Reaction between [Ru₃(CO)₁₂] and the Tridentate Phosphine Ligand HC(PPh₂)₃; X-Ray Crystal Structures of Complexes [Ru₃(CO)₉{Ph₂PCHP(Ph)C₆H₄PPh}], [Ru₂H(CO)₄(Ph₂PCHPPh₂){PhPC₆H₄C(O)}], and [Ru₂(CO)₄Cl(PPh₂)(dppm)] †

Jennifer A. Clucas, Majorie M. Harding, Barry S. Nicholls, and Anthony K. Smith*
Department of Inorganic, Physical and Industrial Chemistry, Donnan Laboratories, University of Liverpool, Liverpool L69 3BX

From the reaction of [Ru₃(CO)₁₂] with HC(PPh₂)₃ the symmetrically capped product [Ru₃(CO)₉{HC(PPh₂)₃}] (1) has been isolated in low yield, together with five other complexes, [Ru₃(CO)₉{Ph₂PCHP(Ph)C₆H₄PPh}] (2), [Ru₂(CO)₅Ph{(Ph₂P)₂C(H)PPh}] (3), [Ru₂(CO)₄Cl(PPh₂)(dppm)] (4) (dppm = Ph₂PCH₂PPh₂), [Ru₂H(CO)₄(Ph₂PCHPPh₂)(PhPC₆H₄)] (5), and [Ru₂H(CO)₄(Ph₂PCHPPh₂){PhPC₆H₄C(O)}] (6). Complexes (1)—(6) have been characterised by i.r., ¹H, ³¹P, and ¹³C n.m.r. spectroscopy. In addition, the structures of complexes (2), (4), and (6) have been determined by single-crystal X-ray diffraction methods. In (2), the HC(PPh₂)₃ ligand has undergone a reaction of which the end result is an *ortho*-substitution of a phenyl ring of one phosphine moiety by the phosphorus atom of a second phosphine moiety, together with the loss of C₆H₆. The resulting Ph₂PC(H)P(Ph)C₆H₄P(Ph) ligand caps the Ru₃ triangle. In (4), the dppm, the PPh₂, and the chloride ligands all bridge the Ru–Ru bond. In (6), the Ph₂PCHPPh₂ ligand bridges the Ru–Ru bond, and the central carbon atom is also bonded to one of the Ru atoms to form a three-membered Ru–P–C ring. Also bridging the Ru–Ru bond is a hydride and a PhPC₆H₄C(O) ligand with which both Ru atoms form bonds to the phosphorus atom and one of the Ru atoms is also bonded to the acyl carbon to form a functional acyl ligand. Pathways to all these complexes are proposed.

The application of transition-metal clusters in catalysis is somewhat restricted by the lack of stability of the metal-atom framework under the conditions required for many catalytic reactions to take place. Many clusters fragment to mononuclear species, for example, under high carbon monoxide pressure,[1] and although there is a large and increasing number of reports of reactions catalysed by clusters,[2] there is in most cases no evidence that the nuclearity of the cluster is maintained throughout the reaction cycle.

To help prevent cluster fragmentation during catalysis, several groups have investigated the use of bridging or capping ligands, and have shown that such ligands increase the stability of the metal-atom framework.[3–8] In particular, the use of tridentate phosphine ligands, capable of co-ordinating to three different metal centres in a cluster complex, has been shown to render the cluster more resistant to fragmentation than the parent compounds. Thus, for example, [Ru₃(CO)₉{SiMe(PBu₂)₃}] is more resistant to dissociation into monomeric species than [Ru₃(CO)₁₂] under CO–H₂ pressure (30 atm, ca. 3 × 10⁶ Pa) at 300 °C.[3] The clusters [M₄(CO)₉{HC(PPh₂)₃}] (M = Co or Rh) are stable at 100 °C under CO (30 atm),[4] whereas the parent carbonyls [M₄(CO)₁₂] are unstable under these conditions.[1,9]

As part of our investigations into the stabilisation of transition-metal cluster complexes with multidentate phosphine

ligands,[10–15] we have carried out a detailed study of the reaction between [Ru₃(CO)₁₂] and HC(PPh₂)₃. A preliminary account of part of this work has been published.[16]

Results and Discussion

The reaction of a tetrahydrofuran solution of [Ru₃(CO)₁₂] with an equimolar quantity of HC(PPh₂)₃ proceeds slowly at 50 °C and gives rise to many products, none of which appears to be particularly favoured, the yield of each product being less than 10%. Reaction at higher temperature (refluxing benzene) leads to an increase in the number of products obtained, and no symmetrically capped product could be isolated. All attempts to reduce the number of products of this reaction, for example by irradiating the reaction mixture rather than using thermal activation, or by adding trimethylamine oxide or sodium diphenylketyl to the reaction mixture, have failed. Chromatography on a Florisil column of the products obtained from the reaction in tetrahydrofuran led to the isolation of six complexes, identified spectroscopically (see below) as [Ru₃(CO)₉{μ₃-HC(PPh₂)₃}] (1), [Ru₃(CO)₉{Ph₂PCHP(Ph)C₆H₄PPh}] (2), [Ru₂(CO)₅Ph{(Ph₂P)₂C(H)PPh}] (3), [Ru₂(CO)₄Cl(PPh₂)-(dppm)] (4) (dppm = Ph₂PCH₂PPh₂), [Ru₂H(CO)₄(Ph₂-PCHPPh₂)(PhPC₆H₄)] (5), and [Ru₂H(CO)₄(Ph₂PCHPPh₂)-{PhPC₆H₄C(O)}] (6). Proposed structures for (1) and (3)—(5) are shown in the Scheme which also gives possible pathways (discussed later) by which (1)—(6) are formed. For complexes (2), (4), and (6) the proposed structures have been confirmed by X-ray diffraction studies. Details of the i.r. spectra of these complexes are given in Table 1, ³¹P and ¹H n.m.r. spectroscopic data in Table 2.

