Carbon–Oxygen and Carbon–Hydrogen Bond Cleavage in the Reaction of $[\{Ru(CO)_2(\eta^5\text{-}C_5H)_5\}_2]$† with Phosphite and Phosphine Ligands

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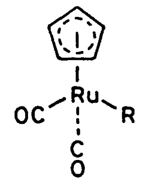
Reaction of $[\{Ru(CO)_2(cp)\}_2]$ (cp = η^5-cyclopentadienyl) with $P(OR)_3$ ligands (R = Me, Et, or Bu^n) yields $[Ru(CO)_2(cp)R]$, $[Ru(cp)\{P(OR)_3\}_2\{P(O)(OR)_2\}]$, and $[Ru(CO)(cp)\{P(OR)_3\}\{P(O)(OR)_2\}]$ complexes resulting from C–O bond cleavage. The former complexes were characterized by reaction with PPh_3 which yields the acyl $[Ru(CO)(cp)(COR)(PPh_3)]$ derivative. Reaction of $[\{Ru(CO)_2(cp)\}_2]$ with PPr_3 and PMe_2Ph proceeds to yield a mixture of the substituted dimer $[Ru_2(CO)_3(cp)_2(PR_3)]$ and the hydrides $[Ru(CO)_x(cp)H(PR_3)_{2-x}]$ (x = 0 or 1) depending on the reaction conditions. The mechanisms of these reactions and the fluxionality of the substituted dimers are discussed.

REACTIONS of tertiary phosphines and phosphites with polynuclear transition-metal carbonyls under relatively mild conditions usually result only in carbonyl substitution, although in some cases, disproportionation may also be observed.[1] Previously unique were the reactions of the dimers $[\{M(CO)_3(cp)\}_2]$ (M = Cr or Mo; cp = cyclopentadienyl) with alkyl phosphites which yield as two of the products the alkyl $[M(CO)_{3-x}(cp)\{P(OR)_3\}_xR]$ (x = 0 or 1) and phosphonate $[M(CO)_2(cp)\{P(OR)_3\}\{P(O)(OR)_2\}]$ complexes.[2,3] We wish to report here a similar reaction between $[\{Ru(CO)_2(cp)\}_2]$ (1) and alkyl phosphites, together with a related reaction of (1) with tertiary alkyl phosphines. Part of this work has been reported as a communication.[4]

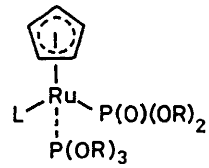
RESULTS AND DISCUSSION

Reaction of $[\{Ru(CO)_2(cp)\}_2]$ (1) *with Phosphites.*—Reaction of (1) with an excess of $P(OR)_3$ proceeds smoothly in refluxing xylene to yield as products the alkyl $[Ru(CO)_2(cp)R]$ (2a—c; R = Me, Et, or Bu) and phosphonate $[Ru(cp)\{P(OR)_3\}_2\{P(O)(OR)_2\}]$ (3a—c; R = Me, Et, or Bu) complexes. The reactions may conveniently be followed by i.r. monitoring of the disappearance of (1). Analysis of the crude mixture (see below) at this point indicates an approximate 1 : 1 mixture of (3a—c) and the monosubstituted derivatives $[Ru(CO)(cp)\{P(OR)_3\}\{P(O)(OR)_2\}]$ (R = Me, Et, or Bu; 6a—c). Although (6b) has been isolated by careful chromatography, the general difficulty in separation was overcome by continuing refluxing until complete substitution had been achieved to yield only (3a, c) as isolated products.

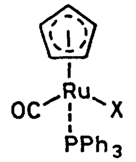
The alkyl complexes $[Ru(CO)_2(cp)R]$ (2a—c) have previously been prepared by reaction of $Na[Ru(CO)_2(cp)]$ with the appropriate alkyl iodide,[5] and i.r. and mass spectroscopic data are in agreement with published results. Because difficulty was experienced in separation of these rather volatile substances from reaction impurities, they were further characterized by reaction with PPh_3, which results in insertion of CO to yield the crystalline $[Ru(CO)(cp)(COR)(PPh_3)]$ complexes (4a—c; R = Me, Et, or Bu). These complexes are identical with specimens prepared by reaction of PPh_3 with authentic $[Ru(CO)_2(cp)R]$ (2a—c). The complexes were characterized by analysis and i.r. and n.m.r. spectroscopy. Particularly characteristic are the ν(CO) acyl stretching frequency at *ca.* 1 600 cm^{-1} and the acyl ^{13}C carbonyl resonance at *ca.* 255 p.p.m. It is of interest to note that in (4b, c) the α-CH_2 protons form an AB system in the n.m.r. spectrum (confirmed by decoupling) due to proximity to the chiral ruthenium centre. Computer-simulated spectra for (4b) confirm the ABX_3P nature of the spectrum. Especially in the case of (2a), prolonged reaction with PPh_3 also yields the alkyl com-



(2a) R = Me
(2b) R = Et
(2c) R = Bu



(3a) L = $P(OMe)_3$, R = Me (6a) L = CO, R = Me
(3b) L = $P(OEt)_3$, R = Et (6b) L = CO, R = Et
(3c) L = $P(OBu)_3$, R = Bu (6c) L = CO, R = Bu



(4a) X = COMe (5) X = Me
(4b) X = COEt
(4c) X = COBu

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† Di-μ-carbonyl-bis[carbonyl(1—5-η-cyclopentadienyl)ruthenium](*Ru–Ru*).

