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Cyclopentadienyl-ruthenium and -osmium chemistry

XXXII *. Some complexes containing tertiary phosphites: X-ray structures of $RuCl\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ and of two isomers of $Ru\{C[{=}C(CN)_2]CPh{=}C(CN)_2\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$

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Abstract

Exchange of tertiary phosphites for PPh_3 in $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ afforded $RuCl\{P(OR)_3\}_2(\eta\text{-}C_5H_5)$ ($R_3 = Me_3$, $(CH_2CF_3)_3$, $(CH_2)_3CEt$). Conventional reactions of the $P(OMe)_3$ complex afforded $RuX\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (X = H, $C(CO_2Me){=}CH(CO_2Me)$, $SnCl_3$, C_2Ph, $\overline{C{=}CPhC(CN)_2C}(CN)_2$, $C\{{=}C(CN)_2\}$-$CPh{=}C(CN)_2$ (red and yellow forms)) or $[Ru(L)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]^+$ [L = NCMe, C = CHPh, $C(OMe)CH_2Ph$, C=CMePh, C=CClPh). The phenylethynyl complex was converted to two copper-containing complexes by coordination of CuCl or Cu^+ to the C≡C triple bond.

Crystals of $RuCl\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ are orthorhombic, space group $Pna2_1$ with unit cell dimensions a 9.606(3), b 14.167(4) and c 12.891(4) Å and $Z = 4$; $Ru\{C[{=}C(CN)_2]CPh{=}C(CN)_2\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ exists as two isomers: yellow form, triclinic, space group $P\bar{1}$, a 9.496(6), b 10.436(6), c 15.216(2) Å, α 90.74(2), β 90.22(3), γ 111.47(4)° and $Z = 2$; red form, orthorhombic, space group $Pbca$, a 14.501(5), b 15.047(2), c 26.658(4) Å and $Z = 4$. The structures were each refined by a full-matrix least-squares procedure to final $R = 0.051$, $R_w = 0.050$ for 1419 reflections with $I > 2.5\sigma(I)$ for $RuCl\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$; $R = 0.037$, $R_w = 0.041$ for 2930 reflections for the yellow isomer of $Ru\{C[{=}C(CN)_2]CPh{=}C(CN)_2\}\{P$-$(OMe)_3\}_2(\eta\text{-}C_5H_5)$; and $R = 0.033$, $R_w = 0.035$ for 1661 reflections for the red isomer.

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* For Part XXXI, see ref. 28.

Introduction

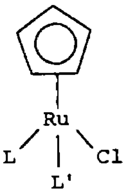
The development of the chemistry of ruthenium and osmium complexes containing η-C_5H_5 groups has resulted in the discovery of complexes containing a wide variety of unusual ligands, much of which has been summarised in recent reviews [1,2]. Also of interest are the variations in chemistry which may occur when ligands [CO, PR_3, $P(OR)_3$; C_5H_5, C_5Me_5] are changed systematically. For example, halide in $RuX(L)_2(\eta\text{-}C_5H_5)$ (X = Cl, Br, I) is tightly bound to the metal when L = CO, but shows a well-defined tendency to ionise when L = PPh_3 [3] or PMe_3 [4]. The ready loss of one PPh_3 ligand from $RuX(PPh_3)_2(\eta\text{-}C_5H_5)$ has been a driving force in the synthesis of unusual chelating ligands. This paper describes the synthesis and reactions of a series of complexes containing tertiary phosphites, most derived from $RuCl\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$.

Results and discussion

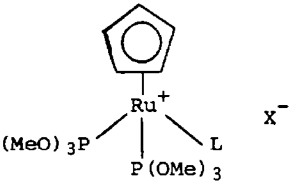
The reaction between $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and trimethyl phosphite, carried out in refluxing xylene, resulted in exchange of both PPh_3 ligands, and yellow $RuCl\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (**1**) was obtained in ~ 90% yield. The complex has been described before [5]: it was identified by the usual spectroscopic methods, the ^1H NMR spectrum containing an OMe resonance at δ 3.59 with the characteristic doublet with unresolved central multiplet arising from an $X_9AA'X'_9$ spin system. In the ^{13}C NMR spectrum, not previously reported, the OMe and C_5H_5 carbons resonate at δ 51.9 and 81.25 ppm, respectively. The C_5H_5 resonances of the $P(OMe)_3$ complexes described herein all show a J(HP) coupling of ~ 1 Hz, and J(CP) of ~ 3 Hz, in contrast with their tertiary phosphine analogues.

The FAB mass spectrum of **1** shows $[M]^+$ as base peak, which fragments by loss of Cl, OMe and $P(OMe)_3$ groups. Several ions are formed by loss of Me from coordinated $P(OMe)_3$, such as those at m/z 245 ($[Ru\{PO(OMe)\}(\eta\text{-}C_5H_5)]^+$), 230 ($[RuPO_2(C_5H_5)]^+$) and 180 ($[Ru\{PO(OMe)\}]^+$). In addition, an ion cluster centred on m/z 865 can be formulated as the ion-molecule aggregate $[\{Ru[P(OMe)_3]_2(C_5H_5)\}_2Cl]^+$, for which there is a precedent in the cation $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2Cl]^+$, obtained as an intermediate in the low-temperature chlorination of $\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2$ to $RuCl(CO)_2(\eta\text{-}C_5H_5)$ [6].

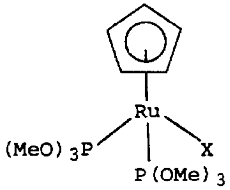
Although $P(OCH_2CF_3)_3$ has been known since 1954 [7], relatively few transition metal complexes containing this ligand have been described: these include $Cr(CO)_2\{P(OCH_2CF_3)_3\}_2(\eta\text{-}C_6H_6)$, $FeI\{P(OCH_2CF_3)_3\}_2(\eta\text{-}C_5H_5)$, $Ni(CO)_2\{P(OCH_2CF_3)_3\}_2$ [8], and the cluster carbonyls $Ru_3(CO)_{12-n}\{P(OCH_2CF_3)_3\}_n$ (n = 1–4) [9]. After an overnight exchange reaction between the fluorophosphite and $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ in refluxing toluene, the complex $RuCl\{P(OCH_2CF_3)_3\}_2(\eta\text{-}C_5H_5)$ (**2**) was obtained in ~ 50% yield, and was identified on the basis of elemental microanalysis and its IR, NMR and mass spectra. Strong ν(CF) bands at 1281 and 1378 cm^{-1}, the ν(PO) band at 1080 cm^{-1}, and a ν(CO) band at 1165 cm^{-1} were found in the IR spectrum, while the ^1H NMR spectrum contains a broad triplet resonance for the CH_2 protons at δ 4.42: the J(HF) coupling was not resolved. The major fragmentation routes of the molecular ion are loss of F, Cl, CF_3 and OCH_2CF_3 fragments.

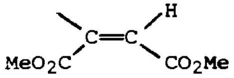


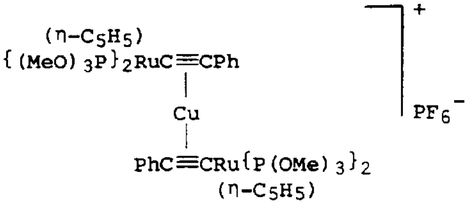
	L	L'
(1)	$\{P(OMe)_3\}_2$	
(2)	$\{P(OCH_2CF_3)_3\}_2$	
(3)	PPh_3	$P(OCH_2)_3CEt$
(4)	$\{P(OCH_2)_3CEt\}_2$	
(5)	$P(OMe)_3$	$P(OCH_2)_3CEt$



	L	X^-
(6)	MeCN	PF_6
(14)	C=CHPh	BF_4
(15)	$C(OMe)CH_2Ph$	BF_4
(16)	C=CMePh	$SbCl_6$
(17)	C=CClPh	$SbCl_6$



	X
(7)	H
(8)	
(9)	$SnCl_3$
(10)	$C\equiv CPh$
(11)	$C\equiv CPh$ ↓ CuCl



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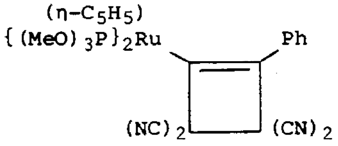

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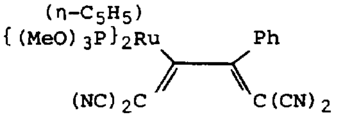

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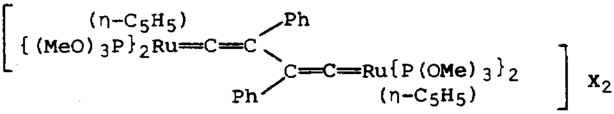


(<u>13a</u>) $X = PF_6$

(<u>13b</u>) $X = BF_4$

We have obtained similarly two complexes containing the cage phosphite ligand, 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, namely $RuCl(PPh_3)\{P(OCH_2)_3CEt\}(\eta\text{-}C_5H_5)$ (**3**) and $RuCl\{P(OCH_2)_3CEt\}_2(\eta\text{-}C_5H_5)$ (**4**); the former predominated after short reaction times, but was largely converted into the latter after heating overnight in xylene. Both yellow complexes were identified on the basis of the usual analytical and spectroscopic data. The FAB MS of (**4**) is notable for the paucity of fragmentation processes: the molecular ion is the base peak, but only slightly more intense than $[M - Cl]^+$; loss of one of the phosphite ligands is the only other process observed, apart from a very weak ion formed by loss of C_2H_4 from $[M - Cl]^+$.

The mixed phosphite complex $RuCl\{P(OMe)_3\}\{P(OCH_2)_3CEt\}(\eta\text{-}C_5H_5)$ (**5**) has also been made from **1** and the cage phosphite, in 53% yield. It forms yellow crystals, readily identified from its spectroscopic properties, which include ^1H NMR absorptions corresponding to those found in **1** and **4**, and an intense molecular ion in the FAB MS spectrum. Interestingly, after loss of Cl from this ion, loss of the cage phosphite is preferred over loss of $P(OMe)_3$ by a factor of 2/1.

Molecular structure of $RuCl\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ *(1)*

Well-formed yellow crystals of complex **1** were suitable for an X-ray structure determination, and Fig. 1 illustrates a plot of the molecular structure. The unit cell contains discrete molecules of **1** separated by normal Van der Waals distances. The ruthenium atom is in a distorted octahedral environment of the C_5H_5 group, the Cl and two $P(OMe)_3$ ligands. Table 1 summarises metal–ligand bond distances and angles in the three complexes $RuCl(L)_2(\eta\text{-}C_5H_5)$, where $L = P(OMe)_3$, PMe_3 and PPh_3 [4]. It can be seen that the average Ru–C(cp) distances increase in the order $PPh_3 \sim PMe_3 < P(OMe)_3$, which reflects the decreasing amount of electron density at the metal.