Complex (1) is identified as the symmetrically capped product [Ru₃(CO)₉{μ₃-HC(PPh₂)₃}] by the marked similarity of its i.r. spectrum with that of the crystallographically characterised complexes [Ru₃(CO)₉{SiMe(PBu₂)₃}] [ν(CO) 2 035s, 1 985s, 1 948w, 1 925s, 1 842m, and 1 800s cm⁻¹][3] and (2), and due to

[Ru₃(CO)₁₂] + HC(PPh₂)₃

Scheme. Possible reaction pathways (assuming P co-ordination to an unsubstituted Ru atom when possible). (*i*) Initial axial co-ordination; (*ii*) initial equatorial co-ordination; (*iii*) second axial co-ordination; (*iv*) second equatorial co-ordination; (*v*) third axial co-ordination; (*vi*) third equatorial co-ordination; (*vii*) −Ru(CO)₄; (*viii*) P–CH bond cleavage and *ortho*-metallation; (*ix*) CH₂Cl₂; (*x*) P–Ph bond cleavage

Table 1. Infrared data (measured in CH_2Cl_2)

Complex	$\tilde{v}(CO)/cm^{-1}$
(1) $[Ru_3(CO)_9\{HC(PPh_2)_3\}]$	2 085vw, 2 048vs, 2 005s, 1 961m, 1 940s, 1 842 (sh), 1 798s
(2) $[Ru_3(CO)_9\{Ph_2PCHP(Ph)C_6H_4PPh\}]$	2 073vw, 2 052vs, 2 002s, 1 960m, 1 941s, 1 852 (sh), 1 807s
(3) $[Ru_2(CO)_5Ph\{(Ph_2P)_2C(H)PPh\}]$	2 061s, 1 992vs, 1 942m,br, 1 828w,br
(4) $[Ru_2(CO)_4Cl(PPh_2)(dppm)]$	2 007m, 1 985s, 1 940s
(5) $[Ru_2H(CO)_4(Ph_2PCHPPh_2)(PhPC_6H_4)]$	2 079s, 2 020s, 2 008vs, 1 995 (sh), 1 962m
(6) $[Ru_2H(CO)_4(Ph_2PCHPPh_2)\{PhPC_6H_4C(O)\}]$	2 035m, 2 020s, 1 970s, 1 603s, 1 568m

vs = Very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, and br = broad.

Table 2. $^{31}P-\{^1H\}$ and ^1H n.m.r. spectroscopic data

Complex	$\delta(^{31}P-\{^1H\})^a$	$\delta(^1H)^b$
(1)	46.92 (s)	6.11 [q, CH, J(PH) 7.8]
(2)	48.8 [d, PPh, J(PP) 84], 37.1 (t, PPh₂)	5.05 [dt, CH, J(PH) 9.6, J(P′H) 7.3]
(3)	136.6 [t, PPh, J(PP) 151], 9.15 (d, PPh₂)	3.7 [q, CH, J(PH) = J(P′H) = 8]
(4)	163.0 [t, PPh₂, J(PP) 187], 29.0 (d, dppm)	3.3 (m, CH₂)
(5)	124.6 [dd, PPh, J(PP′) 109, J(PP″) 12.2],	−13.6 (m, Ru–H)
	23.9 [dd, PPh₂, J(P″P) 12.2, J(P″P′) 4.9],	
	12.4 [dd, P′Ph₂–Ru]	
(6)	136.8 [dd, PPh, J(PP′) 119.6, J(PP″) 7.3],	−13.6 (m, Ru–H), 1.55 [dd, CH,
	24.5 [d, PPh₂, J(P″P) 7.3, J(P″P′) 0],	J(PH) 5.2, J(P′H) 7.0]
	13.1 [d, PPh₂–Ru]	

^{a} Measured in CH_2Cl_2–CD_2Cl_2 or $CDCl_3$; chemical shifts, δ/p.p.m., are relative to 85% H_3PO_4 (external). Coupling constants, J/Hz. s = Singlet, d = doublet, t = triplet, and dd = doublet of doublets. ^{b} Measured in CD_2Cl_2 or $CDCl_3$. q = Quartet, dt = doublet of triplets, and m = multiplet.