plex $[Ru(CO)(cp)Me(PPh_3)]$ (5) resulting from decarbonylation of $[Ru(CO)(cp)(COMe)(PPh_3)]$ (4a); characteristic of this complex and the parent derivative $[Ru(CO)_2(cp)Me]$ (2a) are the high-field ^{13}C and ^1H resonances of the methyl group. Both the carbonyl insertion and decarbonylation reactions are well established for the analogous iron complexes.[6a, b]

The new complexes $[Ru(cp)\{P(OR)_3\}_2\{P(O)(OR)_2\}]$ (3a—c) form part of a small but growing number of covalent transition-metal phosphonate derivatives. They are isolated as slightly hygroscopic white solids (3a) or oils (3b, c) which are unstable in air. All the complexes exhibit molecular ions in the mass spectrum; fragmentation occurs mainly by loss of R or OR, but fragments due to $[Ru(cp)\{P(OR)_3\}_2]^+$, $[Ru(cp)\{P(OR)_3\}]^+$, and $[Ru(cp)\{P(OR)_3\}\{P(O)(OR)_2\}]^+$ may be identified. A band at *ca.* 1 155 cm^{-1} in the thin film i.r. spectra of (3a—c) may be assigned to $\nu(P{=}O)$ although some overlap with C–O vibrations may be present; a corresponding assignment has been made to bands at 1 165 cm^{-1} in the spectra of $[Mo(CO)_2(cp)\{P(OR)_3\}\{P(O)(OR)_2\}]$,[2] and at 1 110—1 180 cm^{-1} in the spectra of $[Fe(CO)_x(cp)\{P(OR)_3\}_{2-x}\{P(O)(OR)_2\}]$ ($x = 1$ or 2) complexes.[7] The ^{31}P n.m.r. spectra show a doublet at *ca.* 160 p.p.m. and a triplet at *ca.* 110 p.p.m. [J(P–P) *ca.* 80 Hz] assignable to co-ordinated phosphite and phosphonate respectively. The complex $[Mo(CO)_2(cp)\{P(OMe)_3\}\{P(O)(OMe)_2\}]$ prepared by the method of Haines and Nolte[2] exhibits doublet ^{31}P resonances at 188.0 and 115.0 p.p.m. [J(P–P) = 36.6 Hz] assignable to phosphite and phosphonate respectively. Resonances in the region of *ca.* 80—120 p.p.m. may thus be characteristic of phosphonate covalently bound to transition metals,[8] and represent a considerable downfield shift from values found for alkyl phosphonates (*ca.* 30 p.p.m.).[9] The proton n.m.r. spectrum of (3a) is also in agreement with this formulation, showing overlapping resonances at δ 3.49 [doublet; J(P–H) = 10.5 Hz] and δ 3.61 (broad peak flanked by two sharp singlets). The former may be assigned to phosphonate, while the latter may be assigned to co-ordinated $P(OMe)_3$ and is characteristic of the $X_9AA'X'_9$ pattern previously observed for $[RuCl(cp)\{P(OMe)_3\}_2]$.[10] The cyclopentadienyl resonance consists of a slightly broadened quartet, consistent with an AXY_2 system in which $J(A{-}X) \approx J(A{-}Y)$. The cyclopentadienyl resonance of $[Ru(CO)(cp)\{P(OEt)_3\}\{P(O)(OEt)_2\}]$ is the triplet expected for an AXY system in which $J(A{-}X) \approx J(A{-}Y)$; non-equivalence of the ethyl substituents of the $P(O)(OEt)_2$ ligand may also be detected.

A scheme accounting for these results is shown by reactions (1)—(5).

If the reaction is stopped immediately after disappearance of (1), ^{31}P analysis of an aliquot reveals doublets at *ca.* 96 p.p.m. and 149 p.p.m. [J(P–P) *ca.* 66 Hz] assignable to phosphonate and co-ordinated phosphite respectively of the monosubstituted $[Ru(CO)(cp)\{P(OR)_3\}\{P(O)(OR)_2\}]$ (6a—c), in addition to signals due to $[Ru(cp)\{P(OR)_3\}_2\{P(O)(OR)_2\}]$ (3a—c); intensities indicate approximately a 1 : 1 ratio of the two complexes. On this basis, the intermediacy of the monosubstituted dimer of equation (1) seems likely although we have neither isolated or detected this complex during the reaction. One cannot, however, dismiss as the reaction pathway an intramolecular decomposition of a disubstituted derivative. Studies

$$[\{Ru(CO)_2(cp)\}_2] + P(OR)_3 \longrightarrow [Ru_2(CO)_3(cp)_2\{P(OR)_3\}] + CO \tag{1}$$

$$[Ru_2(CO)_3(cp)_2\{P(OR)_3\}] \rightleftharpoons [Ru(CO)_2(cp)] + [Ru(CO)(cp)\{P(OR)_3\}] \tag{2}$$

$$[Ru(CO)_2(cp)] + P(OR)_3 \longrightarrow [Ru(CO)_2(cp)R] + P(O)(OR)_2 \tag{3}$$

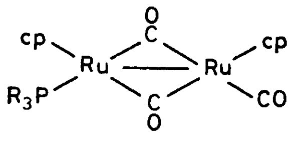
$$[Ru(CO)(cp)\{P(OR)_3\}] + P(O)(OR)_2 \longrightarrow [Ru(CO)(cp)\{P(OR)_3\}\{P(O)(OR)_2\}] \tag{4}$$

$$[Ru(CO)(cp)\{P(OR)_3\}\{P(O)(OR)_2\}] + P(OR)_3 \longrightarrow [Ru(cp)\{P(OR)_3\}_2\{P(O)(OR)_2\}] + CO \tag{5}$$