The Ru–P distances increase in the order $L = P(OMe)_3 < PMe_3 < PPh_3$, that is, in order of increasing cone angle. The two Ru–P separations show marked inequivalence in the PMe_3 and $P(OMe)_3$ complexes; while the origin of the former is not clear at present, that in **1** probably results from the close approach of Cl to a hydrogen attached to C(6). A concomitant effect is the opening of Cl–Ru–P(2) to 95.0(1)°. The calculated Ru–P single bond separation is 2.43 Å; it is evident that there is a substantial degree of back-bonding into the empty P(3*d*) orbitals of the Group 15 ligands in **1**. The P(1)–Ru–P(2) angle is much closer to the ideal

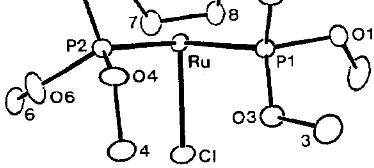


Fig. 1. Molecular structure of $RuCl\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (1), showing atom numbering scheme.

Table 1

Metal–ligand bond distances (Å) and angles (deg) in $RuCl(L)_2(\eta\text{-}C_5H_5)$

	L		
	* PPh_3 [a,b]	† PMe_3 [a,b]	* $P(OMe)_3$ [a,c]
Bond distances (Å)			
Ru–P(1)	2.337(1)	2.373(5)	2.234(2)
Ru–P(2)	2.335(1)	2.280(6)	2.199(3)
Ru–Cl	2.453(2)	2.451(6) 2.440(5)	2.393(3)
Average Ru–C(cp)	2.207	2.20	2.282
Bond angles (deg)			
P–Ru–P	103.99(4)	94.7(2) 95.0(2)	91.2(1)
P(1)–Ru–Cl	89.05(3)	89.7(2)	91.8(1)
P(2)–Ru–Cl	90.41(4)	90.1(2)	95.0(1)
Cone angle (deg)	145	118	107

[a] Asymmetric unit contains * one molecule of the complex † two molecules. [b] Ref. 4. [c] This work.

octahedral angle in **1**, and reflects the smaller cone angle of $P(OMe)_3$ compared with those of PMe_3 and PPh_3.

The Ru–Cl separations also increase as the cone angle of the Group 15 ligand increases, although those in **1** are ca. 0.05 Å shorter than those found in the tertiary phosphine complexes. This suggests that the effect may be more electronic than steric in origin; certainly, the chemical consequence is that the Cl atom which is closest to the ruthenium is more tightly bound and shows much less tendency to ionise.

Chemistry of the $Ru\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ system

We have briefly examined the reactivity of $RuCl\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (**1**) in order to compare it with other $RuCl(L)_2(\eta\text{-}C_5H_5)$ complexes, such as L = CO or PPh_3. In general, the Ru–Cl and Ru–P bonds are more difficult to break than those in the PPh_3 analogue, as would be expected in view of their shorter lengths (see above). In all, there are few surprises: formation and characterisation of the new complexes followed established patterns, and with one exception, the ^1H NMR spectra contained the characteristic $X_9AA'X'_9$ resonance for the OMe protons already described for the chloro complex. FAB mass spectra have been obtained for all complexes studied, and are characterised by loss of X, Me, OMe and $P(OMe)_3$ groups; several ions are formulated as containing PO, PO_2, POMe or PO(OMe) fragments, the latter being formed by Michaelis–Arbuzov-like rearrangements [10].

Although **1** gives yellow solutions in acetonitrile, addition of NH_4PF_6 or $TlPF_6$ and attempted crystallisation did not afford $[Ru(NCMe)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][PF_6]$ (**6**), in contrast to the PPh_3 complex [11]. Complex **6** was obtained, however, when mixtures of **1** and $AgPF_6$ were heated in refluxing acetonitrile; the yellow crystals are soluble in $CHCl_3$ and MeCN, but only sparingly soluble in CH_2Cl_2 and MeOH and insoluble in less polar solvents. The $\nu(CN)$ absorption is found at 2295 cm^{-1}, above that of free MeCN (2252 cm^{-1}) and also of the PPh_3 analogue (2100 cm^{-1}), reflecting the lower electron density on ruthenium in **1**.

Conversion of **1** into $RuH\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (**7**) was readily achieved by heating the former with NaOMe in refluxing methanol; complex **7** forms a white powder, which has ν(RuH) at 1975 cm^{-1}, and a high-field triplet resonance at δ −13.2 ppm. Compared with the PPh_3 analogue, which is formed within 1 h [12], complete conversion of **1** to **7** required 16 h; conversely, **7** is stable in chloroform solution for at least 8 h, whereas H–Cl exchange occurs immediately upon dissolution of $RuH(PPh_3)_2(\eta\text{-}C_5H_5)$ in this solvent.

Insertion of $C_2(CO_2Me)_2$ into the Ru–H bond of **7** gave $Ru\{C(CO_2Me)\text{=}CH(CO_2Me)\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (**8**) as off-white crystals. As described recently [13], initial *cis* addition of $RuH(PPh_3)_2)(\eta\text{-}C_5H_5)$ is followed by rapid isomerisation, and displacement of a PPh_3 ligand occurs to give a chelate monophosphine complex. Complex **8** does not undergo analogous transformations, and we cannot assign the stereochemistry of the vinyl group unequivocally: the vinylic proton exhibits *J*(HP) of ca. 1.2 Hz, in between the 0.9 and 2.0 Hz couplings found for the *cis* and *trans* isomers, respectively, of the PPh_3 complexes [13], but we are inclined to assign the *cis* configuration to (**8**).

The reaction between **1** and $SnCl_2$ afforded yellow crystals of $Ru(SnCl_3)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (**9**) in a reaction entirely analogous to that found for $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ [11]. The major peak in the FAB mass spectrum is $[Ru\{P(OMe)_3\}_2(C_5H_5)\}^+$ (*m/z* 415), formed by loss of Cl and $SnCl_2$ fragments from the molecular ion.

Difficulties in replacement of the Cl in **1** by MeCN are paralleled in other ligand exchange reactions. It proved impossible to replace either the Cl or MeCN ligands by phenylacetylene or phenylvinylidene; the usual route to σ-acetylide complexes, by deprotonation of the corresponding vinylidene cation formed directly from the alkyne [14], is thus not available in this system. Such reactions were found to give the hydride **7**, contaminated with small amounts of the desired acetylide complex **10**. Other attempted syntheses were also unsuccessful, including reactions between **1** and HC_2Ph in the presence of NH_4PF_6, $TlPF_6$ or CuI in diethylamine.

Complex **10** can be obtained in high yield from the reaction between **1** and AgC_2Ph; it was previously prepared by $PPh_3/P(OMe)_3$ exchange in $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ [15]. Pale yellow $Ru(C_2Ph)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ has ν(C≡C) at 2085 cm^{-1}, and is readily oxidised to unidentified products, either in solution or during chromatography on silica or alumina.

The C≡C triple bond in **10** readily complexes copper(I). The complex $Ru\{C_2Ph(CuCl)\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (**11**) was formed by heating **1** with CuC_2Ph in refluxing methanol as pale yellow crystals, while the reaction between **10** and $[Cu(NCMe)_4][PF_6]$ afforded $[[Ru\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)(C_2Ph)]_2Cu]PF_6$ (**12**) as a white crystalline solid. These complexes have precedents in the structurally-characterised complexes $Ru\{C_2Ph(CuCl)\}(PPh_3)_2(\eta\text{-}C_5H_5)$ [16] and $[\{Mn(CO)_3(dppe)(C_2Bu^t)\}_2Cu][PF_6]$ [17] and undoubtedly have similar structures. In both cases, FAB mass spectra have been obtained. The major fragmentation found for **11** is loss of the CuCl moiety; the resulting $[Ru(C_2Ph)\{P(OMe)_3\}_2(C_5H_5)]^+$ (*m/z* 516) then breaks down in a manner similar to that found for the molecular ion of **10**. For **12**, the parent ion $[M]^+$ loses $P(OMe)_3$ ligands stepwise, and one $Ru\{P(OMe)_3\}_2(C_5H_5)$ moiety; a strong ion at *m/z* 516, as found for **11**, is also observed.

A red by-product from the synthesis of **12** was identified as the copper-free binuclear product $[\{Ru[P(OMe)_3]_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C_4Ph_2)][PF_6]_2$ (**13a**). This compound was obtained in very low yield, and was characterised primarily on the basis of its FAB mass spectrum, which contained an ion centred on m/z 1177, assigned to $[Ru_2\{P(OMe)_3\}_4(C_5H_5)_2(C_4Ph_2) + PF_6]^+$; the spectrum of corresponding tetrafluoroborate salt **13b** contained the analogous ion at m/z 1117. Other spectroscopic and microanalytical results were consistent with the proposed formulation of the cation in salts **13**, which has precedent in the crystallographically characterised complex $[\{Fe(dppe)(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C_4Me_2)][BF_4]_2$, obtained by oxidation of $[Fe(CCHMe)(dppe)(\eta\text{-}C_5H_5)][BF_4]$ with iodosobenzene [18]. A similar oxidation (by Cu^{2+}) of traces of the corresponding vinylidene in **10** probably gave **13**. It is of interest that the FAB mass spectrum also contains very weak ions at m/z 2496 and 1837, corresponding to the higher aggregates $[Ru_4\{P(OMe)_3\}_8(C_5H_5)_4(C_8Ph_4) + 3PF_6]^+$ and $[Ru_3\{P(OMe)_3\}_6(C_5H_5)(C_8Ph_3) + 2PF_6]^+$, respectively.

Our interest in the reactivity of σ-bonded acetylide ligands prompted us to investigate selected protonation, alkylation and cycloaddition reactions of **10**. Addition of excess $HBF_4 \cdot OEt_2$ to **10** gave the air-sensitive, orange complex $[Ru(C{=}CHPh)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ (**14**), previously obtained as the PF_6 salt [15]. The extremely low chemical shift of the C_5H_5 protons (δ 5.7) and carbons (δ 91.4) indicates a considerable deficiency of electron density on the metal in this complex, induced by the efficiently π-accepting vinylidene ligand.