(2)

(4)

(6)
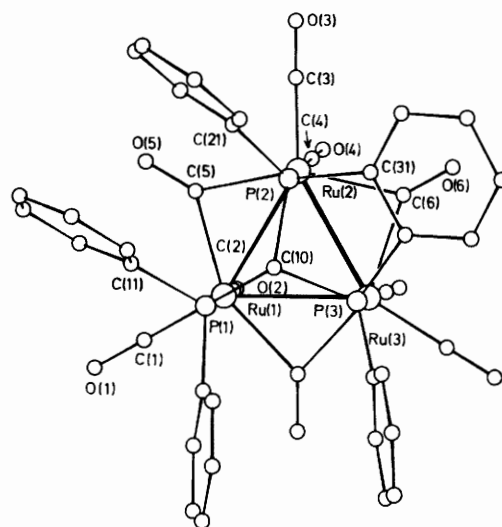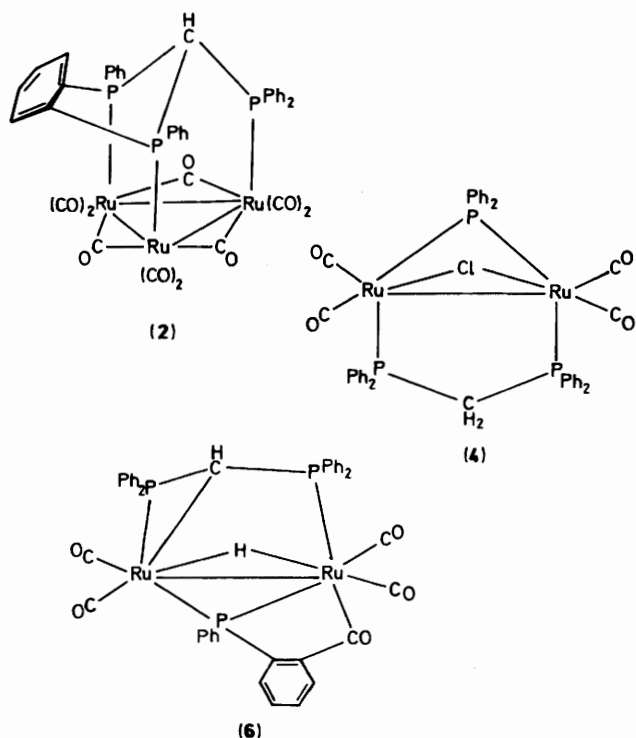
Figure 1. Molecular structure of $[Ru_3(CO)_9\{Ph_2PCHP(Ph)C_6H_4-PPh\}]$ (2). Hydrogen atoms have been omitted

the fact that its ^{31}P n.m.r. spectrum shows all three P atoms to be equivalent. This is substantiated by the ^1H n.m.r. spectrum in which the methine-proton resonance appears as a quartet due to coupling to three equivalent P atoms.

The i.r. spectrum of complex (2) is very similar to that of (1), but the ^{31}P n.m.r. spectrum indicates the presence of one unique and two equivalent P atoms, and the ^1H n.m.r. spectrum shows a triplet of doublets for the methine proton, again indicating non-equivalent P atoms. Since a complete structural character-

isation using spectroscopic methods was not possible, the structure of (2) was determined by X-ray diffraction methods.

The structure is shown in Figure 1 (all H atoms have been omitted), selected bond lengths and angles in Table 3, and atom co-ordinates in Table 4. The essential features are a triangular array of Ru atoms capped by a tridentate phosphine ligand in which two P atoms are equivalent and the third P atom, P(1), unique, as expected from the spectroscopic data. In addition, there are six terminal and three bridging CO groups. P(1) has undergone no change from the parent ligand $HC(PPh_2)_3$. However, P(2) and P(3), in addition to being linked by the methine carbon C(10), are linked *via* C(31) and C(36), to form an *ortho*-disubstituted benzene ring. This has been achieved by the overall loss of benzene from the parent ligand. The *ortho*-

disubstituted benzene introduces some distortion from three-fold symmetry in the ligand; the angles at C(10) are different [P(2)–C(10)–P(3) 96.0(6), P(1)–C(10)–P(2) 110.9(5)°], as are the distances Ru(1)–P(1) and Ru(2)–P(2) [2.407(3) and 2.365(2) Å, respectively]. In turn, the distances Ru(1)–Ru(2) and Ru(2)–Ru(3) differ significantly [2.903(1) and 2.878(1) Å, respectively] and there is slight asymmetry (only possibly significant) in the bridging carbonyl groups that do not lie across the mirror plane [Ru(1)–C(5) 2.146(10), Ru(2)–C(5) 2.103(9) Å]. The ^{13}C n.m.r. spectrum of complex (2) shows only three resonances at room temperature (at δ 199.3, 198.4, and 198.9 p.p.m.) indicating that the molecule is fluxional, but a limiting spectrum is obtained at −71 °C. This shows two resonances due to bridging CO groups at 257.2 [2 CO, J(PC) = 3.4 Hz] and 250.9 p.p.m. [1 CO, J(PC) = 6.8 Hz], and a complex set of resonances between 201.4 and 198.0 p.p.m. due to the six terminal CO groups. The methine carbon gives rise to a doublet of triplets at 69.9 p.p.m. [J(PC) = 7, J(P'C) = 23 Hz].