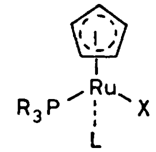
on the reaction of the $[\{M(CO)_3(cp)\}_2]$ dimers (M = Cr or Mo) show that the C–O bond cleavage probably takes place by two competing pathways, one analogous to the scheme above (although involving a disubstituted dimer as the immediate precursor) and the other involving a Michaelis–Arbusov rearrangement of the initially formed disproportionation product $[M(CO)_2(cp)\{P(OR)_3\}_2][M(CO)_3(cp)]$. In the case where M = Cr, the former pathway is preferred, and it is known[3] that disubstitution of $[\{Cr(CO)_3(cp)\}_2]$ to yield the symmetrically substituted $[\{Cr(CO)(cp)[P(OMe)_3]\}_2]$ results in significant lengthening of the M–M bond and an increase in the concentration of monomeric paramagnetic $[Cr(CO)_2(cp)\{P(OMe)_3\}]$ in solution, as compared to $[Cr(CO)_3(cp)]$. Although a Michaelis–Arbusov type reaction involving a disproportionated intermediate of the type $[Ru(CO)(cp)\{P(OR)_3\}_2][Ru(CO)_2(cp)]$ cannot be dismissed here, we prefer the mechanism outlined above in view of the reactions described in the following section which seem more characteristic of radical intermediates. Radicals $[M(CO)_2(cp)]$ (M = Fe or Ru) have been cited as the primary photoproduct of the irradiation of the $[\{M(CO)_2(cp)\}_2]$ dimer,[11] although recent work on the photosubstitution of $[\{Fe(CO)_2(cp)\}_2]$ by $P(OR)_3$ ligands indicates that this may not be the case.[12]

Thermal reaction of $[\{Fe(CO)_2(cp)\}_2]$ with $P(OR)_3$ ligands yields only monosubstituted dimers,[13] albeit under less vigorous reaction conditions than those used here. Reaction of $[FeCl(CO)_2(cp)]$ with $P(OR)_3$ proceeds to yield a mixture of $[Fe(CO)(cp)\{P(OR)_3\}\{P(O)(OR)_2\}]$ and $[Fe(CO)_2(cp)\{P(O)(OR)_2\}]$ probably *via* an Arbusov rearrangement of a $[Fe(CO)_2(cp)\{P(OR)_3\}]Cl$ intermediate,[7] while $[Fe(CO)_2(cp)(\sigma\text{-}cp)]$ undergoes reaction with $P(OMe)_3$ to yield $[Fe(CO)(cp)\{P(OMe)_3\}\{P(O)(OMe)_2\}]$ and methylcyclopentadiene.[14,15] The latter reaction is thought to proceed *via* an Arbusov rearrangement of the intermediate $[Fe(CO)(cp)(\sigma\text{-}cp)\{P(OMe)_3\}]$ in which a free double bond of the σ-cp ligand acts as a nucleophile, and has a precedent in the rearrangement of $[Mo(CO)_2(cp)(AsMe_2)\{P(OMe)_3\}]$ to $[Mo(CO)_2(cp)(AsMe_3)\{P(O)(OMe)_2\}]$, although this reaction is intermolecular.[8]

Reaction of $[\{Ru(CO)_2(cp)\}_2]$ (1) *with Tertiary Phosphines* (PPr_3 *and* PMe_2Ph).—Reaction of the above phosphines with $[\{Ru(CO)_2(cp)\}_2]$ in refluxing toluene followed by chromatography on alumina using CH_2Cl_2 as eluant yields a mixture of the complexes $[Ru_2(CO)_3(cp)_2(PR_3)]$ (7a, b) and $[RuCl(CO)(cp)(PR_3)]$ (8a, b). The proportion of (8a, b) formed increases with increasing excess of PR_3 and longer reaction time. Reaction of isolated $[Ru_2(CO)_3(cp)_2(PR_3)]$ (7a, b) with PR_3 proceeds smoothly to yield ultimately $[RuCl(CO)(cp)(PR_3)]$ (8a, b) and in the case of PMe_2Ph, the $[RuCl(cp)(PMe_2Ph)_2]$ derivative (9) as well. Complexes (8) and (9) were characterized by analysis and spectroscopy and were identical with samples prepared by carbonyl substitution of $[RuCl(CO)_2(cp)]$. In the ^1H n.m.r. spectra of (8b), the methyl resonances are observed as two doublets due to proximity to the chiral ruthenium centre. The methyl resonances of (9) occur as two multiplets, each having the characteristic shape (broad inner peak flanked by two sharp singlets) of the $X_3AA'X_3'$ system previously observed for $[RuCl(cp)(PMePh_2)_2]$.[10]



