Reduction–Oxidation Properties of Organotransition-metal Complexes. Part 29.[1] Pentaphenylcyclopentadienyl Complexes of Ruthenium *

Neil G. Connelly and Ian Manners
Department of Inorganic Chemistry, The University, Bristol BS8 1TS

The complex $[Ru_3(CO)_{12}]$ reacts with C_5Ph_5Br in toluene under reflux to give $[RuBr(CO)_2(\eta\text{-}C_5Ph_5)]$ (**1**) which undergoes carbonyl substitution with P-donor ligands, in acetone in the presence of $ONMe_3{\cdot}2H_2O$, to yield $[RuBr(CO)L(\eta\text{-}C_5Ph_5)]$ [**2**; L = PPh_3, PEt_3, or $P(OMe)_3$]. The halide abstraction reactions of (**2**) with $AgPF_6$ and L^1 afford $[Ru(CO)L(L^1)(\eta\text{-}C_5Ph_5)][PF_6]$ [**3**; L = PEt_3 or $P(OMe)_3$; L^1 = CO, C_2H_4, or MeC≡CMe], and the dicarbonyls $[Ru(CO)_2L(\eta\text{-}C_5Ph_5)][PF_6]$ [L = PEt_3 or $P(OMe)_3$] react with L^1, in acetone with $ONMe_3{\cdot}2H_2O$, to give [**3**; L = L^1 = PEt_3 or $P(OMe)_3$]. Complexes (**1**) and (**2**; L = PEt_3) react with LiMe in tetrahydrofuran, giving $[RuMe(CO)_2(\eta\text{-}C_5Ph_5)]$ (**4**) and $[RuR(CO)(PEt_3)(\eta\text{-}C_5Ph_5)]$ (**5**; R = Me) respectively, and (**5**; R = Et, COMe, or CMe=CMe$_2$) are prepared from (**3**; L = PEt_3, L^1 = C_2H_4) and $[NBu^n_4][BH_4]$ or from (**3**; L = PEt_3, L^1 = CO or MeC≡CMe) and LiMe. The neutral compounds (**1**), (**2**), (**4**), and (**5**) undergo diffusion-controlled one-electron oxidation at a platinum bead electrode in CH_2Cl_2. In most cases the electron-transfer process is fully reversible, but (**1**), (**4**), and $[FeMe(CO)_2(\eta\text{-}C_5Ph_5)]$ show only irreversible cyclic voltammetric waves. The chemical oxidation of (**2**) with $[N(C_6H_4Br\text{-}p)_3][SbCl_6]$ in CH_2Cl_2 gives the 17-electron cation ($\mathbf{2}^+$), and ($\mathbf{5}^+$) have also been characterised in solution after generation from (**5**) by $AgPF_6$ oxidation. Complexes (**1**) and (**3**) undergo diffusion-controlled but chemically irreversible reduction at the platinum electrode; reduction by $[Co(\eta\text{-}C_5H_5)_2]$ (*i*) of [**3**; L = $P(OMe)_3$, L^1 = CO] gives a mixture of (**4**), $[Ru\{P(O)(OMe)_2\}(CO)_2(\eta\text{-}C_5Ph_5)]$, and $[RuCl(CO)\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)]$, (*ii*) of [**3**; L = $P(OMe)_3$, L^1 = MeC≡CMe] gives $[RuH(CO)\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)]$, and (*iii*) of (**1**) gives *trans*-$[\{Ru(\mu\text{-}CO)(CO)(\eta\text{-}C_5Ph_5)\}_2]$ (**6**).

There is widespread general interest in 17- and 19-electron species as intermediates in organotransition-metal chemistry.[2] For iron, both iron(I)[3–9] and iron(III)[10–19] species have been postulated, the latter almost invariably resulting from the one-electron oxidation of the iron(II) complexes $[FeX(CO)_{2-n}L_n(\eta\text{-}C_5H_5)]$ (*n* = 0—2, X = halide, thiolate, alkyl, acyl, *etc.*; L = tertiary phosphine, isocyanide, *etc.*).[10–19] The alkyliron(III) carbonyls[11,14–18] are of particular interest in undergoing migratory insertion to the corresponding acyl derivatives far faster[15] than the iron(II) precursors; in addition, the oxidative conversion of $[FeMe(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ into $[Fe(COMe)(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ is electron-transfer catalysed[14] in the presence of CO.

The mechanism of this oxidatively induced, acyl-forming reaction is understood in general terms[14] but the paramagnetic intermediates have been only partially characterised. 17-Electron species such as $[FeX(dppe)(\eta\text{-}C_5H_5)]^+$ (X = halide, Me, $SnMe_3$, *etc.*; dppe = $Ph_2PCH_2CH_2PPh_2$)[19] and the β-lactam $[Fe(CO)\{NH(CH_2Ph)C(Me)CH_2C(O)\}(\eta\text{-}C_5H_5)]^+$[13] have been isolated as analytically pure solids, but 17-electron intermediates such as $[FeX(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$ (X = Me or COMe) and 19-electron cations such as $[FeMe(CO)(py)(PPh_3)(\eta\text{-}C_5H_5)]^+$ [when the reaction is carried out in the presence of pyridine (py)][11] have both been postulated in the catalysed insertion reaction.

The $\eta\text{-}C_5Ph_5$ ligand stabilises[20,21] paramagnetic complexes (cations, anions, and neutral molecules) formed by one-electron oxidation or reduction. We have therefore investigated the redox reactions of $\eta\text{-}C_5Ph_5$ complexes of ruthenium(II) in an attempt to stabilise ruthenium-(I) and -(III) radicals in general and to shed further light on the nature of the paramagnetic intermediates in the acyl-forming reaction in particular.

Results and Discussion

Synthetic Studies.—On heating a solution of $[Ru_3(CO)_{12}]$ and C_5Ph_5Br (1:3 ratio) in toluene under reflux, a deep purple colour, characteristic of the C_5Ph_5 radical,[22] rapidly developed. After 1 h, however, the reaction mixture was orange-brown, and on cooling to 0 °C yellow crystals of $[RuBr(CO)_2(\eta\text{-}C_5Ph_5)]$ (**1**) were deposited. The complex was characterised by elemental analysis and by routine spectroscopic methods;† the i.r. carbonyl bands at 2 047 and 2 000 cm^{-1} (CH_2Cl_2) are similar in frequency to those of $[RuBr(CO)_2(\eta\text{-}C_5H_5)]$ [$\tilde{\nu}(CO)(CH_2Cl_2)$ = 2 055 and 2 005 cm^{-1}] indicating the similar donor–acceptor properties of the two C_5 ligands.

As with $[FeBr(CO)_2(\eta\text{-}C_5Ph_5)]$,[23] carbonyl substitution of (**1**) by PPh_3 could not be achieved by thermolysis or u.v. photolysis. However, in boiling acetone in the presence of $ONMe_3{\cdot}2H_2O$ the dicarbonylruthenium complex reacted rapidly with P-donor ligands to give the orange mono-substituted derivatives $[RuBr(CO)L(\eta\text{-}C_5Ph_5)]$ [**2**; L = PPh_3, PEt_3, or $P(OMe)_3$] in 65—80% yields (Table 1).