Complex (3) is tentatively assigned the structure shown in the Scheme, on the basis of i.r. and n.m.r. spectroscopic data. The i.r. spectrum (Table 1) shows only three v(CO) bands in the terminal CO region, and a weak band at 1 828 cm⁻¹ due to a bridging CO group. The ^{31}P n.m.r. spectrum shows a triplet (1P) at 136.57 p.p.m. and a doublet (2P) at 9.15 p.p.m. [J(PP) =

151 Hz]. The chemical shift of the triplet resonance is characteristic of a bridging phosphido-group [see complex (6) below], while the doublet resonance at 9.15 p.p.m. is indicative of co-ordinated phosphine groups. The assignment that all three P atoms remain bonded to the methine carbon atom, in contrast to complexes (4) and (6), is based on the ^1H n.m.r. spectrum of (3) in which the resonance due to the methine hydrogen appears as a binomial quartet [δ 3.7, J(PH) = J(P'H) = 8 Hz]. Thus the phosphine ligand is identified as HC(PPh)(PPh₂)₂. The ^{13}C n.m.r. spectrum of (3) [in CD₂Cl₂ solution: δ 202.1 (s) at 25 °C; 236.7, 203.7, 203.1, 196.9, and 187.9 p.p.m. at −123 °C] shows that the molecule is fluxional in solution, but that the fluxional behaviour is frozen out at −123 °C revealing the presence of one bridging CO ligand (236.7 p.p.m.) and four terminal CO ligands. Such a spectrum is consistent with the formulation of (3) as a binuclear complex. Since the carbonyl and phosphine ligands as formulated contribute a total of only 17 electrons to the binuclear complex we looked closely for the presence of a hydride ligand which would supply the extra electron required in order for both Ru atoms to achieve an 18-electron configuration. We found no evidence for such a hydride ligand. However, the integration of the ^1H n.m.r. resonances of the phenyl-group protons in comparison with that of the CH proton is exactly in the ratio of 30:1. This leads us to suggest that the extra electron required in complex (3) is supplied by a bridging phenyl group as depicted in the Scheme. An edge-bridging phenyl group derived from fragmentation of the PPh₃ ligand on an Os₃ cluster has been previously observed.[17]

The remaining complexes, (4)—(6), isolated from the reaction mixture are all binuclear. The structure of (4) is shown in Figure 2 (all H atoms have been omitted), selected bond lengths and angles in Table 5, and atom co-ordinates in Table 6. The molecule contains two Ru atoms bridged by a diphenyl-phosphido-group, a dppm group, and a chloride. In addition there are two terminal CO ligands on each Ru atom. The diphenylphosphido-group and dppm are presumably derived from HC(PPh₂)₃ by cleavage of a P–C bond to give PPh₂ and HC(PPh₂)₂ and protonation of the central carbon atom on HC(PPh₂)₂ to give dppm. The only source of chloride in the reaction is the dichloromethane present as solvent of crystallisation in the solid HC(PPh₂)₃. However, the abstraction of Cl⁻ from dichloromethane is well known.

Complexes (5) and (6) are related in that (6) is derived from (5) by CO insertion into a Ru–C bond. Since complex (6) has

Table 3. Selected bond lengths (Å) and angles (°) for [Ru₃(CO)₉{Ph₂-PCHP(Ph)C₆H₄PPh}]·CHCl₃ (2)

Ru(1)–Ru(2)	2.903(1)	Ru(2)–C(3)	1.867(11)
Ru(2)–Ru(3)	2.878(1)	Ru(2)–C(4)	1.929(9)
Ru(1)–P(1)	2.407(3)	Ru(2)–C(6)	2.156(11)
Ru(2)–P(2)	2.365(2)	P(1)–C(10)	1.815(13)
Ru(1)–C(1)	1.841(15)	P(2)–C(10)	1.874(9)
Ru(1)–C(2)	1.869(15)	P(1)–C(11)	1.841(7)
Ru(1)–C(5)	2.146(10)	P(2)–C(21)	1.802(7)
Ru(2)–C(5)	2.103(9)	P(2)–C(31)	1.814(9)
Ru(2)–Ru(1)–Ru(3)	59.4(1)	Ru(1)–P(1)–C(10)	110.6(4)
P(1)–Ru(1)–Ru(2)	91.4(1)	Ru(1)–P(1)–C(11)	118.0(2)
P(1)–Ru(1)–C(1)	89.7(5)	Ru(2)–P(2)–C(10)	112.2(4)
P(1)–Ru(1)–C(2)	176.7(4)	Ru(2)–P(2)–C(31)	111.2(3)
P(1)–Ru(1)–C(5)	91.5(2)	P(1)–C(10)–P(2)	110.9(5)
P(2)–Ru(2)–Ru(1)	91.8(1)	P(2)–C(10)–P(3)	96.0(6)
P(2)–Ru(2)–C(3)	86.2(3)	Ru(1)–C(5)–Ru(2)	86.2(3)
P(2)–Ru(2)–C(4)	174.8(3)	Ru(2)–C(6)–Ru(3)	83.7(5)
P(2)–Ru(2)–C(6)	89.1(4)		

Table 4. Atom co-ordinates (× 10⁴) for complex (2)

