} = 1.22$ V] with a peak current, $(i_p)_{ox}$, at least twice that found for [1; M = Fe, *n* = 1 or 2, L = $P(OMe)_3$].

Synthetic Studies.—The electrochemically determined values of E_p (Table 2) suggest that chemical oxidation of (1), particularly when *n* = 2 or 3, should be readily achieved. The reactions of (1) with a range of one-electron oxidants have therefore been studied.

TABLE 2

Cyclic voltammetric data for $[M(CO)_{3-n}L_n(C_4Ph_4)]^z$

M	L	*n*	*z*	E_p[a]/V	$(E_p)_{ox}-(E_p)_{red}$ / mV	$(E_p)_{ox}-(E_{p/2})_{ox}$ / mV	$(E_p)_{red}-(E_{p/2})_{red}$ / mV	$\frac{(i_p)_{ox}}{(i_p)_{red}}$	$(i_p)_{ox}$ / μA
Fe	PPh_3	1	0	0.60	60	58	62	0.98	5.3
Fe	$P(OMe)_3$	1	0	0.76	63	62	66	0.98	6.3
Fe	$P(OMe)_3$	2	0	0.22	61	60	65	0.93	5.2
Fe	$P(OMe)_3$	2	1	0.20	56	58	62	1.00	5.0
Ru	$P(OMe)_3$	2	0	0.36[b]	55	57	56	0.91	5.9
Ru	$P(OMe)_3$	3	0	0.02[c]	65	64	76	0.95	3.6

[a] Relative to a calomel electrode, 1 mol dm^{-3} in LiCl. [b] Second, irreversible one-electron oxidation at 0.73 V (scan rate = 100 mV s^{-1}). [c] Second, irreversible one-electron oxidation at 0.55 V (scan rate = 100 mV s^{-1}).

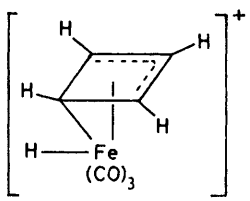
Nitrosonium and arenediazonium ions may oxidise metal carbonyl substrates, or undergo substitution reactions.[2,3] For [1; M = Fe or Ru, *n* = 1—3, L = $P(OMe)_3$] oxidation was not observed using either reagent and only $[Fe(CO)(NO)\{P(OMe)_3\}(\eta^4\text{-}C_4Ph_4)]^+$ [ν(CO) (CH_2Cl_2) at 2 061, ν(NO) at 1 817 cm^{-1}], analogues of which are known,[15] could be identified as a product.

Two paramagnetic, radical cations of iron [2: M = Fe, *n* = 1, L = PPh_3; M = Fe, *n* = 2, L = $P(OMe)_3$] (Table 1) were, however, successfully synthesised using silver(I) salts or the cation $[N(C_6H_4Br\text{-}p)_3]^+$. Addition of an excess of $Ag[BF_4]$ to $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$ in CH_2Cl_2 resulted in the deposition of metallic silver and the formation of an orange solution from which orange crystalline $[Fe(CO)\{P(OMe)_3\}_2(C_4Ph_4)][BF_4]\cdot CH_2Cl_2$ was

isolated. The complex has been characterised, as a CH_2Cl_2 solvate, by elemental analysis (Table 1), by the observation of one carbonyl-stretching absorption in the i.r. spectrum shifted to higher energy by *ca.* 80 cm^{-1} from that of $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$, and by cyclic voltammetry (see above) which verifies the reversible one-electron reduction of (2) to (1). The second example of (2), namely $[Fe(CO)_2(PPh_3)(C_4Ph_4)]^+$, has been isolated as the scarlet $[PF_6]^-$ salt by treating $[Fe(CO)_2(PPh_3)(\eta^4\text{-}C_4Ph_4)]$ with $[N(C_6H_4Br\text{-}p)_3][PF_6]$ in CH_2Cl_2. The cation is readily reduced in solution, as expected from the E_p value (0.60 V) associated with its formation, and characterisation by elemental analysis has not been achieved. However, its identity follows from its ready reduction to $[Fe(CO)_2(PPh_3)(\eta^4\text{-}C_4Ph_4)]$, the observation of two carbonyl absorptions [ν(CO)(CH_2Cl_2) at 2 037 and 2 005 cm^{-1}] shifted, to higher energy, by *ca.* 80 cm^{-1} from those of the neutral precursor, and its e.s.r. spectrum, discussed below.