In the presence of a second ligand, L^1, the bromides [**2**; L = PEt_3 or $P(OMe)_3$] undergo halide abstraction with $AgPF_6$ in CH_2Cl_2 to give the white or yellow cationic complexes $[Ru(CO)L(L^1)(\eta\text{-}C_5Ph_5)][PF_6]$ (**3**; L^1 = CO, C_2H_4, or MeC≡CMe). The dicarbonyls made by this route, namely [**3**; L^1 = CO, L = PEt_3, or $P(OMe)_3$], also undergo carbonyl substitution with L and $ONMe_3{\cdot}2H_2O$ in boiling acetone to give [**3**; L^1 = L = PEt_3 or $P(OMe)_3$].

---

* *Non-S.I. unit employed:* G = 10^{-4} T.

† All of the new complexes were characterised by elemental analysis and i.r. carbonyl spectroscopy (Table 1), by mass spectrometry (for neutral complexes), and by ^1H, ^{13}C, and ^{31}P n.m.r. spectroscopy. Most of the n.m.r. spectroscopic data (chemical shifts, coupling constants, *etc.*) are unremarkable, serving only to confirm the nature and relative abundance of the ligands present. For brevity, these data are not given; non-routine results are discussed in the text where appropriate.

Table 1. I.r. spectroscopic and analytical data for pentaphenylcyclopentadienyl–iron and –ruthenium complexes

Compound	Colour	Yield (%)	Analysis[a] (%)		$\tilde{\nu}$(CO)[b]/cm^{-1}
			C	H	
$[RuBr(CO)_2(\eta\text{-}C_5Ph_5)]$	Yellow	68	64.9 (65.1)	3.8 (3.7)	2 047, 2 000
$[RuBr(CO)(PEt_3)(\eta\text{-}C_5Ph_5)]$	Orange	75	64.8 (65.3)	5.3 (5.2)	1 942
$[RuBr(CO)(PPh_3)(\eta\text{-}C_5Ph_5)]$	Orange	65	70.3 (70.7)	4.7 (4.4)	1 944
$[RuBr(CO)\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)]$	Orange	80	57.5 (57.8)	4.4 (4.3)[c]	1 962
$[Ru(CO)_2(PEt_3)(\eta\text{-}C_5Ph_5)][PF_6]$	White	56	59.7 (59.6)	4.7 (4.7)	2 050, 2 004
$[Ru(CO)_2\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)][PF_6]$	White	64	55.1 (55.1)	3.8 (3.9)	2 072, 2 025
$[Ru(CO)(PEt_3)_2(\eta\text{-}C_5Ph_5)][PF_6]$	Yellow	79	56.5 (56.5)	5.7 (5.5)[d]	1 958
$[Ru(CO)\{P(OMe)_3\}_2(\eta\text{-}C_5Ph_5)][PF_6]$	White	67	48.8 (49.1)	4.3 (4.3)[d]	1 994
$[RuMe(CO)_2(\eta\text{-}C_5Ph_5)]$	White	58	73.7 (73.9)	4.6 (4.6)	2 014, 1 954
$[FeMe(CO)_2(\eta\text{-}C_5Ph_5)]$	Yellow	55	80.1 (79.7)	5.1 (4.9)	2 002, 1 946
$[RuH(CO)\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)]$	White	47	66.1 (66.9)	4.9 (5.1)	1 937
$[RuMe(CO)(PEt_3)(\eta\text{-}C_5Ph_5)]$	Yellow	51	73.3 (73.0)	6.6 (6.1)	1 900
$[RuEt(CO)(PEt_3)(\eta\text{-}C_5Ph_5)]$	Yellow	68	72.9 (73.2)	6.8 (6.3)	1 900
$[Ru(COMe)(CO)(PEt_3)(\eta\text{-}C_5Ph_5)]$	Yellow	65	71.6 (71.8)	5.9 (5.9)	1 915
$[Ru(CO)(C_2H_4)(PEt_3)(\eta\text{-}C_5Ph_5)][PF_6]$	White	73	58.8 (58.8)	5.0 (4.9)[c]	1 996
$[Ru(CO)(C_2H_4)\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)][PF_6]$	White	68	56.5 (56.5)	4.4 (4.4)	2 014
$[Ru(CO)(MeC{\equiv}CMe)(PEt_3)(\eta\text{-}C_5Ph_5)][PF_6]$	Yellow	74	61.9 (61.9)	5.1 (5.2)	1 987
$[Ru(CO)(MeC{\equiv}CMe)\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)][PF_6]$	Yellow	82	57.6 (57.5)	4.6 (4.5)	2 002
$[Ru(CMe{=}CMe_2)(CO)(PEt_3)(\eta\text{-}C_5Ph_5)]$	Yellow	57	74.2 (74.1)	6.4 (6.5)	1 904
$[\{Ru(\mu\text{-}CO)(CO)(\eta\text{-}C_5Ph_5)\}_2]$	Orange	40	69.7 (69.8)	4.3 (4.1)[d]	1 962, 1 769[e]
$[\{Fe(\mu\text{-}CO)(CO)(\eta\text{-}C_5Ph_5)\}_2]$	Green				1 954, 1 774[e]

[a] Calculated values in parentheses. [b] In CH_2Cl_2 unless otherwise stated. [c] Analysed as a 0.5 CH_2Cl_2 solvate. [d] Analysed as a 1.0 CH_2Cl_2 solvate. [e] In Nujol.

σ-Bonded hydrocarbon derivatives are also simply synthesised. The reaction between (**1**) and LiMe in tetrahydrofuran (thf) gives $[RuMe(CO)_2(\eta\text{-}C_5Ph_5)]$ (**4**), and although direct carbonyl substitution of this species was not observed, the monocarbonyl derivatives were prepared from (**2**) or (**3**). Thus, (**2**; L = PEt_3) and LiMe give $[RuR(CO)(PEt_3)(\eta\text{-}C_5Ph_5)]$ (**5**; R = Me), and (**3**; L = PEt_3, L^1 = C_2H_4) reacts with $[NBu^n_4][BH_4]$ to yield (**5**; R = Et). Finally, the cations (**3**; L = PEt_3, L^1 = CO or MeC≡CMe) react with LiMe in thf to give respectively the pale yellow acetyl and trimethylvinyl complexes (**5**; R = COMe or CMe=CMe$_2$) *via* nucleophilic attack at L^1.

Although the n.m.r. spectra of (**5**; R = Me, Et, or COMe) were unremarkable, those of (**5**; R = CMe=CMe$_2$) indicated the presence in solution of two isomers. The ^{13}C n.m.r. spectrum showed two doublets due to phosphorus-coupled carbonyl carbons [δ 210.88 p.p.m., $J(^{13}C^{31}P)$ 19 Hz; δ 210.57 p.p.m., $J(^{13}C^{31}P)$ 23 Hz] and two singlets for the C_5-ring nuclei (δ 105.65 and 105.82 p.p.m.). In addition, the ^{31}P n.m.r. spectrum showed two singlets (δ 20.22 and 19.62 p.p.m.) of similar intensity. These data are consistent with the presence of two rotamers (Figure 1) in an approximate 1:1 ratio, the rotamerism resulting from restricted rotation about the Ru–C(vinyl) bond. The existence of rotamers of $[M(\sigma\text{-}CR{=}CRR)(CO)L(\eta\text{-}C_5H_5)]$ (M = Fe or Ru, L = P-donor ligand, R = alkyl, *etc.*) has been noted[24] previously, and *X*-ray structural studies on $[Fe\{Z\text{-}CMe{=}C(Ph)Me\}(CO)\{P(OPh)_3\}(\eta\text{-}C_5H_5)]$[25] and $[Fe\{E\text{-}C(CO_2Et){=}CHMe\}(CO)(PPh_3)(\eta\text{-}C_5H_5)]$[26] have revealed conformations analogous to those in Figure 1(*a*) and (*b*) respectively.