Atom	x	y	z	Atom	x	y	z
Ru(1)	−915(1)	250	−44(1)	C(12)	−3 285(3)	1 338(4)	1 224(3)
Ru(2)	−87(1)	1 528(1)	1 181(1)	C(13)	−3 758(3)	578(4)	1 156(3)
C(1)	−1 500(8)	250	−952(9)	C(14)	−3 677(3)	0(4)	511(3)
O(1)	−1 828(7)	250	−1 545(7)	C(15)	−3 124(3)	182(4)	−66(3)
C(2)	−45(9)	250	−697(8)	C(16)	−2 651(3)	941(4)	1(3)
O(2)	473(7)	250	−1 131(7)	C(21)	−1 744(4)	560(4)	2 205(4)
C(3)	155(6)	426(7)	1 656(6)	C(22)	−2 260(4)	542(4)	2 837(4)
O(3)	318(4)	−243(5)	1 944(5)	C(23)	−2 726(4)	−214(4)	2 960(4)
C(4)	856(5)	1 477(6)	575(5)	C(24)	−2 676(4)	−952(4)	2 451(4)
O(4)	1 422(4)	1 444(5)	256(4)	C(25)	−2 159(4)	−934(4)	1 819(4)
C(5)	−725(5)	1 094(7)	195(5)	C(26)	−1 693(4)	−178(4)	1 696(4)
O(5)	−870(5)	422(5)	−128(4)	C(31)	−926(5)	2 021(6)	2 987(5)
C(6)	474(8)	250	1 937(9)	C(32)	−678(5)	1 537(8)	3 649(5)
O(6)	875(6)	250	2 466(6)	C(33)	−466(6)	2 027(8)	4 333(6)
P(1)	−2 082(2)	250	731(2)	C(50)	3 817(13)	250	1 602(17)
P(2)	−1 174(1)	1 559(2)	2 027(1)	Cl(1)	3 195(6)	250	810(7)
C(10)	−1 856(8)	250	1 777(7)	Cl(2)	4 364(4)	1 540(5)	1 518(4)
C(11)	−2 731(3)	1 519(4)	647(3)				

been characterised both spectroscopically and crystallographically, it is convenient to describe this complex before (5) which has been characterised by a comparison of spectroscopic data with (6).

The structure of complex (6) is shown in Figure 3, selected bond lengths and angles in Table 7, and atom co-ordinates in Table 8. It is a remarkable complex with three-, four-, and five-membered metallacycles containing Ru, P, and C atoms. Thus there are $\overline{\text{Ru-C-P}}$, $\overline{\text{Ru-P-C-Ru}}$, and $\overline{\text{Ru-C-C-C-P}}$ units. It is probable that complex (6) is formed by cleavage of a P–C bond in HC(PPh$_2$)$_3$, in a similar way to that postulated for

(4), but that instead of being protonated the central carbon atom co-ordinates to a Ru atom to form $\overline{\text{Ru-C-P}}$ and $\overline{\text{Ru-P-C-Ru}}$ rings. Similar behaviour has been observed previously with the iron complex [Fe$_2$(CO)$_7$(dppm)] which reacts with LiMe to form [(OC)$_3$Fe(μ-Ph$_2$PCHPPh$_2$)-FeH(CO)$_3$].[18] The bridging diphenylphosphido-group formed by P–C bond cleavage in HC(PPh$_2$)$_3$ undergoes further reaction with the ruthenium centre. Ortho-metallation of one of the phenyl rings occurs to give complex (5) (see below), followed by carbonyl-ligand insertion into the Ru–C bond to give the acyl derivative. The acyl-carbon atom in complex (6) gives rise to a resonance at δ 251.1 p.p.m. [dd, J(CP) 78, J(CP') 7.6 Hz] in the ^{13}C n.m.r. spectrum, and is further characterised by stretching frequencies at 1 603 and 1 568 cm^{-1}. The structural details of this acyl group are worthy of comment since only
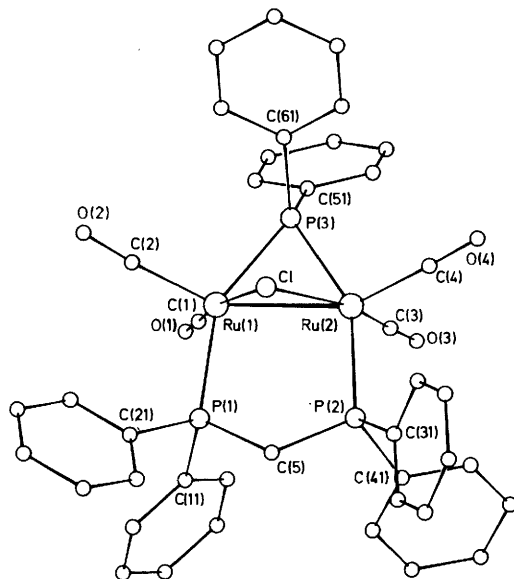

Figure 2. Molecular structure of [Ru$_2$(CO)$_4$Cl(PPh$_2$)(dppm)] (4). Hydrogen atoms have been omitted

Table 5. Selected bond lengths (Å) and angles (°) for [Ru$_2$(CO)$_4$-Cl(PPh$_2$)(dppm)] (4)

Ru(1)–Ru(2)	2.730(1)	Ru(2)–C(4)	1.885(6)
Ru(1)–P(1)	2.380(1)	P(1)–C(5)	1.856(5)
Ru(2)–P(2)	2.365(1)	P(2)–C(5)	1.839(5)
Ru(1)–P(3)	2.318(1)	P(1)–C(11)	1.841(4)
Ru(2)–P(3)	2.322(1)	P(1)–C(21)	1.840(4)
Ru(1)–Cl	2.474(1)	P(2)–C(31)	1.841(3)
Ru(2)–Cl	2.473(1)	P(2)–C(41)	1.829(4)
Ru(1)–C(1)	1.837(5)	P(3)–C(51)	1.829(3)
Ru(1)–C(2)	1.898(5)	P(3)–C(61)	1.842(5)
Ru(2)–C(3)	1.821(5)		