Ruthenium analogues of (2) have not been directly observed, possibly because of the more complex electrochemical behaviour of (1; M = Ru), but are implicated in the reactions of (1; M = Ru) with halogens (see Scheme 2).

Although the structure of $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$ has been determined by single-crystal *X*-ray diffraction studies,[16] that of $[Fe(CO)\{P(OMe)_3\}_2(C_4Ph_4)]^+$, as the CH_2Cl_2-solvated $[BF_4]^-$ salt, has not, due to ready solvent loss in the crystalline state. Hence a comparative study allowing comment to be made on the effect of electron removal on structure and bonding in (1) has not been possible. We have therefore not specified the bonding mode of the C_4Ph_4 ligand when giving the formula of (2). Photoelectron spectroscopy [17,18] coupled with *ab initio* SCF molecular-orbital calculations [18] suggests that the first electron to be removed from $[Fe(CO)_3(\eta^4\text{-}C_4H_4)]$ is from an orbital mainly metal in character. If this is the case and, as seems likely, chemical oxidation in solution involves a similar process, the bonding in (2) may be regarded as involving the C_4Ph_4 ring as a four-electron ligand and an electron-deficient metal centre. Distortion of the ring from square planar, as found [16] in $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$, to rectangular, as proposed [19] for free cyclobutadiene, or to the σ, η^3 structure found [20] when $[Fe(CO)_3(\eta^4\text{-}C_4H_4)]$ is protonated at the metal (see below) is, however, possible.



Although the paramagnetism of [2: M = Fe, n = 1, L = PPh_3; M = Fe, n = 2, L = $P(OMe)_3$] is confirmed by e.s.r. spectroscopy the spectra are otherwise uninformative, showing no hyperfine splitting [at 0 °C in CH_2Cl_2; n = 1, L = PPh_3, $\langle g_{av.}\rangle$ = 2.065, ΔH = 48 G; n = 2, L = $P(OMe)_3$, $\langle g_{av.}\rangle$ = 2.067, ΔH = 65 G].* The frozen-solution spectra (in CH_2Cl_2) are also poorly defined but three $\langle g\rangle$ values may be assigned for each complex, with $\langle g_{av.}\rangle$ in moderate agreement with that found at 0 °C [n = 1, L = PPh_3, $\langle g_1\rangle$ = 2.012, $\langle g_2\rangle$ = 2.033, $\langle g_3\rangle$ = 2.132, $\langle g_{av.}\rangle$ = 2.059, −130 °C; n = 2, L = $P(OMe)_3$, $\langle g_1\rangle$ = 2.017, $\langle g_2\rangle$ = 2.053, $\langle g_3\rangle$ = 2.156, $\langle g_{av.}\rangle$ = 2.075, −160 °C].

The reaction of $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$ with $Ag[NO_3]$ in CH_2Cl_2 differs from that with $Ag[BF_4]$ in that the final product is $[Fe(CO)(NO)\{P(OMe)_3\}(\eta^4\text{-}C_4Ph_4)]^+$. The route by which nitrate ion is reduced to the co-ordinated nitrosyl ligand is not clear. The observation in the carbonyl i.r. spectrum of the formation of $[Fe(CO)\{P(OMe)_3\}_2(C_4Ph_4)]^+$ in the early stages of the reaction, however, suggests initial one-electron transfer is followed by reaction of the radical cation with $[NO_3]^-$. Related oxidation, and oxygen-transfer reactions, are thought [21] to occur when *cis*-$[Mo(CO)_2(dmpe)_2]$ or *trans*-$[Mo(CO)_2(dmpe)_2]^+$ (dmpe = $Me_2PCH_2CH_2PMe_2$) reacts with $Ag[NO_2]$ to give $[Mo(CO)(NO)(NO_2)(dmpe)_2]$ and $[Mo(CO)(NO)(dmpe)_2]^+$ respectively.