The Electron-transfer Reactions of Complexes (**1**)—(**5**).—All of the complexes (**1**)—(**5**) have been studied by cyclic voltammetry at a platinum bead electrode in CH_2Cl_2 (Table 2). Specific conditions are given in the Experimental section.

Oxidation. Each of the complexes [**2**; L = PPh_3, PEt_3 or $P(OMe)_3$] and (**5**; R = Me, Et, COMe, or CMe=CMe$_2$) undergoes diffusion controlled $[(i_p)_{ox}/v^{\frac{1}{2}}$ = constant for scan rates $50 \leqslant v \leqslant 500$ mV s^{-1}] one-electron oxidation in the potential range 0.0 to 1.8 V. In all cases but for (**5**; R = CMe=CMe$_2$), the electron-transfer process is fully reversible $[(i_p)_{red}/(i_p)_{ox} = 1]$ at all of the scan rates used. Reversibility was only observed for the trimethylvinyl complex for $v \geqslant 500$ mV s^{-1}, indicating $[Ru(\sigma\text{-}CMe{=}CMe_2)(CO)(PEt_3)(\eta\text{-}C_5Ph_5)]^+$ (**5**$^+$, R = CMe=CMe$_2$) to be less stable than the other 17e$^-$ cations, with a maximum lifetime of *ca.* 1 s at 25 °C in CH_2Cl_2. The dicarbonyls (**1**), (**4**), and $[FeMe(CO)_2(\eta\text{-}C_5Ph_5)]$ show irreversible oxidation waves at all scan rates.

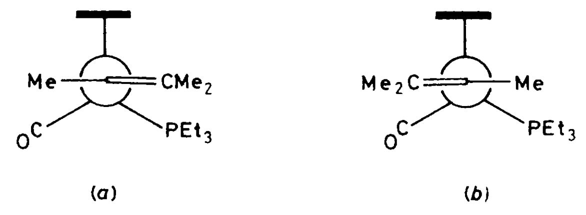

Figure 1. The rotational isomers of $[Ru(\sigma\text{-}CMe{=}CMe_2)(CO)(PEt_3)(\eta\text{-}C_5Ph_5)]$ (**5**; R = CMe=CMe$_2$)

These cyclic voltammetric data show that the C_5Ph_5 ligand stabilises the ruthenium(III) cations (**2**$^+$) and (**5**$^+$; R = Me, Et, or COMe). Only a limited comparison with C_5H_5 analogues can be made, but the oxidation of $[RuX(CO)_{2-n}(PPh_3)_n(\eta\text{-}C_5H_5)]$ is described[27] as irreversible for (X = Me, n = 0 or 1) and only partially reversible for (X = Me, n = 2; X = Cl, n = 1).

The potentials for the oxidation of complexes (**1**)—(**5**) (Table 2) show the expected trends in that (*i*) CO substitution by L lowers the E^0 value by *ca.* 0.7 V, (*ii*) the bromides are more difficult to oxidise than the complexes of σ-bound hydrocarbons (by *ca.* 0.3 V), and (*iii*) there is a small dependence of E^0 on the P-donor ligand substituent. Surprisingly, the E^0 values for the oxidations of (**5**; R = Me) and (**5**; R = COMe) are very similar, with the acetyl complex the easier to oxidise. For $[FeR(CO)(PPh_3)(\eta\text{-}C_5H_5)]$, the oxidatively induced migratory insertion

Table 2. Cyclic voltammetric[a] data for pentaphenylcyclopentadienyl-iron and -ruthenium carbonyl complexes

Complex	E_{ox}[b]/V	E_{red}[c]/V
$[RuBr(CO)_2(\eta\text{-}C_5Ph_5)]$	1.76[d]	−1.46
$[RuMe(CO)_2(\eta\text{-}C_5Ph_5)]$	1.49[d]	
$[FeMe(CO)_2(\eta\text{-}C_5Ph_5)]$	1.18[d,e]	
$[RuBr(CO)(PPh_3)(\eta\text{-}C_5Ph_5)]$	1.07	
$[RuBr(CO)(PEt_3)(\eta\text{-}C_5Ph_5)]$	1.01	
$[RuBr(CO)\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)]$	1.12	
$[RuMe(CO)(PEt_3)(\eta\text{-}C_5Ph_5)]$	0.73	
$[RuEt(CO)(PEt_3)(\eta\text{-}C_5Ph_5)]$	0.71	
$[Ru(COMe)(CO)(PEt_3)(\eta\text{-}C_5Ph_5)]$	0.67	
$[Ru(CMe{=}CMe_2)(CO)(PEt_3)(\eta\text{-}C_5Ph_5)]$	0.59[f]	
$[Ru(CO)_2(PEt_3)(\eta\text{-}C_5Ph_5)]^+$		−1.25
$[Ru(CO)_2\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)]^+$		−1.23
$[Ru(CO)(PEt_3)(C_2H_4)(\eta\text{-}C_5Ph_5)]^+$		−1.37
$[Ru(CO)\{P(OMe)_3\}(C_2H_4)(\eta\text{-}C_5Ph_5)]^+$		−1.33
$[Ru(CO)(PEt_3)(MeC{\equiv}CMe)(\eta\text{-}C_5Ph_5)]^+$		−1.33
$[Ru(CO)\{P(OMe)_3\}(MeC{\equiv}CMe)(\eta\text{-}C_5Ph_5)]^+$		−1.32

[a] Potentials are *versus* the aqueous saturated calomel electrode, measured at a platinum bead in CH_2Cl_2 with 0.1 mol dm^{-3} $[NBu^n_4][PF_6]$ as supporting electrolyte. Under these conditions, the E^0 value for the couple $[Fe(\eta\text{-}C_5H_5)_2]^+$–$[Fe(\eta\text{-}C_5H_5)_2]$ is 0.47 V. [b] Unless otherwise stated, E_{ox} is the potential for a reversible one-electron oxidation. [c] E_{red} is the peak potential for an irreversible reduction, measured at a scan rate of 200 mV s^{-1}. [d] Irreversible process; E_{ox} is the oxidation peak potential at 200 mV s^{-1}. [e] In thf. [f] Reversible process only for scan rates ⩾500 mV s^{-1}.