(7a) $PR_3 = PPr_3$ (7b) $PR_3 = PMe_2Ph$



(8a) $PR_3 = PPr_3$, L = CO, X = Cl

(8b) $PR_3 = PMe_2Ph$, L = CO, X = Cl

(9) PR_3 = L = PMe_2Ph, X = Cl

(10) $PR_3 = PPr_3$, L = CO, X = Br

(11a) $PR_3 = PPr_3$, L = CO, X = H

(11b) $PR_3 = PMe_2Ph$, L = CO, X = H

(12) PR_3 = L = PMe_2Ph, X = H

If CH_2Br_2 is used as chromatography solvent in the reaction of $[\{Ru(CO)_2(cp)\}_2]$ with PPr_3 the analogous bromide $[RuBr(CO)(cp)(PPr_3)]$ (10) is isolated. Thus, $[RuCl(CO)(cp)(PR_3)]$ (8a, b) are not initial reaction products; analysis of the crude reaction mixtures shows a band in the i.r. spectrum at *ca.* 1 930 cm^{-1} and n.m.r. resonances at *ca.* δ −12 [doublet, J(P–H) *ca.* 35 Hz] and δ −12.7 [triplet, J(P–H) = 36.2 Hz; only for PMe_2Ph] which identify the immediate reaction products as the hydrides $[Ru(CO)(cp)H(PR_3)]$ (11a, b) and $[Ru(cp)H(PMe_2Ph)_2]$ (12). The hydrides (11a, b) may be prepared unambiguously in solution by reaction of $[Ru(CO)_2(cp)H]$ synthesized *in situ* from $[Ru_3(CO)_{12}]$ and cyclopentadiene,[16] with one equivalent of PR_3. Although identified by i.r. and n.m.r. spectroscopy, the hydrides could not be isolated analytically pure and were characterized by conversion to the chlorides (8a, b) by stirring in $CHCl_3$. Prolonged reaction of $[Ru(CO)_2(cp)H]$ with PMe_2Ph yielded a mixture of $[Ru(CO)(cp)H(PMe_2Ph)]$ (11b) and $[Ru(cp)H(PMe_2Ph)_2]$ (12); although characterized spectroscopically, the latter could also not be isolated in the pure state and was converted to $[RuCl(cp)(PMe_2Ph)_2]$ (9) by stirring in $CHCl_3$. The hydrides (11a, b) and (12) exhibit characteristic high-field proton resonances in the n.m.r. spectrum; the pattern of the methyl resonances for (11b) and (12) is also analogous to that observed for the chlorides (8) and (9). The pathway which we propose for this reaction is shown in equations (6)—(11).

$$[\{Ru(CO)_2(cp)\}_2] + PR_3 \longrightarrow [Ru_2(CO)_3(cp)_2(PR_3)] + CO \quad (6)$$

$$[Ru_2(CO)_3(cp)_2(PR_3)] \rightleftharpoons [Ru(CO)_2(cp)] + [Ru(CO)(cp)(PR_3)] \quad (7)$$

$$[Ru(CO)(cp)(PR_3)] + PR_3 \longrightarrow [Ru(CO)(cp)H(PR_3)] + [P] \quad (8)$$

$$2\,[Ru(CO)_2(cp)] \rightleftharpoons [\{Ru(CO)_2(cp)\}_2] \quad (9)$$

$$[Ru(CO)_2(cp)] + PR_3 \longrightarrow [Ru(CO)(cp)(PR_3)] + CO \quad (10)$$

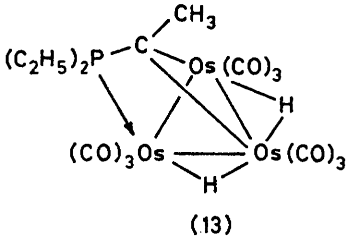
$$[Ru(CO)(cp)H(PMe_2Ph)] + PMe_2Ph \longrightarrow [Ru(cp)H(PMe_2Ph)_2] + CO \quad (11)$$

Thermolysis of $[Ru_2(CO)_3(cp)_2(PMe_2Ph)]$ (8b) in toluene in the absence of an excess of phosphine yields mainly $[Ru(CO)(cp)H(PMe_2Ph)]$ (identified by n.m.r.) and $[\{Ru(CO)_2(cp)\}_2]$ (identified by n.m.r. and i.r.). Heating of (7b) in [$^2H_8$]toluene in the absence of an excess of phosphine yields, in addition to $[\{Ru(CO)_2(cp)\}_2]$, a compound exhibiting a cp resonance at δ 4.84 assignable to the deuteride $[Ru(CO)(cp)D(PMe_2Ph)]$ since no high-field resonance is observed; addition of $CHCl_3$ converts this to the chloride (8b). These reactions (carried out *in situ* in the n.m.r. tube) thus show that no $[Ru(CO)_2(cp)H]$ is formed, and that the formation of $[Ru(CO)(cp)H(PMe_2Ph)]$ is not the result of an intramolecular decomposition. The thermal decomposition in the absence of an excess of phosphine is not totally clean, however; small additional cyclopentadienyl resonances may be observed, and the proton n.m.r. of the residue in $CDCl_3$ shows a multiplet at *ca.* δ 6.64 which may be indicative of an *o*-metallation product.[17] Reaction of $[Ru_2(CO)_3(cp)_2(PMe_2Ph)]$ (7b) with PMe_2Ph in either toluene or [$^2H_8$]toluene yields exclusively a mixture of $[Ru(CO)(cp)H(PMe_2Ph)]$ and $[Ru(cp)H(PMe_2Ph)_2]$, showing that in the presence of an excess of phosphine, hydrogen abstraction from the solvent and *o*-metallation are not competitive with equation (8).

Analysis of aliquots from the reaction of $[\{Ru(CO)_2(cp)\}_2]$ with PMe_2Ph using both ^{31}P and ^{1}H n.m.r. spectra show that the only metal-containing products formed are $[Ru_2(CO)_3(cp)_2(PMe_2Ph)]$, $[Ru(CO)(cp)H(PMe_2Ph)]$, and $[Ru(cp)H(PMe_2Ph)_2]$. The fate of the organic radical of equation (8), [P], has not been completely determined. The ^{31}P n.m.r. spectrum of the crude reaction product does show several additional small resonances in the region −45 to −47 p.p.m. characteristic of a free phosphine, and the reaction is accompanied by the formation of some brown phosphorus-containing insoluble organic material.