Ru(1)–Ru(2)–P(2)	95.9(1)	Ru(1)–Ru(2)–C(4)	151.2(2)
Ru(2)–Ru(1)–P(1)	94.6(1)	Ru(2)–Ru(1)–C(1)	110.9(2)
Ru(1)–Ru(2)–P(3)	53.9(1)	Ru(2)–Ru(1)–C(2)	148.2(2)
Ru(2)–Ru(1)–P(3)	54.0(1)	P(1)–Ru(1)–P(3)	148.3(1)
Ru(1)–Ru(2)–Cl	56.5(1)	P(2)–Ru(2)–P(3)	149.7(1)
Ru(2)–Ru(1)–Cl	56.5(1)	P(1)–Ru(1)–Cl	86.5(1)
Ru(1)–Ru(2)–C(3)	105.9(2)	P(2)–Ru(2)–Cl	85.6(1)

Table 6. Atom co-ordinates (× 10^4) for complex (4)

Atom	x	y	z	Atom	x	y	z
Ru(1)	2 020(1)	3 571(1)	1 314(1)	C(26)	2 813(5)	5 713(2)	2 834(3)
Ru(2)	2 046(1)	1 920(1)	2 005(1)	C(31)	2 671(3)	1 847(2)	4 912(3)
P(1)	1 402(1)	4 142(1)	2 852(1)	C(32)	2 361(3)	2 016(2)	5 897(3)
P(2)	1 519(1)	2 231(1)	3 669(1)	C(33)	3 247(3)	1 750(2)	6 846(3)
P(3)	2 349(1)	2 375(1)	348(1)	C(34)	4 444(3)	1 315(2)	6 810(3)
Cl	4 033(1)	2 959(1)	2 580(1)	C(35)	4 755(3)	1 146(2)	5 825(3)
C(1)	337(6)	3 794(3)	403(4)	C(36)	3 868(3)	1 412(2)	4 876(3)
O(1)	−703(5)	3 959(3)	−173(3)	C(41)	−169(4)	1 815(2)	3 846(3)
C(2)	2 958(6)	4 491(3)	777(4)	C(42)	−325(4)	925(2)	3 845(3)
O(2)	3 553(5)	5 010(3)	417(4)	C(43)	−1 608(4)	537(2)	3 883(3)
C(3)	308(6)	1 461(3)	1 433(4)	C(44)	−2 735(4)	1 039(2)	3 923(3)
O(3)	−787(5)	1 147(3)	1 061(4)	C(45)	−2 579(4)	1 929(2)	3 924(3)
C(4)	2 874(6)	848(4)	2 221(4)	C(46)	−1 296(4)	2 316(2)	3 885(3)
O(4)	3 353(6)	183(3)	2 284(4)	C(51)	1 129(4)	2 037(2)	−904(3)
C(5)	1 662(6)	3 382(3)	3 987(4)	C(52)	559(4)	2 637(2)	−1 672(3)
C(11)	−405(4)	4 478(2)	2 685(3)	C(53)	−354(4)	2 368(2)	−2 629(3)
C(12)	−704(4)	5 267(2)	3 066(3)	C(54)	−696(4)	1 500(2)	−2 818(3)
C(13)	−2 086(4)	5 503(2)	2 914(3)	C(55)	−126(4)	900(2)	−2 049(3)
C(14)	−3 168(4)	4 951(2)	2 379(3)	C(56)	786(4)	1 169(2)	−1 092(3)
C(15)	−2 870(4)	4 162(2)	1 998(3)	C(61)	4 048(4)	2 240(2)	19(3)
C(16)	−1 488(4)	3 925(2)	2 150(3)	C(62)	4 651(4)	1 442(2)	142(3)
C(21)	2 434(5)	5 085(2)	3 494(3)	C(63)	5 939(4)	1 336(2)	−105(3)
C(22)	2 871(5)	5 170(2)	4 607(3)	C(64)	6 624(4)	2 026(2)	−474(3)
C(23)	3 688(5)	5 883(2)	5 060(3)	C(65)	6 021(4)	2 824(2)	−597(3)
C(24)	4 067(5)	6 512(2)	4 399(3)	C(66)	4 733(4)	2 930(2)	−351(3)
C(25)	3 630(5)	6 427(2)	3 286(3)				

crystal structures of η^2-acylruthenium complexes of the type [Ru{C(R)O}I(CO)(PPh$_3$)$_2$] (R = Me or p-tolyl) have been reported.[19] The angle at the acyl-carbon atom [Ru(1)–C(5)–O(5) 124.1(4)°] and the long C–O bond length [C(5)–O(5) 1.215(7) Å] compared to that of the carbonyl ligands [mean C–O 1.132(9) Å] are as expected for an acyl ligand.