The vinylidene complex reacts readily with methanol to give the expected methoxy(benzyl)carbene complex, $[Ru\{C(OMe)CH_2Ph\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ (**15**), also found to be air-sensitive; compared with the PPh_3 analogue, formation of **15** occurs as soon as the reaction mixture reaches reflux point, presumably reflecting the ease of access of MeOH to the vinylidene α-carbon.

Alkylation of **10** with $[Me_3O][SbCl_6]$ afforded a red solution which rapidly deepened in colour and exhibited red/blue dichroism. The product was isolated as a dark purple oil: FAB mass spectra indicated the presence of both the expected $[Ru(C{=}CMePh)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][SbCl_6]$ (**16**) and the chlorovinylidene complex $[Ru(C{=}CClPh)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][SbCl_6]$ (**17**); however, neither were obtained in a pure state, rapid decomposition occurring on attempted purification.

Reactions between the phenylacetylide complex **10** and tetracyanoethene (TCNE) produced three complexes. The white cyclobutenyl derivative, $\overline{Ru\{C{=}CPhC(CN)_2\text{-}C}(CN)_2\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (**18**), formed by a formal [2 + 2]-cycloaddition of the olefin to the acetylide, was isolated from a reaction carried out in diethyl ether. This complex was identified by the characteristic loss of $C_2(CN)_4$ from $[M]^+$ in the FAB mass spectrum [19], as well as from other analytical and spectroscopic data: the IR spectrum contains two weak ν(CN) absorptions at 2249 and 2236 cm^{-1}. Dissolution of **18** causes isomerisation to the butadienyl derivative, $Ru\{C[{=}C(CN)_2]CPh{=}C(CN)_2\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (**19**); the reaction occurs immediately in CH_2Cl_2 or $CHCl_3$, but more slowly in diethyl ether or benzene. This complex is also formed directly from **10** and $C_2(CN)_4$ in benzene, and is characterised by medium intensity ν(CN) bands between 2230–2206 cm^{-1}, and an $[M]^+$ ion which fragments by loss of OMe, CN or Ph groups, but not of the intact $C_2(CN)_4$ molecule.

The ^1H NMR spectrum of **19** is unusual in that the OMe resonance has an unusual quintet structure (relative intensities ca. 2/3/2/3/2) (Fig. 2). We have not

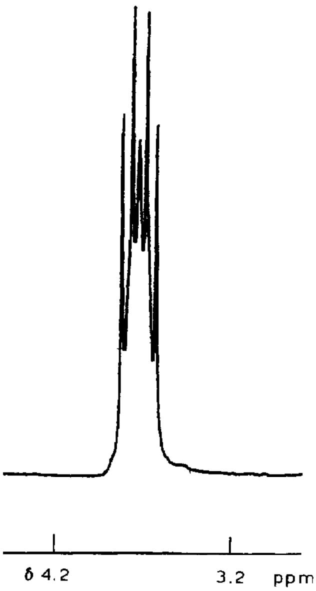


Fig. 2. Methyl resonance (δ 3.56) in ^1H NMR spectrum of $Ru\{C[=C(CN)_2]CPh{=}C(CN)_2\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (**19**).

been able to analyse this in terms of the usual $X_9AA'X_9'$ spin system, and suspect that the extra structure arises as a result of the presence of the asymmetric butadienyl ligand, which in turn allows the individual OMe groups to become magnetically inequivalent. In the ^{13}C NMR spectrum of **19**, the OMe carbons are found as a triplet at δ 52.7, the C_5H_5 group at δ 84.6 and the Ph carbons between δ 128–132 ppm. Only three of the four carbons of the butadienyl ligand were observed, at δ 72.7, 93.9 and 181.8 ppm, assigned to C(1), C(4) and C(2), respectively. The CN groups resonated as four singlets between δ 113–118 ppm.

Slow recrystallisation of **19** from dichloromethane/hexane mixtures gave a mixture of red-orange (**19R**) and yellow (**19Y**) crystals. These were hand separated, and were found to give identical IR and FAB mass spectra: the yellow form was identical with the complex **19** obtained from the cyclo-addition reaction in benzene. Single crystal X-ray studies have shown that the two crystal forms result from different conformations of the $P(OMe)_3$ ligands, as postulated to exist for $RuCl(CO)\{P(OMe)_3\}(\eta\text{-}C_5H_5)$, the IR ν(CO) spectrum of which shows two strong absorptions [20], and for $Cr(CO)_2\{P(OMe)_3\}(\eta\text{-}C_6H_6)$, which also shows an anomalous ν(CO) spectrum [21].

We have not been able to effect conversion of **19** to the allylic complex $Ru\{\eta^3\text{-}C(CN)_2CPh{=}C(CN)_2\}\{P(OMe)_3\}(\eta\text{-}C_5H_5)$ by expulsion of one of the $P(OMe)_3$ ligands, as found in the PPh_3 system. This is another result of the presence of stronger Ru–P bonds, and consequent reduced tendency for dissociation of the tertiary phosphite ligands.

Molecular structures of the two forms of complex 19

The molecular structures and numbering schemes used for the yellow and red forms of Ru{C[=C(CN)$_2$]CPh=C(CN)$_2$}{P(OMe)$_3$}$_2$(η-C$_5$H$_5$) (**19**) are shown in Fig. 3 and Table 2 lists selected interatomic parameters for the two compounds, together with some related data for the complexes Ru{C[=C(CN)$_2$]CPh=C(CN)$_2$}-(L)(L′)(η-C$_5$H$_5$) (L = CNBu^t, L′ = PPh$_3$ and LL′ = dppe) [22].

The ruthenium atoms in both isomers exist in distorted octahedral environments. One octahedral face is occupied by a η-cyclopentadienyl group (Ru–C(cp) 2.230(5)–2.258(5), av. 2.246 Å for (**19Y**); Ru–C(cp) 2.228(8)–2.259(5), av. 2.241 Å in (**19R**)) while the opposite face is occupied by the two P(OMe)$_3$ ligands (Ru–P(1) 2.232(1) and 2.231(2); Ru–P(2) 2.237(1) and 2.238(2) Å; P(1)–Ru–P(2) 89.1(1) and 88.8(1)) and the cyanocarbon group (Ru–C(12) 2.059(4) and 2.063(6) Å; P(1)–Ru–C(12) 94.9(1) and 97.1(2); P(2)–Ru–C(12) 91.5(1) and 90.8(2)°).

Within the cyanocarbon ligand, the butadienyl framework has the familiar localised short-long-short pattern of C–C separations, with the torsion angles Ru–C(12)–C(13)–Ph (69.5 and 65.7°) and C(17)–C(12)–C(13)–C(14) (79.4 and 77.2°) showing the non-planarity of the diene system.

Clearly there are no significant differences in the ruthenium atom geometries in the isomers nor, as can be seen from Table 2, are there any outstanding features associated with either of the unsaturated fragments. The two forms arise as a result of a twist about the Ru–P(1) vector and different orientations of the OMe groups bound to the P(1) atom; these differences are best illustrated in Fig. 3. It is also of interest that the conformational changes, whereby the two P(OMe)$_3$ ligands are rendered inequivalent, appear to be reflected in the ^{1}H NMR spectrum, with its unusual five-line signal for the Me protons.

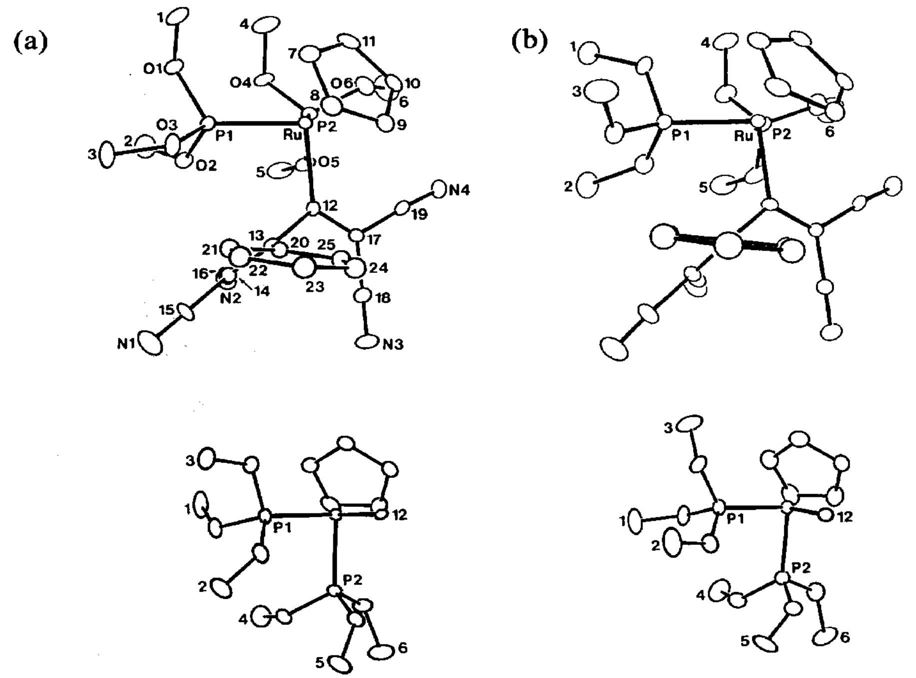
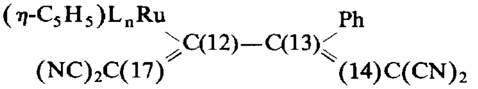


Fig. 3. Molecular structures of Ru{C[=C(CN)$_2$]CPh=C(CN)$_2$}{P(OMe)$_3$}$_2$(η-C$_5$H$_5$) (**19**) showing atom numbering schemes: (a) yellow form; (b) red form.