On adding tcne to $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$ in CH_2Cl_2 an intense green solution is formed from which green-black crystals of neutral $[Fe(CO)\{P(OMe)_3\}(\eta^2\text{-tcne})(\eta^4\text{-}C_4Ph_4)]\cdot 0.33CH_2Cl_2$ (3) (Table 1) are isolable. The formation of (3) from (1) also involves the initial formation of $[Fe(CO)\{P(OMe)_3\}_2(C_4Ph_4)]^+$. Although the carbonyl-stretching frequencies of (3) and the radical cation are very similar (Table 1), the formation of $[tcne]^-$ [and therefore (2)] as an intermediate is clearly shown by the appearance of ν(CN) at 2 185 and 2 143 cm^{-1}, and by the strong e.s.r. spectrum † of the anion.[22] On completion of the reaction the cyanide-stretching region of the i.r. spectrum shows bands at 2 215w and 2 195s cm^{-1}, due to (3), and the e.s.r. spectrum of $[tcne]^-$ was absent. Neither $[Fe(CO)_3(\eta^4\text{-}C_4Ph_4)]$ nor $[Fe(CO)_2(PPh_3)(\eta^4\text{-}C_4Ph_4)]$, which are more difficult to oxidise than $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$, reacts with tcne, further evidence that oxidation precedes substitution in the formation of (3).

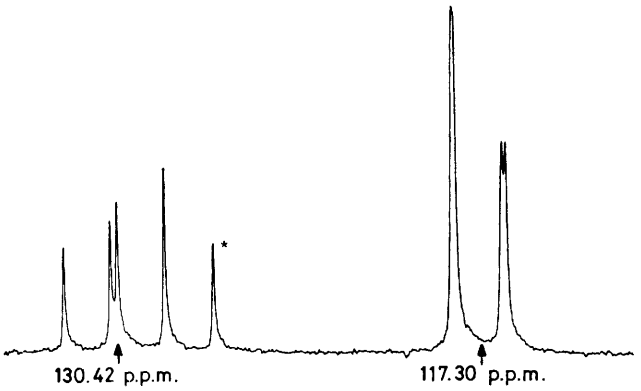
That the monocation $[Fe(CO)\{P(OMe)_3\}_2(C_4Ph_4)]^+$ and the neutral complex (3) have such similar carbonyl-stretching frequencies (Table 1) is a reflection of the strong electron-withdrawing power of the tcne ligand. This property is also reflected in the electrochemical behaviour of (3) for which one-electron oxidation does not occur in the region +1.5 V (*vs.* calomel electrode, 1 mol dm^{-3} in LiCl). If (3) were to be regarded as an analogue of $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$, in which one two-electron donor, $P(OMe)_3$, is replaced by another, tcne, then ready one-electron oxidation of (3) might have been expected.

The reaction of (1) with halogens is complex, but similar to that of $[Fe(CO)_3L_2]$ (L = P- or As-donor) for

* Throughout this paper: 1 G = 10^{-4} T.

† The broad and relatively weak e.s.r. signal of $[Fe(CO)\{P(OMe)_3\}_2(C_4Ph_4)]^+$ could not be detected.