Complete conversion to $[Ru(CO)(cp)H(PMe_2Ph)]$ and $[Ru(cp)H(PMe_2Ph)_2]$ is observed on reaction of $[Ru_2(CO)_3(cp)_2(PMe_2Ph)]$ with an excess of PMe_2Ph; whether this is a result of recycling through the $[\{Ru(CO)_2(cp)\}_2]$ dimer [equations (9) and (6)] or direct substitution of the $[Ru(CO)_2(cp)]$ radical [equation (10)] cannot be determined; the enhanced lability of 17-electron species with respect to carbonyl substitution has been demonstrated, however.[18]

The C–H bond cleavage thus observed is consistent with the presence of the radical intermediates of equations (7) and (8), and it is of interest to compare these reactions to transformations of phosphine and phosphite co-ordinated to trinuclear clusters of the iron group. A similar hydrogen transfer has been observed in the thermolysis of $[Os_3(CO)_{11}(PEt_3)]$ to yield (13).[19] Thermolyses of $[Ru_3(CO)_{11}\{P(OPh)_3\}]$ [20] and $[Os_3(CO)_{11}\{P(OMe)_3\}]$ [21] yield polymetallic species containing co-ordinated phosphonate. Thus, it is tempting to speculate that these formal oxidative additions to metal–metal bonds may proceed *via* the intermediacy of radical species resulting from M–M cleavage in which the integrity of the cluster is maintained by the presence of more than one M–M bond. In a recent kinetic study,[22] it has been shown that the reaction of $[Ru_3(CO)_9(PBu_3)_3]$ with PBu_3 to yield mononuclear fragments proceeds *via* a rate-determining loss of CO to yield an $[Ru_3(CO)_8(PBu_3)_3]$ species; one structure proposed for this intermediate is a diradical arising from cleavage of one Ru–Ru bond.



(13)

Structure and Fluxional Character of $[Ru_2(CO)_3(cp)_2(PR_3)]$ (7a, b) *Complexes.*—It was originally our intention to prepare these complexes to compare their structure and fluxional behaviour with that of the $[Ru_2(CO)_3(cp)_2(CNR)]$ series.[23] The two i.r. bands at 1 943 and 1 762 cm^{-1} in the spectrum of (7a) may be assigned to terminal and bridging carbonyl vibrations, thus indicating the presence of only the $[(cp)(CO)Ru(\mu\text{-}CO)_2Ru(PR_3)(cp)]$ isomer, in contrast to the parent dimer (1) where concentrations of the non-bridged isomer may be detected in solution.[24] The complexes $[Fe_2(CO)_3(cp)_2(PR_3)]$ exhibit analogous spectra,[13] indicating the presence of either the *cis* or *trans* isomer, although a definite assignment is not possible. The complexes show fluxional behaviour involving bridge–terminal carbonyl exchange. Thus in the ^{13}C spectrum of (7b), the two carbonyl signals observed at −70 °C broaden and coalesce to give a single broadened resonance at 238.2 p.p.m. at 25 °C. In the absence of detectable

TABLE 1

Analytical data

	Compound	Analysis (%) *	
		C	H
(3a)	$[Ru(cp)\{P(OMe)_3\}_2\{P(O)(OMe)_2\}]$	29.0 (29.8)	5.4 (5.5)
(3b)	$[Ru(cp)\{P(OEt)_3\}_2\{P(O)(OEt)_2\}]$	40.3 (39.7)	7.1 (7.1)
(3c)	$[Ru(cp)\{P(OBu)_3\}_2\{P(O)(OBu)_2\}]$	51.9 (51.7)	9.4 (9.0)
(4a)	$[Ru(CO)(cp)(COMe)(PPh_3)]$	62.7 (62.5)	4.7 (4.6)
(4b)	$[Ru(CO)(cp)(COEt)(PPh_3)]$	63.2 (63.2)	5.0 (4.9)
(4c)	$[Ru(CO)(cp)(COBu)(PPh_3)]$	64.3 (64.3)	5.4 (5.4)
(5)	$[Ru(CO)(cp)Me(PPh_3)]$	63.8 (63.7)	4.9 (4.9)
(6b)	$[Ru(CO)(cp)\{P(OEt)_3\}\{P(O)(OEt)_2\}]$	39.2 (38.6)	6.5 (6.1)
(7a)	$[Ru_2(CO)_3(cp)_2(PPr_3)]$	46.4 (46.0)	5.5 (5.4)
(7b)	$[Ru_2(CO)_3(cp)_2(PMe_2Ph)]$	45.3 (45.5)	3.7 (3.8)
(8a)	$[RuCl(CO)(cp)(PPr_3)]$	45.7 (46.2)	6.5 (6.7)
(8b)	$[RuCl(CO)(cp)(PMe_2Ph)]$	45.8 (45.7)	4.4 (4.4)
(9)	$[RuCl(cp)(PMe_2Ph)_2]$	53.2 (52.8)	6.0 (5.7)
(10)	$[RuBr(CO)(cp)(PPr_3)]$	42.2 (41.3)	6.0 (6.0)

* Calculated values are given in parentheses.