Table 2

Selected bond parameters for butadienyl complexes



$$\begin{array}{ccc}(\eta\text{-}C_5H_5)L_nRu & & Ph \\ & \!\!\!\!>C(12)-C(13)<\!\!\!\! & \\ (NC)_2C(17) & & (14)C(CN)_2\end{array}$$

	LL′			
	$\{P(OMe)_3\}_2$ **(19Y)** [a]	$\{P(OMe)_3\}_2$ **(19R)** [a]	$(CNBu^t)(PPh_3)$ [b]	dppe [b]
Bond distances (Å)				
Ru–Cp(av.)	2.246	2.241		2.235
Ru–P	2.232(1)	2.231(2)		2.280(1)
	2.237(1)	2.238(2)		2.340(1)
Ru–C(12)	2.059(4)	2.063(6)	2.074(3)	2.068(4)
C(12)–C(17)	1.348(6)	1.34(1)	1.382(5)	1.370(6)
C(12)–C(13)	1.501(6)	1.48(1)	1.478(4)	1.484(6)
C(13)–C(14)	1.343(6)	1.360(9)	1.362(4)	1.346(6)
Bond angles (deg)				
C(13)–C(12)–C(17)	114.2(4)	115.2(6)	112.8(3)	114.4(4)
C(12)–C(13)–C(14)	121.2(4)	122.9(7)	117.9(3)	124.3(4)
Torsion angles (deg)				
Ru–C(12)–C(13)–Ph	69.5	65.7	70.0	70.2
C(17)–C(12)–C(13)–C(14)	79.4	77.2	81.5	80.6

[a] This work. [b] Ref. 22; C atoms renumbered to conform with this work.

An interesting feature arising from a comparison of the two forms of $Ru\{C[=C(CN)_2]CPh{=}C(CN)_2\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ is that there is a significant difference in the calculated density for each of their respective unit cells; the yellow form has D_c 1.523 g cm^{-3} compared with 1.470 g cm^{-3} for the red crystals. In this context it is noteworthy that under normal crystallizing conditions, the yellow form predominates over the red form in an approximate ratio of 3/1; however, if the solution is allowed to stand for prolonged periods only yellow crystals are recovered. These observations reflect the more efficient crystal packing characteristics of the yellow form. That two quite different densities are found suggests an efficient method of separation. Thus when a sample of the mixed crystals is suspended in an inert solvent with a density of ca. 1.50 g cm^{-3} (e.g. a mixture of CCl_4 and 60–80 °C light petroleum) the yellow crystals, by virtue of their greater density, sink to the bottom of the flask and the red crystals float on the surface of the solvent; in our hands, equilibrium, i.e. separation, was achieved for a sample of 35 mg in approximately five minutes.

The striking colour change resulting from a small conformational difference in the ligands is not unusual: two recent, but unrelated, examples are to be found in the red and blue isomers of $[Cu(L)](ClO_4)_2$ (L = *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), which have differing orientations (by inversion) of one of the nitrogen atoms [23], and red and yellow forms of $MnPt(\mu\text{-}\overline{C{=}CHCH_2CH_2O})(CO)_4(PMe_3)_2$, which differ mainly in the orientations of the PMe_3 groups [24].

Conclusions

The molecular structure and reactivity of $RuCl\{P(OMe)_3\}_2(\eta-C_5H_5)$ have been studied, and the results are consistent with the presence of a sterically small Group 15 ligand with good π-accepting properties. Thus the reactions are typical of $RuCl(CO)_2(\eta-C_5H_5)$, with its covalently-bound chloride, and reluctance to dissociate even one 2e-donor ligand. In contrast, the PMe_3 and PPh_3 analogues, with longer Ru–Cl bonds, show a greater tendency to lose chloride and form cationic complexes, and in the case of PPh_3, to lose one of the tertiary phosphine ligands.

Experimental

General conditions. All reactions were carried out under nitrogen; no special precautions were taken to exclude air during work-up, since most complexes proved to be stable in air as solids, and for short times in solution.

Instruments. Perkin–Elmer 683 double-beam spectrometer, NaCl optics (IR); Bruker WP80 spectrometer (^1H NMR at 80 MHz, ^{13}C NMR at 20.1 MHz); GEC-Kratos MS3074 mass spectrometer (mass spectra at 70 eV ionising energy, 4 kV accelerating potential).

FAB mass spectra were obtained on a VG ZAB 2HF instrument equipped with a FAB source. Argon was used as the exciting gas, with source pressure typically 10^{-6} mbar; the FAB gun voltage was 7.5 kV, current 1 mA. The ion accelerating potential was 8 kV. The matrix was 3-nitrobenzyl alcohol. The complexes were made up as ca. 0.5 *M* solutions in acetone or dichloromethane; a drop was added to a drop of matrix and the mixture was applied to the FAB probe tip.

Starting materials. $RuCl(PPh_3)_2(\eta-C_5H_5)$ [25] and $RuCl(CO)\{P(OMe)_3\}(\eta-C_5H_5)$ [20] were made by the cited procedures. Silver phenylacetylide was obtained by addition of phenylacetylene to a solution of $AgNO_3$ in aqueous ammonia. $P(OCH_2CF_3)_3$ (Aldrich) and $P(OCH_2)_3CEt$ (Strem) were used as received.

Preparation of $RuCl\{P(OR)_3\}_2(\eta-C_5H_5)$

(a) $P(OMe)_3$. A solution of $RuCl(PPh_3)_2(\eta-C_5H_5)$ (1.00 g, 1.38 mmol), trimethylphosphite (500 mg, 4.00 mmol), and xylene (30 ml) was refluxed for 4 h. Evaporation to dryness yielded a yellow oil which was extracted with CH_2Cl_2 and the solution was chromatographed, the xylene and excess $P(OMe)_3$ being washed through with 4/1 light petroleum/CH_2Cl_2. Elution with CH_2Cl_2 gave a yellow band, which was crystallized from light petroleum, yielding yellow crystals of $RuCl\{P(OMe)_3\}_2(\eta-C_5H_5)$ (**1**) (554 mg, 89%) identified from its m.p. (126 °C; lit. [5] 126–129 °C) and IR spectrum (nujol: $\nu(PO)$ 1040 cm^{-1}; lit. [5] 1040 cm^{-1}). ^1H NMR ($CDCl_3$): δ 3.59 (t, $J(HP)^*$ 11.7 Hz, 18H, OMe), 4.78 (t, $J(HP)$ 0.98 Hz, 5H, C_5H_5). ^{13}C NMR ($CDCl_3$): δ 51.92 (s, OMe), 81.25 (t, $J(CP)$ 3.1 Hz, C_5H_5). FAB MS: 865, $[\{Ru[P(OMe)_3]_2(C_5H_5)\}_2Cl]^+$, 5.3; 450, $[M]^+$, 100; 415, $[M-Cl]^+$, 52; 384, $[M-Cl-OMe]^+$, 9.5; 326, $[M-P(OMe)_3]^+$, 76; 291, $[Ru\{P(OMe)_3\}(C_5H_5)]^+$, 33; 260, $[Ru\{P(OMe)_2\}(C_5H_5)]^+$, 24; 245, $[Ru\{PO(OMe)\}(C_5H_5)]^+$, 38;

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* $J(HP)^*$ refers to the separation (Hz) of the two most intense absorptions of the XX′ part of the $X_9AA'X'_9$ spectrum; it corresponds to $|J(AX)+J(AX')|$.

230, $[Ru(PO_2)(C_5H_5)]^+$, 9.5; 214, $[Ru(PO)(C_5H_5)]^+$, 1; 202, $[RuCl(C_5H_5)]^+$, 1; 180, $[Ru\{PO(OMe)\}]^+$, 9.5; 167, $[Ru(C_5H_5)]^+$, 33.

(b) $P(OCH_2CF_3)_3$. A mixture of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (100 mg, 0.14 mmol) $P(OCH_2CF_3)_3$ (107 mg, 0.33 mmol) and toluene (25 ml) was refluxed for 16 h. After removal of solvent, the remaining yellow oil was purified by preparative TLC (silica, 1/4 CH_2Cl_2/light petroleum). The yellow fraction (R_f 0.22) was crystallised (CH_2Cl_2/light petroleum) to give yellow $RuCl\{P(OCH_2CF_3)_3\}_2(\eta\text{-}C_5H_5)$ (**2**) (57 mg, 47%), m.p. 71°C. Found: C, 24.01; H, 2.05%; *M* (mass spectrometry), 858; $C_{17}H_{17}ClF_{18}O_6P_2Ru$ calcd.: C, 23.80; H, 2.00%; *M*, 858. IR (nujol): ν(CF) 1378s, 1281s; ν(CO) 1165s; ν(PO) 1080s(br); other bands at 1420m, 1105m, 1067(sh), 1052m, 912m, 907(sh), 851m, 840(sh), 791m cm^{-1}. ^1H NMR: δ ($CDCl_3$) 4.42 (t, *J*(PH) 4 Hz, 12H, CH_2), 5.04 (s, 5H, C_5H_5). FAB MS: 858, $[M]^+$, 65; 839, $[M-F]^+$, 7; 823, $[M-Cl]^+$, 100; 804 $[M-F-Cl]^+$, 20; 770, $[M-F-CF_3]^+$, 23; 759, $[M-OCH_2CF_3]^+$, 12; 740, $[M-F-OCH_2CF_3]^+$, 11; 721, $[M-2F-OCH_2CF_3]^+$, 5; 659, $[M-2(OCH_2CF_3)]^+$, 1; 640, $[M-F-2(OCH_2CF_3)]^+$, 1; 631, ?, 1; 615, ?, 1; 530, $[M-3(OCH_2CF_3)]^+$, 90; 495, $[M-Cl-3(OCH_2CF_3)]^+$, 95; 202, $[RuCl(C_5H_5)]^+$, 70.

(c) $P(OCH_2)_3CEt$. A mixture of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (100 mg, 0.14 mmol) $P(OCH_2)_3CEt$ (56 mg, 0.34 mmol), and toluene (25 ml) was refluxed for 2 h, after which time the major product was $RuCl(PPh_3)\{P(OCH_2)_3CEt\}(\eta\text{-}C_5H_5)$ (TLC identification; see below). Replacement of toluene by xylene (25 ml), heating the mixture overnight at reflux point, purification by preparative TLC (silica, 1/1 acetone/light petroleum), and crystallisation (CH_2Cl_2/light petroleum) of the two fractions gave:

(i) yellow $RuCl(PPh_3)\{P(OCH_2)_3CEt\}(\eta\text{-}C_5H_5)$ (**3**) (R_f 0.6) (11 mg, 13%), m.p. 236°C. Found: C, 55.88; H, 5.27%; *M* (mass spectrometry), 626; $C_{29}H_{31}ClO_3P_2Ru$ calcd.: C, 55.63; H, 5.00%; *M* 626. IR (nujol): ν(PO) 1039s(br), ν(CO) 1178m; other bands at 1158m, 1092m, 966m, 950s, 854m, 788m, 778(sh), 767m, 759(sh), 747m, 695m, 650m cm^{-1}. ^1H NMR: δ ($CDCl_3$) 0.80 (m, 3H, CH_3), 1.26 (m, 2H, CH_2), 3.94 (d, *J*(PH) 4.2 Hz, 6H, OCH_2), 4.54 (s, 5H, C_5H_5), 7.34 (m, 15H, Ph). FAB MS: 626, $[M]^+$, 98; 591, $[M-Cl]^+$, 72; 550, $[M-Cl-C_3H_3]^+$, 1; 464, $[M-P(OCH_2)_3CEt]^+$, 20; 443, ?, 6; 429, $[Ru(PPh_3)(C_5H_5)]^+$, 100; 387, ?, 8; 364, $[M-PPh_3]^+$, 20; 350, ?, 18; 328, $[M-Cl-PPh_3]^+$, 3; 244, ?, 8; 167, $[Ru, C_5H_5]^+$, 8.