Table 3. E.s.r. spectra data[a] for $[RuX(CO)(PEt_3)(\eta\text{-}C_5Ph_5)]^+$

X	g_1	g_2	g_3	g_{av}
Br	2.292	2.140	1.992[b]	2.141
Me	2.083[c]			2.083[d]
Et	2.078[c]			2.078
COMe	2.063	2.036	1 992	2.030
$CMe{=}CMe_2$	2.039[c]			2.039

[a] In frozen CH_2Cl_2 at −196 °C. [b] This component shows $^{79,81}Br$ hyperfine coupling of 120 G. [c] $g_1 = g_2 = g_3$. [d] 2.085 in CH_2Cl_2 at 25 °C.

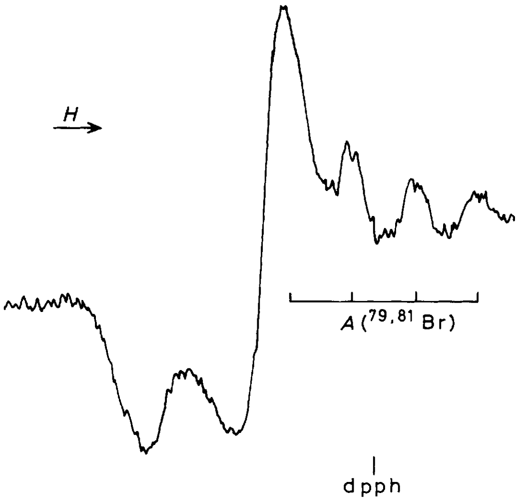

Figure 2. The e.s.r. spectrum of $[RuBr(CO)(PEt_3)(\eta\text{-}C_5Ph_5)]^+$ ($\mathbf{2}^+$; L = PEt_3), in CH_2Cl_2 at −196 °C

reaction which converts the methyl (R = Me, E^0 = 0.38 V) into the acyl (R = COMe, E^0 = 0.47 V) is only catalytic because the latter is more difficult to oxidise than the former.[14]

The reaction of $[N(C_6H_4Br\text{-}p)_3]^+$ (E^0 = 1.25 V), as the $[SbCl_6]^-$ salt, with (**2**) in CH_2Cl_2 gave dark brown solutions which undoubtedly contain the cations ($\mathbf{2}^+$). Although no solid products could be isolated, the solutions each show one i.r. carbonyl band shifted to higher wavenumber by *ca.* 75 cm^{-1} [$\mathbf{2}^+$; L = PPh_3, $\tilde{\nu}$(CO) = 2 016 cm^{-1}; L = PEt_3, $\tilde{\nu}$(CO) = 2 018 cm^{-1}; L = $P(OMe)_3$, $\tilde{\nu}$(CO) = 2 033 cm^{-1}]; the oxidation of $[FeMe(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ [$\tilde{\nu}$(CO) = 1 904 cm^{-1}] to $[FeMe(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$ [$\tilde{\nu}$(CO) = 1 966 cm^{-1}] is accompanied by a similar change.[11]

The formation of ($\mathbf{2}^+$; L = PEt_3) is also supported by the anisotropic e.s.r. spectra observed at −196 °C. When (**2**; L = PEt_3) was oxidised with $[N(C_6H_4Br\text{-}p)_3][SbCl_6]$, the e.s.r. spectrum of ($\mathbf{2}^+$; L = PEt_3) was partly obscured by the signal due to the ammonio cation itself. However, the addition of CH_2Cl_2 to a solid mixture of (**2**; L = PEt_3) and $[NO][PF_6]$, and rapid cooling of the product to −196 °C, gave the spectrum of only ($\mathbf{2}^+$; L = PEt_3), shown in Figure 2. Of the three g values (g_1 = 2.292, g_2 = 2.140, g_3 = 1.992; g_{av} = 2.141) that to highest field shows hyperfine coupling (120 G) to the bromine atom [the fourth line of the expected quartet (^{79,81}Br, $I = \frac{3}{2}$) is obscured by the central component at g = 2.140].

The E^0 values of complexes (**5**) are such that ($\mathbf{5}^+$) can be generated chemically more readily than ($\mathbf{2}^+$). The addition of $AgPF_6$ to (**5**; R = Me) in CH_2Cl_2 rapidly gave a deep violet solution of ($\mathbf{5}^+$; R = Me) with one i.r. carbonyl band at 1 996 cm^{-1} [*cf.* (**5**; R = Me), $\tilde{\nu}$(CO) = 1 900 cm^{-1}] and a single-line e.s.r. spectrum both at room temperature (g = 2.085) and at −196 °C (g = 2.083). Although ($\mathbf{5}^+$; R = Me) could not be isolated, the e.s.r. spectrum and the deep purple colour of the solution persist at room temperature for at least 10 min so that the stability of this 17-electron cation contrasts markedly with the reactivity of $[FeMe(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$. In the presence of CO, the latter rapidly undergoes[14] migratory insertion to $[Fe(COMe)(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$, a reaction which could not be induced for ($\mathbf{5}^+$; R = Me).

The room temperature reaction of complexes (**5**; R = Et, COMe, or $CMe{=}CMe_2$) with $AgPF_6$ in CH_2Cl_2 also results in the formation of ($\mathbf{5}^+$) but the intense colours of the cations fade, in minutes in the cases of the purple acetyl and ethyl complexes, and more rapidly for the green-blue vinyl. The cations ($\mathbf{5}^+$) are more persistent at lower temperatures however, with the vinyl stable for 30 min at −78 °C.

The e.s.r. spectra of ($\mathbf{5}^+$; R = Et, COMe, or $MeC{=}CMe_2$) were recorded (Table 3) using samples prepared by adding precooled (0 °C) CH_2Cl_2 to a solid mixture of (**5**) and $AgPF_6$, and subsequent rapid further cooling of the reaction product to −196 °C in liquid nitrogen. The single-line spectra of ($\mathbf{5}^+$; R = Et or $CMe{=}CMe_2$) are similar to that of ($\mathbf{5}^+$; R = Me), but the acetyl cation ($\mathbf{5}^+$; R = COMe) shows an asymmetric spectrum with three g values at 2.063, 2.036, and 1.992 (g_{av} = 2.030).

It is difficult to make even qualitative comparisons between the e.s.r. spectra of the $Ru(\eta\text{-}C_5Ph_5)$ complexes and those of their $Fe(\eta\text{-}C_5H_5)$ analogues in that published data for the latter are inconsistent [no data exist for $Ru(\eta\text{-}C_5H_5)$ complexes]. The low temperature (−80 °C) spectra of $[Fe(CH_2OH)(CO)_2(\eta\text{-}C_5H_5)]^+$ and $[FeMe(CO)_2(\eta\text{-}C_5H_5)]^+$ each show[12] three g values with g_{av} (2.06 and 2.05 respectively) in good agreement with the room temperature data for the more stable complexes $[Fe(CO)\{CH_2C(Me)N(CH_2Ph)C(O)\}(\eta\text{-}C_5H_5)]$ (g = 2.0518)[13] and $[Fe(CN)(COR)(CO)(\eta\text{-}C_5H_5)]$ (R = Me, g = 2.059; R = Ph, g = 2.060).[18] However, the spectrum recently reported[11] for $[FeMe(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$ [g = 2.009,

$A(^{31}P)$ = 120 G, −20 °C] is most unusual, and those for the acetyl analogues $[Fe(COMe)(CO)L(\eta\text{-}C_5H_5)]^+$ (L = NCMe or PPh_3) are described[17] only as 'asymmetric', with widely different g values of 2.04 and 2.24 respectively. More definitive studies are required.