TABLE 2

Infrared data (cm^{-1})

Compound	ν(M–*CO*) [a]	ν(M–*COR*) [b]	ν(P=O) [c]
(3a)			1 175
(3b)			1 155
(3c)			1 145
(4a)	1 935	1 596	
(4b)	1 933	1 596	
(4c)	1 928	1 600	
(5)	1 928		
(6b)	1 978		1 140
(7a)	1 943 (t) [d] 1 762 (b)		
(7b)	1 940 (t) 1 740 (b)		
(8a)	1 953		
(8b)	1 959		
(10)	1 958		
(11a)	1 927		
(11b)	1 931		

[a] Hexane solution, except (7b) which is in CS_2. [b] Nujol mull. [c] Thin film. [d] t = Terminal, b = bridging.

concentrations of both geometric isomers, little information can be gained with respect to the mechanism of exchange, except to note that the activation energy for the exchange process is considerably less than that observed for the similar $[Fe_2(CO)_3(cp)_2\{P(OR)_3\}]$ derivatives.[25]

TABLE 3

Proton n.m.r. data (p.p.m. from $SiMe_4$)

Compound	Cyclopentadienyl	Others
(3a)	5.02 [q; J(P–H) *ca.* 1.0 Hz]	$P(O)(OMe)_2$ 3.49 [d; J(P–H) = 10.5 Hz] $P(OMe)_3$ 3.61 (m)
(3b)	4.88 [q; J(P–H) *ca.* 0.9 Hz]	$\left.\begin{array}{l}\mathrm{P(O)(O}\mathit{CH}_2\mathrm{CH_3)_2}\\ \mathrm{P(O}\mathit{CH}_2\mathrm{CH_3)_3}\end{array}\right\}$ 3.78—4.03 (m) $\left.\begin{array}{l}\mathrm{P(O)(OCH_2}\mathit{CH}_3\mathrm{)_2}\\ \mathrm{P(OCH_2}\mathit{CH}_3\mathrm{)_3}\end{array}\right\}$ 1.15 (m)
(3c)	4.95 [q; J(P–H) *ca.* 1.0 Hz]	$\left.\begin{array}{l}\mathrm{P(O)(O}\mathit{CH}_2\mathrm{CH_2CH_2CH_3)_2}\\ \mathrm{P(O}\mathit{CH}_2\mathrm{CH_2CH_2CH_3)_3}\end{array}\right\}$ 3.97 (m) $\left.\begin{array}{l}\mathrm{P(O)(OCH_2}\mathit{CH}_2\mathit{CH}_2\mathrm{CH_3)_2}\\ \mathrm{P(OCH_2}\mathit{CH}_2\mathit{CH}_2\mathrm{CH_3)_3}\end{array}\right\}$ 1.42 (m) $\left.\begin{array}{l}\mathrm{P(O)(OCH_2CH_2CH_2}\mathit{CH}_3\mathrm{)_2}\\ \mathrm{P(OCH_2CH_2CH_2}\mathit{CH}_3\mathrm{)_3}\end{array}\right\}$ 0.90 (m)
(4a)	4.99 [d; J(P–H) = 0.4 Hz]	CH_3 2.08 [d; J(P–H) = 0.5 Hz] PPh_3 7.40 (m)
(4b)	4.98 [d; J(P–H) = 0.4 Hz]	CH_2 2.4 (m) CH_3 0.52 (t) PPh_3 7.40 (m)
(4c)	4.95 [d; J(P–H) = 0.4 Hz]	$\mathit{CH}_2\mathrm{CH_2CH_2CH_3}$ 2.35 (m) $\mathrm{CH_2}\mathit{CH}_2\mathit{CH}_2\mathit{CH}_3$ 0.73—1.40 (m) PPh_3 7.40 (m)
(5)	4.80 [d; J(P–H) = 0.5 Hz]	CH_3 0.07 [d; J(P–H) = 5.3 Hz] PPh_3 7.36 (m)
(6b)	5.16 [t; J(P–H) *ca.* 0.9 Hz]	$\left.\begin{array}{l}\mathrm{P(O)(O}\mathit{CH}_2\mathrm{CH_3)_2}\\ \mathrm{P(O}\mathit{CH}_2\mathrm{CH_3)_3}\end{array}\right\}$ 3.80—4.07 (m) $\left.\begin{array}{l}\mathrm{P(OCH_2}\mathit{CH}_3\mathrm{)_3}\\ \mathrm{P(O)(OCH_2}\mathit{CH}_3\mathrm{)_2}\end{array}\right\}$ 1.23 (m)
(7a)	$\left.\begin{array}{l}5.22\\ 4.99\end{array}\right\}$	CH_2CH_2 1.40 (m) CH_3 1.03 (t)
(7b)	$\left.\begin{array}{l}5.24\\ 4.71\end{array}\right\}$	CH_3 1.42 [d; J(P–H) = 9.4 Hz] Ph 7.45 (m)
(8a)	5.03 [d; J(P–H) = 0.4 Hz]	CH_2CH_2 1.22—1.98 (m) CH_3 1.03 (t)
(8b)	4.84	CH_3 $\left.\begin{array}{l}\text{1.94 (d)}\\ \text{1.84 (d)}\end{array}\right\}$ J(P–H) = 12.6 Hz Ph 7.44 (m)
(9)	4.27	CH_3 1.51 (m) 1.67 (m) Ph 7.27 (m)
(10)	5.04 [d; J(P–H) = 0.4 Hz]	CH_2CH_2 1.33—2.01 (m) CH_3 1.03 (t)
(11a) *	4.84	CH_2CH_2 1.41 (m) CH_3 0.93 (m) Ru–H −12.10 [d; J(P–H) = 33.2 Hz]
(11b) *	4.82	CH_3 $\left.\begin{array}{l}\text{1.56 (d)}\\ \text{1.47 (d)}\end{array}\right\}$ J(P–H) = 9.4 Hz Ph 7.22—7.72 (m) Ru–H −11.70 [d; J(P–H) = 35.1 Hz]
(12) *	4.77	Me 1.44 (m) Ph 7.18—7.67 (m) Ru–H —12.68 [t; J(P–H) = 36.2 Hz]

* In C_6D_6 solution; all other spectra are in $CDCl_3$.