(ii) Yellow $RuCl\{P(OCH_2)_3CEt\}_2(\eta\text{-}C_5H_5)$ (**4**) (R_f 0.23) (58 mg, 79%), m.p. 264°C (dec), obtained as a $0.5CH_2Cl_2$-solvate. Found: C, 35.66; H, 4.75%; *M* (mass spectrometry), 526; $C_{17}H_{27}ClO_6P_2Ru \cdot 0.5CH_2Cl_2$ calcd.: C, 35.92; H, 4.80%; *M* (unsolvated), 526. IR (nujol): ν(CO) 1166s, ν(PO) 1028s; other bands at 1285m, 1040(sh), 996m, 915m, 948s, 857s, 801s, 793s, 785(sh), 771s, 761s, 753s, 720m, 654s, 641s cm^{-1}. ^1H NMR: δ ($CDCl_3$) 0.84 (m, 6H, Me), 1.26 (m, 4H, CH_2), 4.27 (t, *J*(HP) 2.4 Hz, 12H, OCH_2), 4.92 (s, 5H, C_5H_5), 5.31 (s, 1H, CH_2Cl_2). FAB MS: 526, $[M]^+$, 100; 491, $[M-Cl]^+$, 95; 462, $[M-C_2H_4]^+$, 1; 364, $[M-P(OCH_2)_3CEt]^+$, 38; 328, $[Ru\{P(OCH_2)_3CEt\}(C_5H_5)]^+$, 34; 167, $[Ru(C_5H_5)]^+$, 1.

Preparation of $RuCl\{P(OMe)_3\}\{P(OCH_2)_3CEt\}(\eta\text{-}C_5H_5)$ (5)

A mixture of $RuCl\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (200 mg, 0.445 mmol) $P(OCH_2)_3CEt$ (112 mg, 0.688 mmol), and xylene (30 ml) was refluxed for 40 h. Evaporation, extraction of the residue with CH_2Cl_2, and purification (silica, 3/7 acetone/light petroleum) gave a yellow fraction which formed yellow crystals (CH_2Cl_2/light petroleum) of RuCl{P(OMe)$_3$}{P(OCH$_2$)$_3$CEt}(η-C_5H_5) (5) (115 mg, 53%), m.p. 125°C (dec.). Found: C, 34.73; H, 5.23%; *M* (mass spectrometry), 488; $C_{14}H_{25}ClO_6P_2Ru$ calcd.: C, 34.47; H, 5.18%; *M*, 488. Infrared (nujol): 1396m, 1390m, 1366m, 1303s, 1184s, 1156s, 1101m, 1065s, 1035s(br), 1005(sh), 994(sh), 974s, 955s, 940s, 856s, 846(sh), 830m, 807(sh), 775s(br), 737s, 649s, 627m cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 0.84 (m, 3H, Me), 3.67 (*d*, *J*(HP)* 11.5 Hz, 9H, OMe), 4.26 (d, *J*(HP)* 5.1 Hz, OCH$_2$), 4.51 (d, *J*(HP)* 6.6 Hz, OCH$_2$), 4.89 (t, *J*(HP) 1.1 Hz, 5H, C_5H_5). FAB MS: 488, $[M]^+$, 100; 453, $[M - Cl]^+$, 46.2; 422, $[M - Cl - Et]^+$, 2.5; 364, $[M - P(OMe)_3]^+$, 7.4; 343, $[M - Cl - PO(OMe)_2]^+$, 5.0; 327, $[M - Cl - P(OMe)_3]^+$, 28.1; 289, $[M - Cl - P(OCH_2)_3CEt]^+$, 14.9.

Preparation of [Ru(NCMe){P(OMe)$_3$}$_2$(η-C_5H_5)][PF$_6$]

A mixture of RuCl{P(OMe)$_3$}$_2$(η-C_5H_5) (500 mg, 1.11 mmol) and $AgPF_6$ (337 mg, 1.33 mmol) was refluxed in MeCN (20 ml) for 6 h. The filtered solution was evaporated to dryness, and the resulting pale yellow oil was crystallized from MeCN/Et_2O to yield pale yellow microcrystals of [Ru(NCMe){P(OMe)$_3$}$_2$(η-C_5H_5)][PF$_6$] (6) (610 mg, 91%), m.p. 161–164°C. Found: C, 26.19; H, 4.46; N, 2.35%; *M* (mass spectrometry), 456. $C_{13}H_{26}O_6F_6NP_3Ru$ calcd.: C, 26.00; H, 4.37; N, 2.33%; *M*, 456. IR (nujol): ν(CN) 2295w, ν(PF) 840 vs(br) cm^{-1}; other bands at 1287(sh), 1280m(br), 1187m, 1067(sh), 1057s, 1037s, 1020s, 1000s(br), 877m, 829(sh), 810s, 800(sh), 785s, 757m, 735s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.37 (s, 3H, CMe), 3.64 (t, *J*(HP)* 11.7 Hz, 18H, OMe), 5.01 (t, *J*(HP) 0.98 Hz, 5H, C_5H_5). ^{13}C NMR ($CDCl_3$): δ 3.46 (s, CMe), 52.16 (t, *J*(CP) 2.4 Hz, OMe), 82.04 (t, *J*(CP) 0.12 Hz, C_5H_5), 128.20 (s, NC). FAB MS: 456, $[Ru(NCMe)\{P(OMe)_3\}_2(C_5H_5)]^+ \equiv [M]^+$, 67.3; 415, $[M - MeCN]^+$, 100.

Preparation of RuH{P(OMe)$_3$}$_2$(η-C_5H_5)

(N.B. Oxygen-free conditions were maintained throughout this preparation.) A mixture of RuCl{P(OMe)$_3$}$_2$(η-C_5H_5) (300 mg, 0.67 mmol) and sodium metal (197 mg, 0.009 g-atom) was refluxed in methanol (20 ml) for 16 h. The solution was placed in an ice-bath and evaporated to dryness. Sublimation of the resulting pale yellow oil (80°/0.1 mmHg) afforded a pure sample of RuH{P(OMe)$_3$}$_2$(η-C_5H_5) (7) as a white powder (107 mg, 38%), m.p. ca. 25°C. Found: C, 32.27; H, 5.83%; M (mass spectrometry), 416. $C_{11}H_{24}O_6P_2Ru$ calcd.: C, 31.87; H, 5.84%; M, 416. IR (nujol): ν(RuH) 1975m(br) cm^{-1}; other bands: 1420(sh), 1262m, 1181s, 1108(sh), 1072s, 1035s(br), 800s, 775s, 721s, 615m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ −13.16 (t, *J*(HP) 35 Hz, 1H, RuH), 3.44 (t, *J*(HP)* 10.9 Hz, 18H, OMe), 4.96 (s, 5H, C_5H_5). FAB MS: 830, $[\{Ru[P(OMe)_3]_2(C_5H_5)\}_2]^+$, 1.2; 416, $[M]^+$, 100; 385, $[M - OMe]^+$, 35.4; 291, $[Ru\{P(OMe)_3\}(C_5H_5)]^+$, 10.3.

Preparation of Ru{C(CO$_2$Me)=CH(CO$_2$Me)}{P(OMe)$_3$}$_2$(η-C_5H_5)

A mixture of RuCl{P(OMe)$_3$}$_2$(η-C_5H_5) (200 mg, 0.44 mmol) and sodium metal (95 mg, 0.004 g-atom) was refluxed in methanol (20 ml) for 16 h. Evaporation of the cooled solution afforded a pale yellow oil, which was identified by TLC as the hydride (7). The residue was taken up in benzene (20 ml), $C_2(CO_2Me)_2$ (96 mg, 0.68 mmol) was added, and the mixture refluxed for 32 h. Evaporation to dryness and preparative TLC (3 : 1 light petroleum/acetone) yielded a major band (colourless,

R_f ca. 0.85) which was crystallized ($\mathrm{Et_2O}$) to yield off-white crystals of $\mathrm{Ru\{C(CO_2Me){=}CH(CO_2Me)\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}$ (**8**) (70 mg, 29%), m.p. 123° C. The other bands oxidised quickly on the plate. Found: C, 37.07; H, 5.42%; *M* (mass spectrometry), 557. $\mathrm{C_{17}H_{30}O_{10}P_2Ru}$ calcd.: C, 36.62; H, 5.44%; *M*, 557. IR (nujol): ν(CO) 1736m, 1692s; ν(C=C) 1540s $\mathrm{cm^{-1}}$; other bands at 1505m, 1435s, 1380m, 1338s, 1190s, 1145s(br), 1070s, 1030s(br), 955m, 870s, 857m, 845m, 835m, 830m, 820m, 800–710s(br), 658s, 631m $\mathrm{cm^{-1}}$. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 3.57 (t, *J*(HP)* 11.7 Hz, 21H, POMe and COMe), 3.79 (s, 3H, COMe), 4.82 (t, *J*(HP) 0.98 Hz, 5H, $\mathrm{C_5H_5}$), 5.93 (t, *J*(HP) 1.2 Hz, 1H, =CH). FAB MS: 558, $[M]^+$, 2.3; 527, $[M-\mathrm{OMe}]^+$, 4.0; 499, $[M-\mathrm{CO_2Me}]^+$, 25.3; 434, $[M-\mathrm{P(OMe)_3}]^+$, 100; 415, $\mathrm{[Ru\{P(OMe)_3\}_2(C_5H_5)]^+}$, 14.7.