Reduction. The cationic complexes (**3**; L = PEt_3, L^1 = CO, C_2H_4, or MeC≡CMe) show no oxidation waves in their cyclic voltammograms, but undergo diffusion-controlled, chemically irreversible reduction at rather negative potentials (*ca.* −1.2 to −1.4 V); the complexes [**3**; L = L^1 = PEt_3 or $P(OMe)_3$] are not redox active in the potential range ±1.7 V. Of the neutral complexes, only (**1**) showed a reduction wave, similarly irreversible and with a peak potential of −1.42 V in CH_2Cl_2 and −1.40 V in thf.

The reaction of $[Co(\eta\text{-}C_5H_5)_2]$ with [**3**; L = $P(OMe)_3$, L^1 = CO] in CH_2Cl_2 gave a mixture of $[RuMe(CO)_2(\eta\text{-}C_5Ph_5)]$, $[RuCl(CO)\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)]$, and the phosphonate complex $[Ru\{P(O)(OMe)_2\}(CO)_2(\eta\text{-}C_5Ph_5)]$. The last shows a singlet ^{31}P n.m.r. resonance with a much lower chemical shift (δ 82.22 p.p.m.) than that found for $P(OMe)_3$ bound to $Ru(\eta\text{-}C_5Ph_5)$ {*e.g.* δ 135.32 for [**2**; L = $P(OMe)_3$]; δ 131.35 for [**3**; L = L^1 = $P(OMe)_3$]}, and the i.r. carbonyl spectrum is very similar to that[28] of $[Fe\{P(O)(OMe)_2\}(CO)_2(\eta\text{-}C_5H_5)]$ [$\tilde{\nu}(CO)(CH_2Cl_2)$ 2 043 and 1 989 cm^{-1}].

The two dicarbonyls appear to result from a Michaelis–Arbusov type rearrangement.[29] Two mechanisms may be proposed for their formation, the first (Scheme 1) involving a novel reaction between the two radicals $[Ru(CO)_2(\eta\text{-}C_5Ph_5)]$ and $[Ru(CO)_2\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)]$, and the second (Scheme 2) nucleophilic attack of $[Ru(CO)_2(\eta\text{-}C_5Ph_5)]^-$ on the starting material [**3**; L = $P(OMe)_3$, L^1 = CO]. It is difficult to distinguish between the two possibilities although the observation[28] that $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ and $[Fe(CO)_2\{P(OMe)_3\}(\eta\text{-}C_5H_5)]^+$ give $[MoMe(CO)_3(\eta\text{-}C_5H_5)]$ and $[Fe\{P(O)(OMe)_2\}(CO)_2(\eta\text{-}C_5H_5)]$ lends support to the mechanism in Scheme 2.

$$[M(CO)_2\{P(OMe)_3\}]^+ \xrightarrow{e^-} [M(CO)_2\{P(OMe)_3\}]^{\cdot}$$

$$[M(CO)_2\{P(OMe)_3\}]^{\cdot} \longrightarrow [M(CO)_2]^{\cdot} + P(OMe)_3$$

$$[M(CO)_2\{P(OMe)_3\}]^{\cdot} + [M(CO)_2]^{\cdot} \longrightarrow [MMe(CO)_2] + [M\{P(O)(OMe)_2\}(CO)_2]$$

Scheme 1. M = $Ru(\eta\text{-}C_5Ph_5)$

$$[M(CO)_2\{P(OMe)_3\}]^+ \xrightarrow{2e^-} [M(CO)_2]^- + P(OMe)_3$$

$$[M(CO)_2]^- + [M(CO)_2\{P(OMe)_3\}]^+ \longrightarrow [MMe(CO)_2] + [M\{P(O)(OMe)_2\}(CO)_2]$$

Scheme 2. M = $Ru(\eta\text{-}C_5Ph_5)$

The reaction of complex [**3**; L = $P(OMe)_3$, L^1 = MeC≡CMe] with $[Co(\eta\text{-}C_5H_5)_2]$ in toluene gave $[RuH(CO)\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)]$, characterised by elemental analysis (Table 1), mass spectrometry, and by a high field, phosphorus-coupled hydride resonance [δ −11.29 p.p.m., $J(^1H^{31}P)$ = 37 Hz] in the ^1H n.m.r. spectrum. The most plausible mechanism for the formation of the hydride complex involves hydrogen atom abstraction by the 17-electron radical $[Ru(CO)\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)]$ (Scheme 3), a reaction well established for organotransition-metal radicals and typified by the formation of $[FeH(CO)(dppe)(\eta\text{-}C_5Me_5)]$ from $[Fe(CO)(dppe)(\eta\text{-}C_5Me_5)]$.[7]

$$\begin{tikzcd}
{[M(CO)\{P(OMe)_3\}(\eta\text{-}MeC{\equiv}CMe)]^+} \arrow[r] & {[M(CO)\{P(OMe)_3\}(\eta\text{-}MeC{\equiv}CMe)]^{\cdot}} \arrow[d, "-\mathrm{MeC{\equiv}CMe}"] \\
{[MH(CO)\{P(OMe)_3\}]} & {[M(CO)\{P(OMe)_3\}]^{\cdot}} \arrow[l, "H^{\cdot}"']
\end{tikzcd}$$

Scheme 3. M = $Ru(\eta\text{-}C_5Ph_5)$

$$[MBr(CO)_2] \xrightarrow{e^-} [MBr(CO)_2]^{\cdot -}$$

$$[MBr(CO)_2]^{\cdot -} \longrightarrow [M(CO)_2]^{\cdot} + Br^-$$

$$2[M(CO)_2]^{\cdot} \longrightarrow [\{M(\mu\text{-}CO)(CO)\}_2]$$

Scheme 4. M = $Ru(\eta\text{-}C_5Ph_5)$

$$[MBr(CO)_2] \xrightarrow{2e^-} [M(CO)_2]^- + Br^-$$

$$[M(CO)_2]^- + [MBr(CO)_2] \longrightarrow [\{M(\mu\text{-}CO)(CO)\}_2] + Br^-$$

Scheme 5. M = $Ru(\eta\text{-}C_5Ph_5)$

In thf, (**1**) reacts slowly with $[Co(\eta\text{-}C_5H_5)_2]$ to give an orange complex which slowly decomposes but which has been characterised as *trans*-$[\{Ru(\mu\text{-}CO)(CO)(\eta\text{-}C_5Ph_5)\}_2]$ (**6**) by elemental analysis (Table 1) and by the i.r. carbonyl spectrum which shows one terminal (1 962 cm^{-1}) and one bridging (1 769 cm^{-1}) absorption {*cf.* *trans*-$[\{Ru(\mu\text{-}CO)(CO)(\eta\text{-}C_5Me_5)\}_2]$, $\tilde{\nu}(CO)$ = 1 925 and 1 744 cm^{-1}};[30] the mass spectrum showed no parent ion (M^+) but peaks were present corresponding to the diruthenium fragments $[M - 4(CO)]^+$ and $[M - 4(CO) - C_5Ph_5]^+$.