The identification of complex (5) is based on its very similar spectroscopic characteristics to (6). Thus, both (5) and (6) show
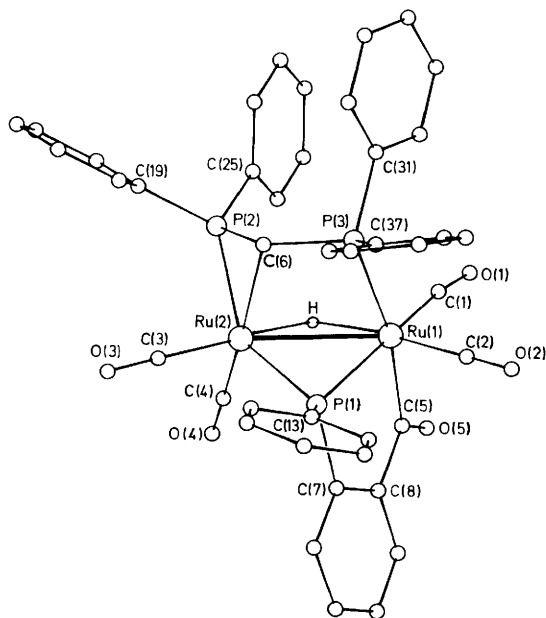
a hydride resonance at δ −13.6 in their ^{1}H n.m.r. spectra, while the ^{31}P n.m.r. spectral data (see Table 2) are also very similar. The i.r. spectrum of (5) shows no bands attributable to an acyl carbonyl group. We therefore assign the structure shown in the Scheme to (5), in which one of the phenyl groups of the μ-PPh$_2$ ligand is ortho-metallated directly to an Ru atom, but otherwise is identical to (6).

Figure 3. Molecular structure of [Ru$_2$H(CO)$_4$(Ph$_2$PCHPPh$_2$){PhPC$_6$-H$_4$C(O)}] (6). Phenyl-hydrogen atoms have been omitted

Table 7. Selected bond lengths (Å) and angles (°) for [Ru$_2$H(CO)$_4$-(Ph$_2$PCHPPh$_2$){PhPC$_6$H$_4$C(O)}] (6)

Ru(1)–Ru(2)	2.972(1)	C(2)–O(2)	1.133(8)
Ru(1)–P(1)	2.333(1)	C(3)–O(3)	1.136(10)
Ru(2)–P(1)	2.319(1)	C(4)–O(4)	1.123(9)
Ru(1)–P(3)	2.404(2)	C(5)–O(5)	1.215(7)
Ru(2)–P(2)	2.290(1)	P(2)–C(6)	1.771(6)
Ru(2)–C(6)	2.251(6)	P(3)–C(6)	1.805(6)
Ru(1)–H	1.80(9)	P(1)–C(7)	1.809(6)
Ru(2)–H	1.87(10)	P(1)–C(13)	1.819(5)
Ru(1)–C(1)	1.921(7)	P(2)–C(19)	1.822(4)
Ru(1)–C(2)	1.877(6)	P(2)–C(25)	1.801(4)
Ru(2)–C(3)	1.878(7)	P(3)–C(31)	1.830(4)
Ru(2)–C(4)	1.909(7)	P(3)–C(37)	1.830(4)
Ru(1)–C(5)	2.128(6)	C(5)–C(8)	1.511(8)
C(1)–O(1)	1.136(8)		

Ru(1)–Ru(2)–P(1)	50.5(1)	P(2)–Ru(2)–C(4)	118.5(2)
Ru(2)–Ru(1)–P(1)	50.1(1)	P(2)–Ru(2)–C(3)	94.2(2)
Ru(1)–P(3)–C(6)	103.8(2)	C(5)–Ru(1)–P(1)	81.2(2)
Ru(2)–P(2)–C(6)	65.9(2)	C(8)–C(5)–Ru(1)	117.8(4)
Ru(2)–C(6)–P(2)	68.2(2)	C(7)–P(1)–Ru(1)	103.5(2)
Ru(2)–C(6)–P(3)	105.1(3)	C(5)–Ru(1)–C(1)	86.3(3)
P(1)–Ru(2)–C(6)	94.1(1)	C(5)–Ru(1)–C(2)	90.7(2)
P(3)–Ru(1)–C(2)	97.1(2)	Ru(1)–C(5)–O(5)	124.1(4)
P(3)–Ru(1)–C(1)	101.2(2)	C(8)–C(5)–O(5)	118.0(5)
P(3)–Ru(1)–P(1)	89.6(1)	C(2)–Ru(1)–C(1)	95.9(3)
P(2)–Ru(2)–P(1)	138.3(1)	C(4)–Ru(2)–C(3)	92.7(3)
P(3)–C(6)–P(2)	123.3(3)		

Table 8. Atom co-ordinates (× 10^4) for complex (6)