EXPERIMENTAL

The compound $[\{Ru(CO)_2(cp)\}_2]$ was prepared from $[Ru_3(CO)_{12}]$ using the method of Knox.[16] The compound $[RuCl(CO)_2(cp)]$ was prepared by reaction of $[\{RuCl_2(CO)_3\}_2]$ with Tl(cp),[26] which also yields amounts of $[\{Ru(CO)_2(cp)\}_2]$. PPr_3 was prepared by literature methods; all other starting materials were obtained commercially. All experiments were carried out under nitrogen using dried and degassed solvents. Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer using 1.0-mm NaCl cells, n.m.r. spectra on a JEOL FX-100 spectrometer, and mass spectra on an AEI MS12 instrument. Carbon-13 spectra were run in the presence of $[Cr(acac)_3]$ (acac = acetylacetonate) as relaxation agent.

(*i*) *Reaction between* $[\{Ru(CO)_2(cp)\}_2]$ *and* $P(OEt)_3$.—The dimer (500 mg) was treated in refluxing xylene (15 cm^3) with a 5 : 1 molar excess of $P(OEt)_3$. The reaction was followed to complete disappearance of dimer (*ca.* 6 h) and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel which had previously been deactivated with diethyl ether and washed with benzene. Using benzene as eluant, a first colourless band was collected which gave the product $[Ru(CO)_2(cp)Et]$ (2b) as a clear oil (200 mg; 36%). This material was further characterized by its reaction with PPh_3 as described below. The remaining products were eluted from the column as a light brown band using methanol. The residue obtained after evaporation of the solvent was further purified by preparative thin-layer chromatography (t.l.c.) on silica plates using 5% methanol–diethyl ether as eluant. A small amount of $[Ru(CO)_2(cp)Et]$ (2b) was eluted with the solvent front, while the two slower moving colourless bands were collected to yield $[Ru(cp)\{P(OEt)_3\}_2\{P(O)(OEt)_2\}]$ (3b) (250 mg; 18%) and $[Ru(CO)(cp)\{P(OEt)_3\}\{P(O)(OEt)_2\}]$ (6b) (150 mg; 14%) in order of elution.

TABLE 4

Carbon-13 and ^{31}P n.m.r. data

Complex	$\delta(^{13}C)$ [a]	$\delta(^{31}P)$ [b]
(2a)	cp 87.4 CO 200.8 CH_3 −33.2	
(3a)		$P(O)(OMe)_2$ 108.5 (t) $P(OMe)_3$ 158.4 (d) $J(P–P)$ = 81.3 Hz
(3b)		$P(O)(OEt)_2$ 106.9 (t) $P(OEt)_3$ 155.3 (d) $J(P–P)$ = 81.3 Hz
(3c)		$P(O)(OBu)_2$ 110.0 (t) $P(OBu)_3$ 155.6 (d) $J(P–P)$ = 81.4 Hz
(4a)	cp 88.7 *C*OR 254.0 [$J(P–C)$ = 12.2 Hz] CO 205.0 [$J(P–C)$ = 19.5 Hz] CH_3 52.0 [$J(P–C)$ = 1.9 Hz]	
(4b)	cp 88.6 *C*OR 255.7 [$J(P–C)$ = 11.7 Hz] CO 205.4 [$J(P–C)$ = 19.5 Hz] CH_2 58.5 [$J(P–C)$ = 2.9 Hz] CH_3 9.4	
(4c)	cp 88.4 *C*OR 255.8 [$J(P–C)$ = 12.2 Hz] CO 205.4 [$J(P–C)$ = 19.6 Hz] $CH_2(\alpha)$ 65.4 [$J(P–C)$ = 2.0 Hz] (β) 27.1 (γ) 22.3 CH_3 14.1	
(5)	cp 87.2 CO 206.6 [$J(P–C)$ = 22.0 Hz] CH_3 −29.6 [$J(P–C)$ = 12.2 Hz]	
(6b)		$P(OEt)_3$ 148.7 $P(O)(OEt)_2$ 94.5 $J(P–P)$ = 66.6 Hz
(7a) [c]	cp 89.6, 90.5 CO_t 208.6 CO_b 258.6 $CH_2(\alpha)$ 30.6 [$J(P–C)$ = 23.0 Hz] CH_2CH_3 17.7	
(7b) [c]	cp 87.5 (coincident) CO_t 204.5 CO_b 255.1 CH_3 14.1 [d; $J(P–C)$ = 19.5 Hz] Ph 126—136	PMe_2Ph 20.4
(8b)		PMe_2Ph 22.3
(9)		PMe_2Ph 16.4
(11b) [d]		PMe_2Ph 31.5
(12) [d]		PMe_2Ph 28.3

[a] Relative to $SiMe_4$; in $CDCl_3$ unless stated otherwise. [b] Relative to 85% H_3PO_4; in $CDCl_3$ unless stated otherwise. [c] −70 °C in CD_2Cl_2. [d] C_6D_6 solution.

In reactions with $P(OMe)_3$ and $P(OBu)_3$, refluxing was continued for an additional 3 h after disappearance of dimer (1) to yield (2a, c) and (3a, c) as the only isolated products after work-up.

(*ii*) *Reaction between* $[Ru(CO)_2(cp)Me]$ *and* PPh_3.—The complex $[Ru(CO)_2(cp)Me]$ (2a) (100 mg), prepared as in (*i*) or from $Na[Ru(CO)_2(cp)]$ and MeI, was treated with a 6 : 1 molar excess of PPh_3 in refluxing xylene (15 cm^3) until reaction was *ca.* 50% complete as judged by i.r. spectroscopy. The solvent was removed and the residue was chromatographed on silica preparative t.l.c. plates using CH_2Cl_2 as eluant. A fast moving band yielded starting material and PPh_3; the second light yellow band gave the product $[Ru(CO)(cp)(COMe)(PPh_3)]$ (4a) (90 mg) as light yellow crystals after recrystallization from CH_2Cl_2–light petroleum.