The analogous reaction between $[Co(\eta\text{-}C_5H_5)_2]$ and $[FeBr(CO)_2(\eta\text{-}C_5Ph_5)]$ afforded an unstable green solid whose i.r. carbonyl spectrum [$\tilde{\nu}(CO)$(Nujol) 1 954 and 1 774 cm^{-1}] suggested the formulation *trans*-$[\{Fe(\mu\text{-}CO)(CO)(\eta\text{-}C_5Ph_5)\}_2]$ {*cf.* (**6**) and *trans*-$[\{Fe(\mu\text{-}CO)(CO)(\eta\text{-}C_5Me_5)\}_2]$ [$\tilde{\nu}(CO)$ 1 932 and 1 764 cm^{-1}][31]}. A complex with similar properties, prepared from $[FeBr(CO)_2(\eta\text{-}C_5Ph_5)]$ and sodium amalgam, was reported[23] in 1965, but its dimeric nature was not established.

Complex (**6**) may be formed *via* the coupling of two $[Ru(CO)_2(\eta\text{-}C_5Ph_5)]$ radicals (Scheme 4) or by nucleophilic attack of $[Ru(CO)_2(\eta\text{-}C_5Ph_5)]^-$ on (**1**) (Scheme 5). Again, it is impossible to distinguish between the possibilities, but the reaction of $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ with $[FeX(CO)_2(\eta\text{-}C_5H_5)]$ (X = Cl or I) to give[32] $[\{Fe(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)\}_2]$ provides some evidence for the mechanism in Scheme 5.

Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. Unless stated otherwise, products (*i*) were purified by dissolving in CH_2Cl_2, filtration, addition of n-hexane, and partial evaporation of the solvent mixture *in vacuo* to induce precipitation, and (*ii*) dissolve in polar solvents such as CH_2Cl_2 or thf to give solutions which slowly decompose in air.

The compounds $[FeBr(CO)_2(\eta\text{-}C_5Ph_5)]$,[23] $[Co(\eta\text{-}C_5H_5)_2]$,[33] C_5Ph_5Br,[22] and $[N(C_6H_4Br\text{-}p)_3][SbCl_6]$[34] were prepared by published methods; the salts $[NO][PF_6]$ and $AgPF_6$ were purchased from Fluorochem Ltd., $[NBu^n{}_4][BH_4]$ from Aldrich Chemical Co., Inc.

Infrared spectra were recorded on a Nicolet FT 7199 spectrometer, or a Perkin-Elmer PE 257 spectrometer with calibration against the absorption band of polystyrene at 1 601 cm^{-1}. Proton n.m.r. spectra were recorded on JEOL PMX 60 or FX 90Q instruments, and ^{13}C n.m.r. spectra on JEOL FX 90Q or FX 200 spectrometers. All were calibrated against tetramethylsilane as internal reference. Phosphorus-31 n.m.r. spectra were recorded on a JEOL FX 90Q instrument using 85% H_3PO_4 as external reference.

Mass spectra were recorded on an AEI MS 902 spectrometer. *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. Electrochemical studies were carried out as described previously.[35] Solutions were 0.5×10^{-3} and 1.0×10^{-3} mol dm^{-3} in complex for voltammetry and controlled potential electrolysis respectively; in both cases the solutions were 0.1 mol dm^{-3} in $[NBu^n{}_4][PF_6]$ as supporting electrolyte. Under these conditions, E^0 for the couple $[Fe(\eta\text{-}C_5H_5)_2]^+\text{–}[Fe(\eta\text{-}C_5H_5)_2]$ is 0.47 V. Microanalyses were carried out by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

Bromodicarbonyl(η-*pentaphenylcyclopentadienyl*)*ruthenium*, $[RuBr(CO)_2(\eta\text{-}C_5Ph_5)]$.—A mixture of $[Ru_3(CO)_{12}]$ (1.48 g, 2.31 mmol) and C_5Ph_5Br (3.63 g, 6.91 mmol) in toluene (90 cm^3) was heated under reflux for 1 h. The orange-brown solution was then filtered and cooled to 0 °C to give a yellow precipitate. Recrystallisation from hot toluene gave the product as a yellow solid, yield 3.20 g (68%).

Bromocarbonyl(η-*pentaphenylcyclopentadienyl*)(*triethylphosphine*)*ruthenium*, $[RuBr(CO)(PEt_3)(\eta\text{-}C_5Ph_5)]$.—To a suspension of $[RuBr(CO)_2(\eta\text{-}C_5Ph_5)]$ (1.01 g, 1.48 mmol) in acetone (95 cm^3) was added an excess of PEt_3 (0.5 cm^3) and $ONMe_3\cdot 2H_2O$ (0.16 g, 1.44 mmol). After heating the mixture under reflux for 15 min, n-hexane (100 cm^3) was added and the solution was cooled to -10 °C to give an orange precipitate. Purification from CH_2Cl_2–hexane gave an orange solid, yield 0.85 g (75%).

The complexes $[RuBr(CO)L(\eta\text{-}C_5Ph_5)]$ [L = PPh_3 or $P(OMe)_3$], the latter as a 0.5 CH_2Cl_2 solvate, were prepared similarly.

(η-*But*-2-*yne*)*carbonyl*(η-*pentaphenylcyclopentadienyl*)(*trimethyl phosphite*)*ruthenium Hexafluorophosphate*, $[Ru(CO)(\eta\text{-}MeC{\equiv}CMe)\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)][PF_6]$.—To a mixture of $[RuBr(CO)\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)]\cdot 0.5CH_2Cl_2$ (0.51 g, 0.62 mmol) and an excess of but-2-yne (0.3 cm^3) in CH_2Cl_2 (40 cm^3) was added $AgPF_6$ (0.16 g, 0.63 mmol). The resulting yellow-orange solution was heated under reflux for 30 min and then filtered through Kieselguhr. Addition of n-hexane (100 cm^3) to the filtrate precipitated the product which was purified from CH_2Cl_2–n-hexane to give a yellow solid, yield 0.46 g (82%).

The complexes $[Ru(CO)L(L^1)(\eta\text{-}C_5Ph_5)][PF_6]$ [L = $P(OMe)_3$, L^1 = CO or C_2H_4; L = PEt_3, L^1 = CO, C_2H_4, or $MeC{\equiv}CMe$] were prepared similarly from $[RuBr(CO)L(\eta\text{-}C_5Ph_5)]$ and L^1, but heating was not necessary for L = PEt_3. The complexes (L^1 = C_2H_4 or $MeC{\equiv}CMe$) are air-sensitive in the solid state and in solution.

Carbonyl(η-*pentaphenylcyclopentadienyl*)*bis*(*trimethyl phosphite*)*ruthenium Hexafluorophosphate–Dichloromethane* (1/1), $[Ru(CO)\{P(OMe)_3\}_2(\eta\text{-}C_5Ph_5)][PF_6]\cdot CH_2Cl_2$.—A mixture of $[Ru(CO)_2\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)][PF_6]$ (0.20 g, 0.23 mmol), an excess of $P(OMe)_3$ (0.3 cm^3), and $ONMe_3\cdot 2H_2O$ (0.03 g, 0.27 mmol) in acetone (50 cm^3) was heated under reflux for 15 min. The solution was then filtered, n-hexane (100 cm^3) was added, and reduction of the solvent volume *in vacuo* precipitated the product. Purification from CH_2Cl_2–n-hexane gave a white solid, yield 0.16 g (67%).