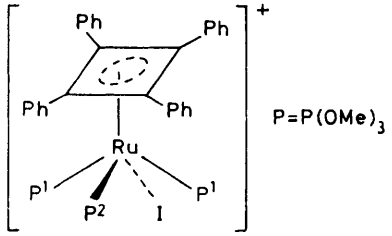
which halogenation yields $[FeX(CO)_3L_2]^+$ and $[FeX_2(CO)_{4-n}L_n]$ ($n = 1$ or 2, X = halide) *via* a mechanism involving one-electron transfer.[23] With iodine in hexane $[Ru\{P(OMe)_3\}_3(\eta^4\text{-}C_4Ph_4)]$ affords $[MX(CO)_{3-n}L_n(\eta^4\text{-}C_4Ph_4)]^+$ [4; M = Ru, X = I, $n = 3$, L = $P(OMe)_3$] as the orange-brown, crystalline tri-iodide salt (Table 1).



Proton-decoupled ^{31}P n.m.r. spectrum of $[RuI\{P(OMe)_3\}_3(\eta^4\text{-}C_4Ph_4)]^+$ in CD_2Cl_2 at −80 °C. The asterisked band is due to an impurity

The structure of (4) may be assigned as square pyramidal with an apical cyclobutadiene ring (see below) on the basis of ^{31}P n.m.r. spectroscopy (Figure, Table 3). Although complicated by second-order effects the spectrum has been simulated (Table 3) with $J(P^1P^2) = 75$ Hz and chemical-shift values of 117.30 (P^1) and 130.42 (P^2), and clearly shows the presence of two equivalent and one inequivalent phosphite ligands.

Similar halogeno-complexes $[RuX(CO)\{P(OMe_3\}_2(\eta^4\text{-}C_4Ph_4)][X_3]$ (4; X = Cl, Br, or I) precipitate from hexane on the addition of the halogen, X_2, to $[Ru(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$. Each shows one carbonyl absorption in the i.r. spectrum [*e.g.* X = Br, ν(CO) at 2 025 cm^{-1} (in Nujol)], but, apart from elemental analysis on the iodo-complex, these have not been further characterised due to instability in solution. In the presence of PPh_3, (4) decomposes to uncharacterised carbonyl-containing complexes and halogenotetraphenylcyclobutenyl radicals the formation of which is best



studied by e.s.r. spectroscopy. Thus, addition of PPh_3 to a suspension of $[RuX(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)][X_3]$ (4; X = Cl, Br, or I) in toluene yields a green solution which exhibits a strong e.s.r. spectrum[24] of free C_4Ph_4X. It is not clear whether the halogen atom of the cyclobutenyl radical originates from the metal or the polyhalide counter anion of $[RuX(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]^+$, although the latter is more likely. Triphenylphosphine will react with $[I_3]^-$ to liberate iodide ion which is then able to attack the co-ordinated cyclobutadiene ring.

The reactions of halogens with (1; M = Fe) are not fully characterised although (4; M = Fe) are undoubtedly formed. Iodine and $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$ in hexane react, in a ratio I : Fe of 4 : 1, to give a black precipitate which exhibits one carbonyl i.r. absorption at 1 995 cm^{-1} (in CH_2Cl_2), shifted to higher energy by *ca.* 90 cm^{-1} from that of $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$. The shift is similar to that observed on

TABLE 3

Proton-decoupled ^{31}P n.m.r. spectrum [a] of $[RuI\{P(OMe)_3\}_3(\eta^4\text{-}C_4Ph_4)]^+$

Chemical shift δ [b]	
132.40 (132.40)	118.16 (118.17)
130.67 (130.68)	118.10 (118.07)
130.42 (130.42)	116.37 (116.37)
128.71 (128.71)	116.22 (116.21)

[a] In CD_2Cl_2, calculated values in parentheses. [b] In p.p.m. to high frequency of H_3PO_4.

iodination of $[Ru(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$; the black precipitate is therefore formulated as $[FeI(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)][I_3]$.