Heating for prolonged periods of time (*ca.* 2—3 weeks) results in almost complete consumption of starting material; the product isolated after chromatography as above is, however, the alkyl derivative $[Ru(CO)(cp)Me(PPh_3)]$ (5).

Complexes (4b, c) may be similarly prepared by reaction of $[Ru(CO)_2(cp)R]$ (2b, c) (R = Et or Bu) with a 5 : 1 molar excess of PPh_3 in refluxing xylene for 48 h followed by chromatography on grade II alumina using CH_2Cl_2 as eluant.

(*iii*) *Reaction between* $[\{Ru(CO)_2(cp)\}_2]$ *and* PPr_3.—The dimer (1) (250 mg) was treated with a 2 : 1 molar excess of PPr_3 in refluxing xylene to complete disappearance of (1) as judged by the i.r. spectrum. The n.m.r. spectrum of an aliquot taken at this point ([$^2H_6$]benzene) showed the presence of $[Ru_2(CO)_3(cp)_2(PPr_3)]$ (7a) and $[Ru(CO)(cp)H(PPr_3)]$ (11a). The solvent was removed under reduced pressure and the residue chromatographed on grade II alumina using CH_2Cl_2 as eluant. The first orange band collected yielded $[Ru_2(CO)_3(cp)_2(PPr_3)]$ (7a) (125 mg) as orange crystals after recrystallization from CH_2Cl_2–light petroleum. The second yellow band eluted gave $[RuCl(CO)(cp)(PPr_3)]$ (8a) (170 mg) as yellow crystals after recrystallization in the same way. If CH_2Br_2 is used as eluant, the second band yields $[RuBr(CO)(cp)(PPr_3)]$ (10) isolated as orange crystals.

Reaction of (1) with PMe_2Ph was carried out in the same way to yield a mixture of $[Ru_2(CO)_3(cp)_2(PMe_2Ph)]$ and $[RuCl(CO)(cp)(PMe_2Ph)]$ (8b).

(*iv*) ***Reaction of*** $[Ru_2(CO)_3(cp)_2(PMe_2Ph)]$ ***with*** PMe_2Ph.—The complex $[Ru_2(CO)_3(cp)_2(PMe_2Ph)]$ (7b) (100 mg) was treated with a 5 : 1 molar excess of PMe_2Ph in refluxing toluene (10 cm^3). After 8 h, starting material had disappeared and i.r. and n.m.r. analysis indicated the presence of $[Ru(CO)(cp)H(PMe_2Ph)]$ (11b) and $[Ru(cp)H(PMe_2Ph)_2]$ (12). The solvent was removed under reduced pressure and the residue chromatographed on grade III alumina using CH_2Cl_2 as eluant. The first yellow band to develop gave $[RuCl(CO)(cp)(PMe_2Ph)]$ (8b) (50 mg) and the second yellow band gave $[RuCl(cp)(PMe_2Ph)_2]$ (9) (30 mg) identical with samples prepared as in (*v*).

(*v*) ***Reaction between*** PR_3 ***and*** $[RuCl(CO)_2(cp)]$.—The complex $[RuCl(CO)_2(cp)]$ (250 mg) was treated with a 2 : 1 molar excess of PPr_3 for 12 h in refluxing toluene. The solvent was removed and the residue was chromatographed on grade III alumina using CH_2Cl_2 as eluant. The product was eluted as a yellow band yielding yellow crystals of $[RuCl(CO)(cp)(PPr_3)]$ (8a) (200 mg). The complex $[RuCl(CO)(cp)(PMe_2Ph)]$ (8b) was prepared in the same way.

Reaction of $[RuCl(CO)(cp)(PMe_2Ph)]$ (8b) (200 mg) with a 2 : 1 molar excess of PMe_2Ph in refluxing toluene for 12 h, followed by chromatography, gave $[RuCl(cp)(PMe_2Ph)_2]$ (9) as a yellow solid in low yield (20 mg).

(*vi*) ***Reaction of*** $[Ru(CO)_2(cp)H]$ ***with*** PR_3.—A heptane solution of $[Ru(CO)_2(cp)H]$ (1.67 mmol) was prepared by the method of Knox.[16] At 80 °C, PPr_3 (2.0 mmol) was added and the solution stirred for 15 min. Infrared and n.m.r. analysis indicated complete conversion to $[Ru(CO)(cp)H(PPr_3)]$ (11a). The solvent was evaporated and the residue dissolved in $CHCl_3$ and stirred overnight. The solvent was evaporated and the residue chromatographed on grade III alumina using benzene as eluant. Collection of the yellow band and recrystallization gave $[RuCl(CO)(cp)(PPr_3)]$ (8a) (400 mg). A solution of $[Ru(CO)(cp)H(PMe_2Ph)]$ (11b) was prepared in the same way and converted to $[RuCl(CO)(cp)(PMe_2Ph)]$ (8b).

More prolonged reaction (*ca.* 2 h) with PMe_2Ph yields a mixture of $[Ru(CO)(cp)H(PMe_2Ph)]$ (11b) and $[Ru(cp)H(PMe_2Ph)_2]$ (12) as judged by n.m.r. analysis. Evaporation of heptane, followed by stirring in $CHCl_3$ and chromatography of the residue, yields $[RuCl(CO)(cp)(PMe_2Ph)]$ (8b) and $[RuCl(cp)(PMe_2Ph)_2]$ (9).

All products were identical with samples prepared as in (*v*). Analytical and spectral data for the compounds are given in Tables 1—4.

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