The complex $[Ru(CO)(PEt_3)_2(\eta\text{-}C_5Ph_5)][PF_6]\cdot CH_2Cl_2$ was prepared similarly.

Carbonyl(*methyl*)(η-*pentaphenylcyclopentadienyl*)(*triethylphosphine*)*ruthenium*, $[RuMe(CO)(PEt_3)(\eta\text{-}C_5Ph_5)]$.—To a stirred, cooled (0 °C) solution of $[RuBr(CO)(PEt_3)(\eta\text{-}C_5Ph_5)]$ (1.01 g, 1.31 mmol) in thf (35 cm^3) was added an excess (1.5:1) of LiMe in diethyl ether. After 30 min the solution was reduced in volume to 5 cm^3 and then transferred to an n-hexane–alumina chromatography column (25 × 2.5 cm). Elution with n-hexane–thf (9:1) gave a yellow solution which was evaporated to dryness. Purification of the residue from thf–n-hexane gave the product as a yellow solid, yield 0.47 g (51%).

The complexes $[MMe(CO)_2(\eta\text{-}C_5Ph_5)]$ (M = Fe or Ru) were prepared similarly except that elution required n-hexane–thf (4:1), and for the iron complex MgMeBr in diethyl ether was used instead of LiMe.

Carbonyl(*ethyl*)(η-*pentaphenylcyclopentadienyl*)(*triethylphosphine*)*ruthenium*, $[RuEt(CO)(PEt_3)(\eta\text{-}C_5Ph_5)]$.—To a stirred solution of $[Ru(CO)(\eta\text{-}C_2H_4)(PEt_3)(\eta\text{-}C_5Ph_5)][PF_6]\cdot 0.5CH_2Cl_2$ (0.52 g, 0.57 mmol) in thf (35 cm^3) was added $[NBu^n{}_4][BH_4]$ (0.15 g, 0.58 mmol). After 10 min the solution was filtered through Kieselguhr and then reduced in volume to 5 cm^3. Chromatography on an n-hexane–alumina column (25 × 2.5 cm) and elution with n-hexane–thf (3:1) gave a yellow solution which was evaporated to dryness. Purification of the residue from CH_2Cl_2–n-hexane gave the product as a yellow solid, yield 0.28 g (68%).

Acetyl(*carbonyl*)(η-*pentaphenylcyclopentadienyl*)(*triethylphosphine*)*ruthenium*, $[Ru(COMe)(CO)(PEt_3)(\eta\text{-}C_5Ph_5)]$.—To a stirred, cooled (0 °C), solution of $[Ru(CO)_2(PEt_3)(\eta\text{-}C_5Ph_5)][PF_6]$ (0.31 g, 0.36 mmol) in thf (30 cm^3) was added an excess (1.5:1) of MgMeBr in diethyl ether. After 30 min the solvent volume was reduced *in vacuo* to 5 cm^3. Chromatography on an n-hexane–alumina column (20 × 2.5 cm) and elution with n-hexane–thf (3:1) gave a yellow solution. Removal of the solvent, and purification of the residue from thf–n-hexane gave the product as a yellow solid, yield 0.17 g (65%).

The complex $[Ru(\sigma\text{-}CMe{=}CMe_2)(CO)(PEt_3)(\eta\text{-}C_5Ph_5)]$ was prepared similarly from $[Ru(CO)(\eta\text{-}MeC{\equiv}CMe)(PEt_3)(\eta\text{-}C_5Ph_5)][PF_6]$ except that elution with n-hexane–thf (6:1) was required.

Reaction of $[Ru(CO)(\eta\text{-}MeC{\equiv}CMe)\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)][PF_6]$ *with* $[Co(\eta\text{-}C_5H_5)_2]$; *Synthesis of* $[RuH(CO)\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)]$.—To an excess (1.4:1) of $[Co(\eta\text{-}C_5H_5)_2]$ (0.07 g, 0.37 mmol) in toluene (20 cm^3) was added $[Ru(CO)(MeC{\equiv}CMe)\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)][PF_6]$ (0.24 g, 0.27 mmol). After 25 min the brown suspension was filtered through a 3 cm thick pad of alumina and the filtrate evaporated to dryness. The orange-brown residue was dissolved in thf (2 cm^3) and transferred to an n-hexane–alumina column (25 × 2.5 cm). Elution with n-hexane–thf (2 : 1) gave a pale yellow solution which was evaporated to dryness. Purification from thf–n-hexane gave the product as a white solid, yield 0.09 g (47%).

Reaction of $[Ru(CO)_2\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)][PF_6]$ *with* $[Co(\eta\text{-}C_5H_5)_2]$.—To a stirred solution of $[Co(\eta\text{-}C_5H_5)_2]$ (19 mg, 0.10 mmol) in CH_2Cl_2 (20 cm^3) was added $[Ru(CO)_2\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)][PF_6]$ (95 mg, 0.11 mmol). After 15 min, the brown solution was evaporated to dryness and the residue was extracted with toluene (15 cm^3). The resulting yellow solution was then filtered, and the solvent removed *in vacuo*. Purification gave a yellow-brown solid, yield 65 mg. I.r. and n.m.r. spectroscopy showed the product to be an approximately equimolar mixture of $[RuMe(CO)_2(\eta\text{-}C_5Ph_5)]$, $[Ru\{P(O)(OMe)_2\}(CO)_2(\eta\text{-}C_5Ph_5)]$, and $[RuCl(CO)\{P(OMe)_3\}(\eta\text{-}C_5Ph_5)]$.

Di-μ-carbonyl-dicarbonylbis(pentaphenylcyclopentadienyl)-diruthenium, $[\{Ru(\mu\text{-}CO)(CO)(\eta\text{-}C_5Ph_5)\}_2]$.—To a stirred solution of $[RuBr(CO)_2(\eta\text{-}C_5Ph_5)]$ (0.68 g, 1.00 mmol) in thf (40 cm^3) was added $[Co(\eta\text{-}C_5H_5)_2]$ (0.19 g, 1.00 mmol). After 1 h the orange precipitate was filtered off, washed with toluene (2 × 25 cm^3) and diethyl ether (2 × 25 cm^3), and dried *in vacuo*, crude yield 0.49 g, (82%). Purification by Soxhlet extraction using CH_2Cl_2 as the solvent gave the product as an orange solid, yield 0.24 g (40%). The complex is slightly soluble in CH_2Cl_2 and hot toluene, but insoluble in all other common solvents.

The complex $[\{Fe(\mu\text{-}CO)(CO)(\eta\text{-}C_5Ph_5)\}_2]$ was prepared similarly but purification was impossible; the compound reacts with any solvent in which it is soluble, for example CH_2Cl_2 or hot toluene.

Acknowledgements

We thank the S.E.R.C. for a Research Studentship (to I. M.), and Johnson Matthey plc for a generous loan of ruthenium trichloride.