Preparation of $\mathit{Ru(SnCl_3)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}$

$\mathrm{SnCl_2}$ (100 mg, 0.44 mmol) was added to a solution of $\mathrm{RuCl\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}$ (100 mg, 0.22 mmol) in a mixture of ethyl acetate (8 ml) and methanol (2 ml). Stirring for 16 h yielded a yellow precipitate. Filtration and crystallization ($\mathrm{CH_2Cl_2}$/light petroleum) afforded pale yellow crystals of $\mathrm{Ru(SnCl_3)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}$ (**9**) (110 mg, 78%), m.p. 302° C. Found: C, 20.66; H, 3.63%; *M* (mass spectrometry), 639. $\mathrm{C_{11}H_{23}O_6Cl_3P_2SnRu}$ calcd.: C, 20.54; H, 3.55%; *M*, 639. IR (nujol): 3110m, 1415m, 1378s, 1368s, 1178s, 1066(sh), 1055s(br), 1039(sh), 1020(sh), 1010s, 849m, 795s, 780m, 751s, 725s $\mathrm{cm^{-1}}$. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 3.63 (t, *J*(HP)* 12.2 Hz, 18H, OMe), 5.08 (s, 5H, $\mathrm{C_5H_5}$). FAB MS: 639, $[M]^+$, 1; 604, $[M-\mathrm{Cl}]^+$, 42.9; 569, $[M-\mathrm{2Cl}]^+$, 6.5; 450, $[M-\mathrm{SnCl_2}]^+$, 100; 415, $\mathrm{[Ru\{P(OMe)_3\}_2(C_5H_5)]^+}$, 64.3.

Preparation of $\mathit{Ru(C_2Ph)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}$

$\mathrm{AgC_2Ph}$ (167 mg, 0.80 mmol) was added to a solution of $\mathrm{RuCl\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}$ (300 mg, 0.67 mmol) in benzene (20 ml), and the mixture was refluxed for 16 h. The filtered solution was evaporated to dryness, and the resulting yellow oil chromatographed on preparative TLC plates (2/1 light petroleum/acetone). A colourless band (R_f 0.43) was collected and crystallized from ether/light petroleum to yield pale yellow microcrystals of $\mathrm{Ru(C{\equiv}CPh)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}$ (**10**) (262 mg, 76%), m.p. 83° C. Found: C, 44.33; H, 5.43%; *M* (mass spectrometry), 515. $\mathrm{C_{19}H_{28}O_6P_2Ru}$ calcd.: C, 44.27; H, 5.49%; *M*, 515. IR (nujol): ν(C≡C) 2085s, 2003w $\mathrm{cm^{-1}}$; other bands at 1597m, 1488m, 1192(sh), 1175s, 1063m, 1033s, 1027s, 785s, 766m, 728s, 700s $\mathrm{cm^{-1}}$. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 3.68 (t, *J*(HP)* 11.7 Hz, 18H, OMe), 4.99 (t, *J*(HP) 1.1 Hz, 5H, $\mathrm{C_5H_5}$), 7.12 (m, 5H, Ph). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 52.04 (s, OMe), 83.32 (t, *J*(CP) 3 Hz, $\mathrm{C_5H_5}$), 123.34, 127.71, 130.63, (3 × s, Ph). FAB MS: 516, $[M]^+$, 100; 485, $[M-\mathrm{OMe}]^+$, 6.0; 415, $[M-\mathrm{C_2Ph}]^+$, 25.0; 392, $[M-\mathrm{P(OMe)_3}]^+$, 7.8; 377, $[M-\mathrm{Me}-\mathrm{P(OMe)_3}]^+$, 18.5; 361, $[M-\mathrm{OMe}-\mathrm{P(OMe)_3}]^+$, 16.8; 330, $\mathrm{[Ru(C_2Ph)(POMe)(C_5H_5)]^+}$, 2.6; 291, $\mathrm{[Ru\{P(OMe)_3\}(C_5H_5)]^+}$, 17.2.

Preparation of $\mathit{Ru\{C_2Ph(CuCl)\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}$

A reaction between $\mathrm{RuCl\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}$ (100 mg, 0.22 mmol) and $\mathrm{CuC_2Ph}$ (40 mg, 0.27 mmol) in refluxing methanol over 16 h led to the precipitation of a fine yellow powder. Evaporation to dryness and crystallization of the residue from acetone/light petroleum afforded light yellow microcrystals of $\mathrm{Ru\{C_2Ph(CuCl)\}}$-

$\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (**11**) (123 mg, 91%), m.p. 138°C. Found: C, 37.33; H, 4.64%; *M* (mass spectrometry), 614. $C_{19}H_{28}O_6ClCuP_2Ru$ calcd.: C, 37.14; H, 4.60%; *M*, 614. IR (nujol): $\nu(C{\equiv}C)$ 1998w, 1954s cm^{-1}; other bands at 1599s, 1488s, 1425(sh), 1181s, 1068s, 1057(sh), 1020s, 849m, 838m, 808s, 769s, 765s, 755(sh), 732s, 698s, 626m cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.64 (t, $J(HP)^\star$ 12.0 Hz, 18H, OMe), 5.18 (t, $J(HP)$ 0.98 Hz, 5H, C_5H_5), 7.21 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ 52.14 (s, OMe), 84.04 (s, C_5H_5), 125.90, 128.09, 130.57 (3 × s, Ph). FAB MS: 1192, ?, 8.3; 1096, $[\{Ru(C_2Ph)[P(OMe)_3]_2(C_5H_5)\}_2Cu]^+$, 5.8; 614, $[M]^+$, 37.5; 599, $[M-Me]^+$, 1; 579, $[M-Cl]^+$, 20.8; 564, $[M-Me-Cl]^+$, 2.5; 516, $[M-CuCl]^+$, 100; 486, $[M-CuCl-OMe]^+$, 8.3; 415, $[M-CuCl-C_2Ph]^+$, 16.7.

Preparation of $[\{(\eta\text{-}C_5H_5)Ru\{P(OMe)_3\}_2(C_2Ph)\}_2Cu][PF_6]$

A solution of $Ru(C_2Ph)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (100 mg, 0.22 mmol) and $[Cu(NCMe)_4][PF_6]$ (41 mg, 0.11 mmol) in CH_2Cl_2 (20 ml) was stirred for 4.5 h. The solvent was removed and the residue was extracted with diethyl ether; the residual yellow oil was crystallised from MeOH to give white microcrystals of $[\{(\eta\text{-}C_5H_5)Ru\{P(OMe)_3\}_2(C_2Ph)\}_2Cu][PF_6]$ (**12**) (78 mg, 57%), m.p. 154°C (dec). Found: C, 36.27; H, 4.42%; *M* (mass spectrometry), 1095. $C_{26}H_{28}CuF_6O_{12}P_5Ru$ calcd.: C, 36.82; H, 4.56%; *M*, 1095. IR (nujol): $\nu(C{\equiv}C)$ 1992m, 1948s; $\nu(CO)$ 1128m, $\nu(PO)$ 1047s(br), $\nu(PF)$ 843s; other bands at 1595s, 790m, 772m, 723s, 698m cm^{-1}. ^1H NMR: δ ($CDCl_3$) 3.61 (t, $J(HP)^\star$ 5.7 Hz, 36H, OMe), 5.80 (s, 10H, C_5H_5), 7.29 (m, 10H, Ph). FAB MS: 1095, $[M]^+$, 92; 971, $[M-P(OMe)_3]^+$, 4; 940, $[M-OMe-P(OMe)_3]^+$, 1; 907, $[M-P(OMe)_3-Cu]^+$, 1; 847, $[M-2P(OMe)_3]^+$, 1; 723, $[M-3P(OMe)_3]^+$, 19; 599, $[M-4P(OMe)_3]^+$, 25; 579, $[CuRu(C_2Ph)\{P(OMe)_3\}_2(C_5H_5)]^+$, 69; 564, $[579-Me]^+$, 11; 516, $[Ru(C_2Ph)\{P(OMe)_3\}_2(C_5H_5)]^+$, 61; 455, $[Ru(C_2Ph)\{P(OMe)_3\}(C_5H_5)]^+$, 25; 415, $[Ru\{P(OMe)_3\}_2(C_5H_5)]^+$, 19; 377, ?, 19; 291, $[Ru\{P(OMe)_3\}(C_5H_5)]^+$, 17; 260, $[Ru\{P(OMe)_2\}(C_5H_5)]^+$, 22; 245, $[Ru\{PO(OMe)\}(C_5H_5)]^+$, 17; 167, $[Ru(C_5H_5)]^+$, 25.

A minor product from this reaction was best isolated from a reaction between equimolar amounts of $Ru(C_2Ph)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ and $[Cu(NCMe)_4]X$ ($X = PF_6$ or BF_4) in methanol for 30 min. Evaporation, extraction of the red oily residue with CH_2Cl_2, and crystallisation by addition of hexane to the extract, gave red needles of $[\{Ru\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C_4Ph_2)]X_2$ (**13a**, $X = PF_6$; **13b**, $X = BF_4$) in 3–5% yields, m.p. 194 and 157°C, respectively. For **13a**: Found: C, 34.14; H, 4.25%; $C_{38}H_{56}O_{12}F_{12}P_4Ru_2$ calcd.: C, 34.56; H, 4.27%. IR (nujol): $\nu(C{=}C)$ 1629s, $\nu(PF)$ 846s; other bands at 1597s, 1496m, 1180m, 1047s(br), 880(sh), 800s, 765m, 756m, 731s, 712m, 642m cm^{-1}. ^1H NMR: δ ($CDCl_3$) 3.66 (t, $J(HP)^\star$ 11.8 Hz, 36H, OMe), 5.99 (s, 10H, C_5H_5), 7.2–7.4 (m, 10H, Ph). ^{13}C NMR: δ ($(CD_3)_2CO$) 54.04 (s, OMe), 91.75 (s, C_5H_5), 126.9–138.9 (m, Ph), other carbons not seen. FAB MS ($Ru\{P(OMe)_3\}_2(C_5H_5) \equiv (Ru)$): 2496, $[(Ru)_4(C_8Ph_4)+3PF_6]^+$, 1; 1837, $[(Ru)_3(C_6Ph_3)+2PF_6]^+$, < 1; 1321, $[(Ru)_2(C_4Ph_2)+2PF_6]^+$, 1; 1177, $[(Ru)_2(C_4Ph_2)+2PF_6]^+$, 11; 1047, $[(Ru)_2(CPh_2)+O?]^+$, 2; 1031, $[(Ru)_2(C_4Ph_2)]^+ \equiv [M]^+$, 2; 1016, $[M-Me]^+$, 3; 766, $[M-C_4Ph_2-2OMe]^+$, 1; 657, $[(Ru)(C_2Ph)+PF_6]^+$, 1; 616, $[M-(Ru)]^+$, 25; 516, $[(Ru)(C_2Ph)]^+$, 41; 443, $[(Ru)+CO]^+$, 4; 414, $[(Ru)]^+$, 100; 291, $[Ru\{P(OMe)\}-(C_5H_5)]^+$, 49. For **13b**: IR (nujol) $\nu(C{=}C)$ 1630m; $\nu(BF)$ 1045s(br); other bands at 1595m, 808m, 799m, 722s, 694m cm^{-1}. FAB MS: 2322, $[(Ru)_4(C_8Ph_4)+3BF_4]^+$, < 1; 1720, $[(Ru)_3(C_6Ph_3)+2BF_4]^+$, < 1; 1205, $[(Ru)_2(C_4Ph_2)+2BF_4]^+$, 1; 1117, $[(Ru)_2(C_4Ph_2)+BF_4]^+$, 14; 1047, $[(Ru)_2(C_4Ph_2)$