Further evidence for iodination at iron arises from the observation that iodine and $[Fe(CO)\{P(OMe)_3\}_2(C_4Ph_4)]^+$ also react to give a product with ν(CO) at 1 995 cm^{-1}. The radical cations $[Fe(CO)_3(PPh_3)_2]^+$ [23] and $[Mn(CO)(dppe)(\eta^5\text{-}C_5H_5)]^+$ [2] (dppe = $Ph_2PCH_2CH_2PPh_2$) undergo similar radical–radical coupling reactions with halogens,

$$[M(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)] + X_2 \rightleftharpoons [M(CO)\{P(OMe)_3\}_2(C_4Ph_4)]^+ + X + X^- \quad \text{(i)}$$

$$[M(CO)\{P(OMe)_3\}_2(C_4Ph_4)]^+ + X^- \longrightarrow [MX(CO)\{P(OMe)_3\}_2(C_4Ph_4)] \quad \text{(ii)}$$
(5)

$$[MX(CO)\{P(OMe)_3\}_2(C_4Ph_4)] + [M(CO)\{P(OMe)_3\}_2(C_4Ph_4)]^+ \rightleftharpoons [MX(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]^+ + [M(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)] \quad \text{(iii)}$$

SCHEME 2

X_2, to give halogenometal complexes $[FeX(CO)_3(PPh_3)_2]^+$ [23] and $[MnX(CO)(dppe)(\eta^5\text{-}C_5H_5)]^+$ [25] respectively.

The reaction of $[FeI(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)][I_3]$ with PPh_3 differs from that with the iodoruthenium complex in that regeneration of $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$ occurs. That PPh_3 again reacts with $[I_3]^-$ to give iodide ions which subsequently react with $[FeI(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]^+$ is confirmed by treating the tri-iodide salt directly with $[NBu^n_4]I$; instant reformation of $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$ occurs.

By analogy with that shown for $[Fe(CO)_3L_2]$ [23] (L = P- or As-donor), the mechanism in Scheme 2 can be proposed for the halogenation of [1; M = Fe or Ru,

$n = 2$, L = $P(OMe)_3$]. The mechanism is complicated, however, in that the reactions described above, between $[FeI(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)][I_3]$ and I^- or PPh_3 show that equilibrium * (iv) also exists.

$$[FeI(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]^+ + I^- \rightleftharpoons [Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)] + I_2 \quad \text{(iv)}$$

The intermediacy of the 19-electron complex (5) and the redox reaction (iii) in the mechanism proposed cannot be fully substantiated. However, the reaction between $[Fe(CO)\{P(OMe)_3\}_2(C_4Ph_4)]^+$ and X^- does afford † $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$, and e.s.r. studies reveal the formation of a paramagnetic intermediate. Thus, addition of $[N(PPh_3)_2]Cl$ or $[PPh_4]Br$ to $[Fe(CO)\{P(OMe)_3\}_2(C_4Ph_4)]^+$ in toluene at 25 °C results in new, broad signals [X = Cl, $\langle g \rangle_{av.} = 2.073$, $\Delta H = 33$ G; X = Br, $\langle g_{av.} \rangle = 2.099$, $\Delta H = 54$ G]. Although unequivocal assignment of these spectra to (5) cannot be made, the dependence of $\langle g_{av.} \rangle$ on X, and the presence of (1) in the reaction mixture after the e.s.r. spectrum has decayed, implicate the 19-electron complex, and therefore steps (ii) and (iii) (Scheme 2), in the formation of (4) from (1) and halogens. It should be noted that the second

$$[Ru(CO)_{3-n}L_n(\eta^4\text{-}C_4Ph_4)] + X_2 \rightleftharpoons [Ru(CO)_{3-n}L_n(C_4Ph_4)]^+ + X + X^- \quad \text{(v)}$$

$$[Ru(CO)_{3-n}L_n(C_4Ph_4)]^+ + X \rightleftharpoons [Ru(CO)_{3-n}L_n(C_4Ph_4)]^{2+} + X^- \quad \text{(vi)}$$

$$[Ru(CO)_{3-n}L_n(C_4Ph_4)]^{2+} + X^- \longrightarrow [RuX(CO)_{3-n}L_n(\eta^4\text{-}C_4Ph_4)]^+ \quad \text{(vii)}$$

SCHEME 3

oxidation wave in the cyclic voltammogram of (1; M = Ru), if assigned to the formation of $[Ru(CO)_{3-n}L_n(C_4Ph_4)]^{2+}$, suggests an alternative mechanism (Scheme 3) for the formation of (4; M = Ru); this mechanism cannot operate for (1; M = Fe).