References

1 Part 28, L. Brammer, N. G. Connelly, J. Edwin, W. E. Geiger, A. G. Orpen, and J. B. Sheridan, *Organometallics*, 1988, **7**, 1259.

2 See, for example, J. K. Kochi, 'Organometallic Mechanisms and Catalysis,' Academic Press, New York, 1978; J. Halpern, *Pure Appl. Chem.*, 1986, **58**, 575; J. K. Kochi, *J. Organomet. Chem.*, 1986, **300**, 139; T. J. Meyer and J. V. Caspar, *Chem. Rev.*, 1985, **85**, 187; A. E. Stiegman and D. R. Tyler, *Acc. Chem. Res.*, 1984, **17**, 61; G. Palyi, F. Ungvary, V. Galamb, and L. Marko, *Coord. Chem. Rev.*, 1984, **53**, 37; K-W. Lee and T. L. Brown, *J. Am. Chem. Soc.*, 1987, **109**, 3269; Y-M. Wuu, C. Zou, and M. S. Wrighton, *ibid.*, p. 5861; C. E. Ash, P. W. Hurd, M. Y. Darensbourg, and M. Newcomb, *ibid.*, p. 3313; R. M. Kowalewski, F. Basolo, W. C. Trogler, R. W. Gedridge, T. D. Newbound, and R. D. Ernst, *ibid.*, p. 4860; A. S. Goldman and D. R. Tyler, *Inorg. Chem.*, 1987, **26**, 253; K. Y. Lee, D. J. Kuchynka, and J. K. Kochi, *Organometallics*, 1987, **6**, 1886; R. Davies, J. L. A. Durrant, and C. C. Rowland, *J. Organomet. Chem.*, 1986, **316**, 147; P. J. Krusic, R. Briere, and P. Rey, *Organometallics*, 1985, **4**, 801; K. M. Doxsee, R. H. Grubbs, and F. C. Anson, *J. Am. Chem. Soc.*, 1984, **106**, 7819.

3 A. J. Dixon, S. J. Gravelle, L. J. van de Burgt, M. Poliakoff, J. J. Turner, and E. Weitz, *J. Chem. Soc., Chem. Commun.*, 1987, 1023.

4 J. P. Blaha and M. S. Wrighton, *J. Am. Chem. Soc.*, 1985, **107**, 2694.

5 P. J. Krusic, P. J. Fagan, and J. San Filippo, jun., *J. Am. Chem. Soc.*, 1977, **99**, 250.

6 M. J. Thomas, T. A. Shackleton, S. C. Wright, D. J. Gillis, J. P. Colpa, and M. C. Baird, *J. Chem. Soc., Chem. Commun.*, 1986, 312.

7 C. Lapinte, D. Catheline, and D. Astruc, *Organometallics*, 1984, **3**, 817.

8 M. C. R. Symons, S. W. Bratt, and J. L. Wyatt, *J. Chem. Soc., Dalton Trans.*, 1983, 1377.

9 D. Miholova and A. A. Vlcek, *Inorg. Chim. Acta*, 1983, **73**, 249.

10 N. G. Connelly and W. E. Geiger, *Adv. Organomet. Chem.*, 1984, **23**, 1 and refs. therein.

11 M. J. Therien and W. C. Trogler, *J. Am. Chem. Soc.*, 1987, **109**, 5127.

12 V. Guerchais and C. Lapinte, *J. Chem. Soc., Chem. Commun.*, 1986, 663.

13 S. Javaheri and W. P. Giering, *Organometallics*, 1984, **3**, 1927.

14 R. H. Magnuson, R. Meirowitz, S. J. Zulu, and W. P. Giering, *Organometallics*, 1983, **2**, 460.

15 R. H. Magnuson, R. Meirowitz, S. Zulu, and W. P. Giering, *J. Am. Chem. Soc.*, 1982, **104**, 5790.

16 W. N. Rogers, J. A. Page, and M. C. Baird, *Inorg. Chem.*, 1981, **20**, 3521.

17 R. H. Magnuson, S. Zulu, W. M. T'sai, and W. P. Giering, *J. Am. Chem. Soc.*, 1980, **102**, 6887.

18 R. J. Klingler and J. K. Kochi, *J. Organomet. Chem.*, 1980, **202**, 49.

19 P. M. Treichel, D. C. Molzahn, and K. P. Wagner, *J. Organomet. Chem.*, 1979, **174**, 191.

20 N. G. Connelly and S. J. Raven, *J. Chem. Soc., Dalton Trans.*, 1986, 1613; N. G. Connelly, W. E. Geiger, G. A. Lane, S. J. Raven, and P. H. Rieger, *J. Am. Chem. Soc.*, 1986, **108**, 6219; N. G. Connelly, S. J. Raven, and W. E. Geiger, *J. Chem. Soc., Dalton Trans.*, 1987, 467.

21 K. Broadley, N. G. Connelly, G. A. Lane, and W. E. Geiger, *J. Chem. Soc., Dalton Trans.*, 1986, 373; G. A. Lane, W. E. Geiger, and N. G. Connelly, *J. Am. Chem. Soc.*, 1987, **109**, 402.

22 K. Zieger and B. Schnell, *Liebigs Ann. Chem.*, 1925, **445**, 266.

23 S. McVey and P. L. Pauson, *J. Chem. Soc.*, 1965, 4312.

24 D. L. Reger, K. A. Belmore, E. Mintz, and P. J. McElligott, *Organometallics*, 1984, **3**, 134; M. I. Bruce, T. W. Hambley, M. R. Snow, and A. G. Swincer, *ibid.*, 1985, **4**, 501.

25 D. L. Reger, K. A. Belmore, E. Mintz, N. G. Charles, E. A. H. Griffith, and E. L. Amma, *Organometallics*, 1983, **2**, 101.

26 D. L. Reger, K. A. Belmore, J. L. Atwood, and W. E. Hunter, *J. Am. Chem. Soc.*, 1983, **105**, 5710.

27 M. F. Joseph, J. A. Page, and M. C. Baird, *Organometallics*, 1984, **3**, 1749.

28 R. J. Haines, A. L. du Preez, and I. L. Marais, *J. Organomet. Chem.*, 1971, **28**, 405.

29 A. K. Bhattacharya and G. Thyagarajan, *Chem. Rev.*, 1981, **81**, 415.

30 R. B. King, M. Z. Iqbal, and A. D. King, jun., *J. Organomet. Chem.*, 1979, **171**, 53.

31 R. B. King and M. B. Bisnette, *J. Organomet. Chem.*, 1967, **8**, 287.

32 D. Miholova and A. A. Vlcek, *Inorg. Chim. Acta*, 1980, **43**, 43; R. E. Dessy and P. M. Weissman, *J. Am. Chem. Soc.*, 1966, **88**, 5124.

33 R. B. King, 'Organometallic Syntheses,' Academic Press, New York, 1965, vol. 1, p. 70.

34 F. A. Bell, A. Ledwith, and D. C. Sherrington, *J. Chem. Soc. C*, 1969, 2719.

35 G. A. Carriedo, V. Riera, N. G. Connelly, and S. J. Raven, *J. Chem. Soc., Dalton Trans.*, 1987, 1769.

Received 5th *February* 1988; *Paper* 8/00510I