+ O?]$^+$, 2; 1031, [(Ru)$_2$(C$_4$Ph$_2$)]$^+$, 3; 1015, [(Ru)$_2$(C$_2$Ph) + BF$_4$]$^+$, 10; 766, [M − C$_4$Ph$_2$ − 20Me]$^+$, 2; 616, [(Ru)(C$_4$Ph$_2$)]$^+$, 18; 603, [(Ru)C$_2$Ph + BF$_4$]$^+$, 14; 516, [(Ru)(C$_2$Ph)]$^+$, 91; 433, [(Ru) + CO]$^+$, 32; 414, [(Ru)]$^+$, 100; 291, [Ru{P(OMe)$_3$}(C$_5$H$_5$)]$^+$, 48.

Reactions of Ru(C$_2$Ph){P(OMe)$_3$}$_2$(η-C$_5$H$_5$)

(a) HBF$_4$. A solution of Ru(C$_2$Ph){P(OMe)$_3$}$_2$(η-C$_5$H$_5$) (150 mg, 0.29 mmol) in CH$_2$Cl$_2$ (20 ml) was treated with HBF$_4$ · OEt$_2$ (117 mg, 0.87 mmol). The resulting pink solution was reduced and filtered into an excess of diethyl ether (50 ml) to give a fine orange powder, [Ru(C=CHPh){P(OMe)$_3$}$_2$(η-C$_5$H$_5$)][BF$_4$] (**14**) (140 mg, 80%), m.p. 97–99 °C. Found: C, 34.49; H, 4.61%; M (mass spectrometry), 517. C$_{19}$H$_{29}$O$_6$BF$_4$Ru calcd.: C, 37.82; H, 4.85%; M, 517. IR (nujol): ν(C=C) 1671s, 1636m; ν(BF) 1065s cm^{-1}; other bands at 1599s, 1578s, 1497m, 1429(sh), 1422(sh), 1181s, 1065s, 1030s(br), 837m, 823s, 792s, 778s, 763s, 741s, 702m cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 3.70 (t, J(HP)* 12.2 Hz, 18H, OMe), 5.69 (s, 5H, C$_5$H$_5$), 5.93 (t, J(HP) 4.6 Hz, 1H, =CH), 7.14 (m, 5H, Ph). ^{13}C NMR (CDCl$_3$): δ 53.75 (d, J(CP) 4.2 Hz, OMe), 91.36 (d, J(CP) 6.3 Hz, C$_5$H$_5$), 117.73 (s, =C), 126.32, 126.95, 128.94 (3 × s, Ph). FAB MS: 517, [M]$^+$, 66.7; 415, [M − C=CHPh]$^+$, 100; a peak at m/z 1120 was present in spectra obtained at the end of a run.

(b) [Me$_3$O][SbCl$_6$]. Addition of [Me$_3$O][SbCl$_6$] (54 mg, 0.14 mmol) to a solution of Ru(C$_2$Ph){P(OMe)$_3$}$_2$(η-C$_5$H$_5$) (70 mg, 0.14 mmol) in CH$_2$Cl$_2$ (15 ml) resulted in the momentary formation of a red solution, which immediately changed to a solution exhibiting red/blue dichroism. Addition of a reduced volume to an excess of diethyl ether gave an oil which was identified as a mixture of the methylvinylidene [Ru(C=CMePh){P(OMe)$_3$}$_2$(η-C$_5$H$_5$)][SbCl$_6$] (**16**) and the chlorovinylidene, [Ru(C=CClPh){P(OMe)$_3$}$_2$(η-C$_5$H$_5$)][SbCl$_6$] (**17**). Found: M (mass spectroscopy), 531, 551 (major). [C$_{20}$H$_{31}$O$_6$P$_2$Ru]$^+$ requires M, 531; [C$_{19}$H$_{28}$O$_6$ClP$_2$Ru]$^+$ requires M, 551. IR (CH$_2$Cl$_2$): ν(C=C) 1167m, 1648 cm^{-1}; other bands at 3055m, 2799w, 2662w, 1735w, 1598m, 1491m, 1452s, 1255s, 1180s, 1112(sh), 1045s(br), 911m, 862m, 758m, 720w, 703w, 691w, 658(sh), 651s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.18 (s, 3H, Me), 3.69 (m, 36H, OMe), 5.69, 5.82 (2 × s, 10H, C$_5$H$_5$), 7.31 (m, 10H, Ph).

(c) C$_2$(CN)$_4$ in diethyl ether. A solution of TCNE (12 mg, 0.10 mmol) in diethyl ether (5 ml) was added to a solution of Ru(C$_2$Ph){P(OMe)$_3$}$_2$(η-C$_5$H$_5$) (50 mg, 0.10 mmol) in the same solvent (15 ml). The mixture was immediately placed in an ice-bath, and the solvent subsequently removed, to leave a white powder identified as $\overline{\mathrm{Ru\{C{=}C(Ph)C(CN)_2C}}\mathrm{(CN)_2\}}$ {P(OMe)$_3$}$_2$(η-C$_5$H$_5$) (**18**) (47 mg, 73%), m.p. 240–245 °C (dec). Found: C, 46.66; H, 4.39; N, 8.52%; M (mass spectrometry), 644. C$_{25}$H$_{28}$O$_6$P$_2$N$_4$Ru calcd.: C, 46.66; H, 4.39; N, 8.71%; M, 644. IR (nujol): ν(CN) 2249(sh), 2236w; ν(C=C) 1570w, 1551w, 1539w cm^{-1}; other bands: 1499(sh), 1445s, 1241m, 1180m, 1060s(br), 1006s, 992(sh), 820m, 786s, 768s, 715s, 700s, 678m, 666(sh), 650m cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 3.24 (t, J(HP)* 11.2 Hz, 18H, OMe), 4.73 (t, J(HP) 0.98 Hz, 5H, C$_5$H$_5$), 7.17 (m, 5H, Ph). FAB MS: 644, [M]$^+$, 21.7; 613, [M − OMe]$^+$, 17.4; 516, [M − C$_2$(CN)$_4$]$^+$, 100; 489, [M − OMe − P(OMe)$_3$]$^+$, 10.9; 415, [M − C$_2$Ph − C$_2$(CN)$_4$]$^+$, 26.1; 392, [M − P(OMe)$_3$ − C$_2$(CN)$_4$]$^+$, 5.2.

(d) C$_2$(CN)$_4$ in benzene. A solution of Ru(C$_2$Ph){P(OMe)$_3$}$_2$(η-C$_5$H$_5$) (100 mg, 0.19 mmol) and TCNE (29 mg, 0.22 mmol) in benzene (20 ml) was stirred for 16 h, yielding a yellow precipitate, which was recrystallized from CH$_2$Cl$_2$/light petroleum

to give yellow crystals of $Ru\{C[=C(CN)_2]C(Ph)=C(CN)_2\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)$ (**19**) (72 mg, 51%), m.p. 240–245 °C (dec). Found: C, 46.53; H, 4.39; N, 8.64%; *M* (mass spectrometry), 644. $C_{25}H_{28}O_6P_2N_4Ru$ calcd.: C, 46.66; H, 4.39; N, 8.71%; *M*, 644. IR (nujol): ν(CN) 2230(sh), 2222s, 2213s, 2206s; ν(C=C) 1580w, 1531s cm^{-1}; other bands at 1499m, 1445s, 1250m, 1180s, 1055s(br), 1025(sh), 1010(sh), 837m, 821m, 810m, 783s, 770s, 738m, 720s, 703s, 662m, 627m cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.59 (qn, *J*(HP)* 15.1, 6.8 Hz, 18H, OMe), 4.80 (t, *J*(HP) 0.97 Hz, 5H, C_5H_5), 7.53 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ 52.71 (t, *J*(CP) 0.21 Hz, OMe), 84.59 (s, C_5H_5), 72.69 (s, C(1)), 93.86 (t, *J*(CP) 5 Hz, C(4)), 113.89, 113.83, 114.61, 117.75 (4 × s, CN), 127.97, 129.31, 131.46, 131.85 (m, Ph), 181.81 (s, C(2)). FAB MS: 644, $[M]^+$, 88.9; 630, $[M-N]^+$?, 2.3; 613, $[M-OMe]^+$, 100; 599, $[M-N-OMe]^+$?, 1.0; 582, $[M-2OMe]^+$, 2.3; 567, $[M-Ph]^+$, 1.0; 536, $[M-OMe-Ph]^+$, < 1; 520, $[M-P(OMe)_3]^+$, 22.2; 505, $[M-Ph-2OMe]^+$, 3.4; 489, $[M-OMe-P(OMe)_3]^+$, 11.1; 415, $[Ru\{P(OMe)_3\}_2(C_5H_5)]^+$, 44.4. Partial evaporation of the supernatant solution from the above, and addition of light petroleum yielded an orange powder (44 mg, 31%), which was identified as **19** from its R_f, IR and FAB mass spectra. These products were found to undergo interconversion readily, the equilibrium favouring the yellow product. Slow recrystallization of the product mixture from CH_2Cl_2/hexane gave a mixture of red-orange and yellow crystals in the ratio of approximately 3/1. These were hand-separated for the X-ray crystallographic study.