EXPERIMENTAL

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. Unless otherwise stated, the solid complexes are stable in air and are soluble in polar solvents such as CH_2Cl_2 or acetone to give moderately air-stable solutions. All the solvents were dried by standard methods and deoxygenated before use. The compounds $[M(CO)_3(\eta^4\text{-}C_4Ph_4)]$ (M = Fe or Ru) [26] were prepared by published procedures; salts of Ag^I and $[NO]^+$ were purchased from Fluorochem Ltd., and tcne from Aldrich Chemical Co. Ltd. Ultraviolet irradiations were carried out using a 250-W mercury lamp (Hanovia, type 504/4) with solutions contained in quartz glassware.

Infrared spectra were recorded on Perkin-Elmer PE 257 or 457 spectrophotometers and calibrated against the absorption band of polystyrene at 1 601 cm^{-1}. Hydrogen-1 n.m.r. spectra were obtained on a JEOL PS100 spectrometer and calibrated against tetramethylsilane as internal reference, ^{31}P n.m.r. spectra on a JEOL PFT 100 spectrometer and calibrated against H_3PO_4 as external reference.

* The equilibrium is pushed to the left in the presence of an excess of iodine which serves to remove I^- as inert $[I_3]^-$.

X-Band e.s.r. spectra were recorded on a Varian Associates 4502/15 instrument and were calibrated against a solid sample of the diphenylpicrylhydrazyl (dpph) radical. Cyclic voltammetric studies were made using the positive feedback capacity of the AMEL Electrochemolab in conjunction with a three-electrode cell. Auxiliary and working electrodes were platinum wires and the reference was a calomel electrode, 1 mol dm^{-3} in LiCl. Solutions were 10^{-3} mol dm^{-3} in complex and 0.05 mol dm^{-3} in $[NEt_4][ClO_4]$ as supporting electrolyte.

Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol. Melting points are uncorrected.

Dicarbonyl(1—4-η-tetraphenylcyclobutadiene)(triphenylphosphine) iron, $[Fe(CO)_2(PPh_3)(\eta^4\text{-}C_4Ph_4)]$.—A solution of $[Fe(CO)_3(\eta^4\text{-}C_4Ph_4)]$ (0.33 g, 0.67 mmol) and PPh_3 (0.22 g, 0.84 mmol) in thf (100 cm^3) was irradiated (u.v. light) for 30 h. The deep yellow solution was evaporated to dryness, and the residue dissolved in CH_2Cl_2 and chromatographed on a Florisil–hexane column. Elution with hexane–CH_2Cl_2 (4 : 1) removed unchanged $[Fe(CO)_3(\eta^4\text{-}C_4Ph_4)]$ and gave a second yellow band from which yellow crystals of $[Fe(CO)_2(PPh_3)(\eta^4\text{-}C_4Ph_4)]$ were isolated by partial removal of the solvent *in vacuo*. Yield 0.24 g (49%), m.p. 220 °C (decomp.).

Carbonyl(1—4-η-tetraphenylcyclobutadiene)bis(trimethyl phosphite) iron, $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$.—The complex $[Fe(CO)_3(\eta^4\text{-}C_4Ph_4)]$ (1.06 g, 2.14 mmol) and $P(OMe)_3$ (5.0 g, 40.3 mmol) in thf (300 cm^3) were treated as above (17 h irradiation). On chromatography, elution with hexane–diethyl ether (20 : 1) gave two yellow bands the first of which gave small amounts of $[Fe(CO)_2\{P(OMe)_3\}(\eta^4\text{-}C_4Ph_4)]$ (m.p. 162—166 °C). The second band gave, on removal of diethyl ether, yellow crystals of $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$. Yield 1.02 g (70%), m.p. 130—132 °C.