Preparation of $[Ru\{C(OMe)(CH_2Ph)\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$

A solution of $[Ru(C=CHPh)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ (100 mg, 0.15 mmol) in methanol (20 ml) was heated to reflux point. The resulting pale yellow solution was evaporated to dryness. The residue was extracted with CH_2Cl_2 and crystallized by addition of light petroleum to yield pale yellow crystals of the methoxycarbene complex, $[Ru\{C(OMe)(CH_2Ph)\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ (**15**) (84 mg, 88%), m.p. 136 °C. Found: C, 36.68; H, 5.11%; *M* (mass spectrometry), 548. $C_{20}H_{33}O_7BF_4P_2Ru$ calcd.: C, 37.80; H, 5.25%; *M* 548. IR (nujol): ν(C–OMe) 1291s; ν(BF) 1060s(br) cm^{-1}; other bands at 1499m, 1302s, 1260m, 1180m, 1137m, 1100(sh), 1050s(br), 958(sh), 803(sh), 788s, 776s, 765s, 735s, 701m cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.65 (t, *J*(HP)* 12.0 Hz, 18H, POMe), 4.10 (s, 3H, COMe), 4.70 (s, 2H, CH_2), 5.27 (s, 5H, C_5H_5), 7.22 (m, 5H, Ph). FAB MS: 548, $[M]^+$, 100; 533, $[M-Me]^+$, 2.6; 518, $[M-OMe]^+$, 1.3; 442, $[M-Me-CH_2Ph]^+$, 34.6; 415, $[Ru\{P(OMe)_3\}_2(C_5H_5)]^+$, 15.4.

Crystallography

Intensity data for the three complexes were measured at room temperature on an Enraf-Nonius CAD 4F diffractometer fitted with Cu-K_α (nickel filter) radiation, $\lambda = 1.5418$ Å, for **1**, and Mo-K_α (graphite monochromator), $\lambda = 0.7107$ Å, for (**19R**) and (**19R**), with the use of the $\omega/2\theta$ scan technique. No significant decomposition of any of the crystals occurred during their respective data collections. Routine corrections were applied for Lorentz and polarization effects [26] and for absorption (analytical procedure) [26]. Relevant data collection parameters are listed in Table 3.

The structures were solved by conventional heavy-atom techniques and refined by a full-matrix least-squares procedure in each case [26]. Non-hydrogen atoms were refined with anisotropic thermal parameters except for phenyl ring carbons which were refined as hexagonal rigid groups with individual isotropic thermal parameters.

Table 3

Crystal data and refinement details for complex (**1**) and the yellow and red forms of complex (**19**)

Complex	**1**	**19** Y	**19** R
Formula	$C_{11}H_{23}ClO_6P_2Ru$	$C_{25}H_{28}N_4O_6P_2Ru$	$C_{25}H_{28}N_4O_6P_2Ru$
MW	449.8	643.5	643.5
Crystal system	orthorhombic	triclinic	orthorhombic
Space group	$Pna2_1$ (C^9_{2v}, No. 33)	$P\bar{1}$ (C^1_i, No. 2)	$Pbca$ (D^{15}_{2h}, No. 61)
a, Å	9.606(3)	9.496(6)	14.501(5)
b, Å	14.167(4)	10.436(6)	15.047(2)
c, Å	12.891(4)	15.216(2)	26.658(4)
α, deg	90	90.74(2)	90
β, deg	90	90.22(3)	90
γ, deg	90	111.47(4)	90
U, Å^3	1754.3	1403.1	5816.7
D_c, g cm^{-3}	1.703	1.523	1.470
$F(000)$	912	868	2624
μ, cm^{-1}	106.04	8.03	6.44
Transmission factors (max/min)	0.2404–0.0324	0.9028–0.7950	0.9208–0.7746
θ limits, deg	1.5–60	1–22.5	1–22.5
No of data collected	2137	3781	7442
No of unique data	1501	3675	3804
No of data with $I \geqslant 2.5\sigma(I)$	1419	2980	1661
R	0.051	0.037	0.033
g	0.017	0.003	0.004
R_w	0.050	0.041	0.035
ρ_{max}, e Å^{-3}	0.96	0.62	0.50

Table 4

Fractional atomic coordinates ($\times 10^5$ for Ru; $\times 10^4$ for others) for (**1**)

Atom	x	y	z
Ru	19163(6)	5775(3)	00000(–)
P(1)	1667(2)	–990(1)	–49(3)
P(2)	3751(3)	450(2)	1010(2)
Cl	285(3)	714(2)	1395(3)
O(1)	533(7)	–1387(4)	–857(5)
C(1)	–850(14)	–1072(9)	–810(16)
O(2)	2949(7)	–1639(5)	–434(8)
C(2)	3876(12)	–1405(8)	–1215(10)
O(3)	1288(7)	–1481(5)	1003(6)
C(3)	1084(17)	–2469(8)	1079(15)
O(4)	4124(9)	–470(6)	1678(6)
C(4)	3301(16)	–657(12)	2602(12)
O(5)	5159(7)	506(5)	325(7)
C(5)	6563(16)	502(11)	801(13)
O(6)	3980(10)	1196(6)	1898(9)
C(6)	3380(13)	2114(8)	1896(13)
C(7)	1301(12)	2011(7)	–677(10)
C(8)	615(11)	1323(8)	–1233(8)
C(9)	1541(17)	775(9)	–1756(11)
C(10)	2849(11)	1064(11)	–1524(13)
C(11)	2724(13)	1872(9)	–839(12)

Hydrogen atoms were included in the models at their calculated positions. After the inclusion of a weighting scheme, $[\sigma^2(F)+g|F|^2]^{-1}$, the refinements were continued until convergence. The absolute configuration of **1** was determined on the basis of differences in Friedel pairs included in the data set. Final refinement details are listed in Table 3.

Scattering factors for neutral Ru (corrected for f' and f'') were from ref. 27 and values for the remaining atoms were those incorporated in SHELX [26]. Data solution and refinement were performed with the SHELX program system on the University of Adelaide's VAX11/785 computer system.

Table 5

Fractional atomic coordinates ($\times 10^5$ for Ru; $\times 10^4$ for others) for **19** Y

Atom	x	y	z
Ru	23160(4)	21163(3)	18496(2)
P(1)	1668(1)	1707(1)	3256(1)
P(2)	4265(1)	1442(1)	2089(1)
O(1)	904(4)	165(4)	3591(2)
O(2)	3001(4)	2250(4)	3955(2)
O(3)	489(4)	2379(4)	3565(2)
O(4)	4073(4)	219(3)	2757(3)
O(5)	5770(4)	2536(3)	2480(3)
O(6)	4712(4)	901(4)	1190(3)
N(1)	2716(7)	6828(6)	4537(3)
N(2)	6147(6)	5204(6)	3996(3)
N(3)	6389(6)	7501(5)	1875(4)
N(4)	6155(6)	3924(5)	411(3)
C(1)	−393(10)	−847(8)	3215(5)
C(2)	3342(8)	1547(8)	4670(4)
C(3)	30(9)	2357(8)	4468(4)
C(4)	3215(10)	−1152(7)	2523(7)
C(5)	6791(7)	2342(6)	3097(5)
C(6)	6108(9)	693(10)	1054(6)
C(7)	7(6)	897(6)	1290(4)
C(8)	353(6)	2299(6)	1108(4)
C(9)	1605(6)	2718(6)	549(3)
C(10)	2068(6)	1626(6)	400(3)
C(11)	1077(7)	474(6)	874(4)
C(12)	3667(5)	4149(4)	2063(3)
C(13)	3054(5)	4969(4)	2663(3)
C(14)	3668(5)	5397(5)	3465(3)
C(15)	3120(6)	6194(6)	4055(3)
C(16)	5029(6)	5232(5)	3759(3)
C(17)	4923(5)	4908(5)	1634(3)
C(18)	5736(5)	6353(5)	1763(3)
C(19)	5586(6)	4319(5)	963(3)
C(20)	1777(3)	5326(3)	2302(2)
C(21)	519(3)	5252(3)	2799(2)
C(22)	−590(3)	5678(3)	2442(2)
C(23)	−441(3)	6178(3)	1588(2)
C(24)	818(3)	6252(3)	1091(2)
C(25)	1926(3)	5826(3)	1448(2)

Table 6

Fractional atomic coordinates ($\times 10^5$ for Ru; $\times 10^4$ for others) for **19 R**

Atom	*x*	*y*	*z*
Ru	−492(3)	23380(4)	15309(2)
P(1)	−571(1)	3584(1)	1176(1)
P(2)	326(2)	3130(2)	2212(1)
O(1)	−1517(3)	3860(4)	1430(2)
O(2)	89(4)	4413(3)	1218(3)
O(3)	−814(4)	3642(4)	586(2)
O(4)	−326(4)	3895(4)	2422(2)
O(5)	1268(4)	3665(5)	2192(2)
O(6)	412(5)	2474(4)	2686(2)
N(1)	2176(6)	3992(6)	−280(4)
N(2)	2617(6)	4576(6)	1240(3)
N(3)	3639(5)	2027(6)	1065(3)
N(4)	2074(5)	1325(6)	2361(3)
C(1)	−2011(7)	4666(7)	1349(4)
C(2)	74(8)	5212(7)	904(6)
C(3)	−1557(7)	3154(9)	368(4)
C(4)	−1247(7)	3704(9)	2618(4)
C(5)	1405(7)	4593(7)	2304(5)
C(6)	815(9)	2781(10)	3162(4)
C(7)	24(6)	856(5)	1413(4)
C(8)	−207(6)	1018(6)	1905(4)
C(9)	−1067(7)	1468(6)	1920(5)
C(10)	−1353(6)	1581(6)	1413(5)
C(11)	−681(7)	1206(6)	1093(4)
C(12)	1287(4)	2422(5)	1268(3)
C(13)	1418(4)	2729(5)	747(3)
C(14)	1836(5)	3495(5)	632(3)
C(15)	2005(7)	3783(6)	117(4)
C(16)	2239(6)	4083(6)	991(4)
C(17)	2050(4)	2075(5)	1491(3)
C(18)	2937(6)	2045(5)	1257(3)
C(19)	2037(5)	1663(6)	1983(4)
C(20)	1106(3)	2119(3)	342(2)
C(21)	574(3)	2433(3)	−56(2)
C(22)	316(3)	1860(3)	−443(2)
C(23)	592(3)	972(3)	−431(2)
C(24)	1125(3)	657(3)	−33(2)
C(25)	1382(3)	1231(3)	353(2)

Fractional atomic coordinates are listed in Tables 4–6 and the numbering schemes used are shown in Figs. 1 and 3. Listing of thermal parameters, hydrogen atom parameters, and of the observed and calculated structure factors are available from the authors.

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