Yellow crystals of $[Ru(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$ (48%), m.p. 164—166 °C, were prepared similarly.

(1—4-η-Tetraphenylcyclobutadiene)tris(trimethyl phosphite)ruthenium, $[Ru\{P(OMe)_3\}_3(\eta^4\text{-}C_4Ph_4)]$.—Ultraviolet irradiation of a solution of $[Ru(CO)_3(\eta^4\text{-}C_4Ph_4)]$ (0.28 g, 0.51 mmol) and $P(OMe)_3$ (3.0 g, 24.2 mmol) in thf (150 cm^3) for 100 h gave a deep yellow solution from which the solvent was removed *in vacuo*. Dissolution of the residue in the minimum volume of diethyl ether and chromatography on Florisil gave small quantities of $[Ru(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$ [eluted with hexane–diethyl ether (10 : 1)] and $[Ru\{P(OMe)_3\}_3(\eta^4\text{-}C_4Ph_4)]$ [eluted with hexane–diethyl ether (1 : 1)]. Recrystallisation from hexane gave the complex as *yellow crystals*. Yield 0.16 g (38%), m.p. 188—192 °C (decomp.).

Carbonyl(tetraphenylcyclobutadiene)bis(trimethyl phosphite)-iron Tetrafluoroborate–Dichloromethane(1/1), $[Fe(CO)\{P(OMe)_3\}_2(C_4Ph_4)][BF_4]\cdot CH_2Cl_2$.—To a stirred, yellow solution of $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$ (0.203 g, 0.30 mmol) in CH_2Cl_2 (60 cm^3) was added solid $Ag[BF_4]$ (0.057 g, 0.30 mmol). After 2 h, more $Ag[BF_4]$ (0.015 g, 0.08 mmol) was added to aid completion of the reaction. After 4 h the red solution was filtered to remove metallic silver, reduced in volume, and treated with hexane to give an orange precipitate, yield 0.18 g (72%). Recrystallisation from CH_2Cl_2–hexane gave an analytically pure sample of the product as

† This reaction cannot involve direct oxidation of X^- to X_2 by (2) as the oxidation potential for the couple (1)—(2) is lower than that of X^-—$\frac{1}{2}X_2$.

red crystals which lose dichloromethane of solvation on standing in air or if washed with diethyl ether.

Carbonyl(1—2-η-tetracyanoethylene)(1—4-η-tetraphenylcyclobutadiene)(trimethyl phosphite)iron—Dichloromethane (3/1), $[Fe(CO)\{P(OMe)_3\}(\eta^2\text{-tcne})(\eta^4\text{-}C_4Ph_4)]\cdot 0.33\ CH_2Cl_2$.—To a stirred, yellow solution of $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$ (0.30 g, 0.44 mmol) in CH_2Cl_2 (70 cm^3) was added tcne (0.057 g, 0.44 mmol). After 3 h the deep emerald-green solution was filtered, reduced in volume, and treated with n-hexane to precipitate a dark green solid. Recrystallisation from CH_2Cl_2–hexane gave the complex as green-black *crystals*. Yield 0.21 g (67%), m.p. >120 °C (decomp.).

Iodo(1—4-η-tetraphenylcyclobutadiene)tris(trimethyl phosphite)ruthenium Tri-iodide, $[RuI\{P(OMe)_3\}_3(\eta^4\text{-}C_4Ph_4)][I_3]$.—A solution of I_2 (0.063 g, 0.25 mmol) in n-hexane (30 cm^3) was added dropwise to $[Ru\{P(OMe)_3\}_3(\eta^4\text{-}C_4Ph_4)]$ (0.103 g, 0.124 mmol) in hexane (70 cm^3). After stirring for 5 min the analytically pure yellow-orange precipitate was filtered off. Yield 0.12 g (70%), m.p. 104 °C (decomp.). The *complex* may be recrystallised from CH_2Cl_2–n-hexane if necessary.

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