Atom	x	y	z	Atom	x	y	z
Ru(1)	11(1)	7 652(1)	8 722(1)	C(17)	5 553(4)	6 150(3)	9 092(2)
Ru(2)	2 006(1)	7 963(1)	7 860(1)	C(18)	4 609(4)	6 684(3)	6 380(2)
P(1)	2 389(1)	7 678(1)	8 865(1)	C(19)	1 747(5)	7 113(2)	6 380(2)
P(2)	907(2)	7 437(1)	7 013(1)	C(20)	2 643(5)	6 494(2)	6 417(2)
P(3)	106(2)	6 525(1)	8 121(1)	C(21)	3 260(5)	6 270(2)	5 920(2)
C(1)	−1 870(7)	7 938(4)	8 549(3)	C(22)	2 981(5)	6 664(2)	5 384(2)
O(1)	−2 956(5)	8 164(3)	8 501(3)	C(23)	2 084(5)	7 283(2)	5 347(2)
C(2)	−200(6)	7 152(3)	9 440(3)	C(24)	1 467(5)	7 507(2)	5 845(2)
O(2)	−290(6)	6 832(3)	9 869(2)	C(25)	−847(4)	7 600(2)	6 729(2)
C(3)	3 746(7)	7 871(5)	7 604(3)	C(26)	−1 553(4)	7 072(2)	6 349(2)
O(3)	4 802(6)	7 841(4)	7 450(3)	C(27)	−2 895(4)	7 220(2)	6 116(2)
C(4)	2 138(7)	9 049(4)	7 914(3)	C(28)	−3 531(4)	7 895(2)	6 262(2)
O(4)	2 227(7)	9 688(3)	7 942(3)	C(29)	−2 825(4)	8 423(2)	6 641(2)
C(5)	278(6)	8 717(3)	9 174(2)	C(30)	−1 482(4)	8 275(2)	6 875(2)
O(5)	−608(5)	9 198(3)	9 180(2)	C(31)	−1 346(4)	6 071(3)	7 684(2)
C(6)	1 292(5)	6 776(3)	7 600(2)	C(32)	−1 113(4)	5 434(3)	7 339(2)
H	274(95)	8 200(55)	8 073(40)	C(33)	−2 202(4)	5 077(3)	7 002(2)
C(7)	2 760(6)	8 439(3)	9 399(2)	C(34)	−3 524(4)	5 356(3)	7 012(2)
C(8)	1 656(6)	8 882(3)	9 509(2)	C(35)	−3 757(4)	5 992(3)	7 357(2)
C(9)	1 837(7)	9 471(4)	9 927(3)	C(36)	−2 668(4)	6 350(3)	7 694(2)
C(10)	3 093(7)	9 596(4)	10 236(3)	C(37)	815(3)	5 680(2)	8 519(2)
C(11)	4 186(7)	9 162(4)	10 125(3)	C(38)	4(3)	5 360(2)	8 922(2)
C(12)	4 044(7)	8 583(4)	9 702(3)	C(39)	431(3)	4 699(2)	9 233(2)
C(13)	3 552(4)	6 929(3)	9 156(2)	C(40)	1 667(3)	4 358(2)	9 140(2)
C(14)	3 437(4)	6 640(3)	9 722(2)	C(41)	2 478(3)	4 678(2)	8 737(2)
C(15)	4 381(4)	6 106(3)	9 974(2)	C(42)	2 051(3)	5 339(2)	8 427(2)
C(16)	5 438(4)	5 861(3)	9 658(2)				

It is notable that, with the exception of complex (2) where a molecule of benzene is lost, all the fragments of the $HC(PPh_2)_3$ ligand remain co-ordinated to the metal atoms in the complexes formed. It seems likely that the preferred initial co-ordination of $HC(PPh_2)_3$ to $[Ru_3(CO)_{12}]$ is *via* two phosphine groups at equatorial sites on two adjacent Ru atoms (Scheme). The third phosphine group is then constrained to co-ordinate at an axial site which leads to an electron-rich Ru atom and induces Ru–Ru bond fission to generate an electron-deficient binuclear species (see Scheme). The electron deficiency of this binuclear species is relieved by intramolecular attack on the $HC(PPh_2)_3$ ligand leading to $P–CH_2$ and P–Ph bond-cleavage reactions resulting in ligand fragmentation, but retention of the fragments in the isolated complexes.

Experimental

Reactions were carried out under a dry oxygen-free nitrogen atmosphere. All solvents were dried and degassed before use. Infrared spectra were recorded for CH_2Cl_2 solutions in 0.5-mm NaCl cells on a Perkin-Elmer 681 spectrophotometer. The n.m.r. measurements were made with Bruker WM250 or JEOL 90Q instruments and measured in CD_2Cl_2 or $CDCl_3$. The compounds $[Ru_3(CO)_{12}]$[20] and $HC(PPh_2)_3$[4] were prepared by published procedures; $HC(PPh_2)_3$ was recrystallised from CH_2Cl_2–light petroleum (b.p. 60—80 °C) before use, resulting in one molecule of CH_2Cl_2 of crystallisation.

Reaction between $[Ru_3(CO)_{12}]$ *and* $HC(PPh_2)_3$.— $[Ru_3(CO)_{12}]$ (1.279 g, 2.0 mmol) and $HC(PPh_2)_3 \cdot CH_2Cl_2$ (1.463 g, 2.2 mmol) in tetrahydrofuran (thf) (100 cm^3) were heated at 50—55 °C for 24 h. The resulting deep red solution was evaporated to dryness under reduced pressure, and the residue chromatographed on a Florisil column. Elution was commenced with light petroleum (b.p. 60—80 °C) as eluant, and the polarity of the eluant was slowly increased by addition of dichloromethane to effect the maximum separation of the products. Six bands were separated, and the products from these bands were further purified by thin-layer chromatography and recrystallisation from dichloromethane–hexane [compounds (1), (3), (5), and (6)], dichloromethane–heptane (2), or thf–heptane (4). The yields of the products obtained and the order of elution from the column were as follows: (3), dark red crystals (48 mg, 3%); (4), yellow crystals (30 mg, 2%); (2), brown crystals (56 mg, 3%); (1), yellow crystals (50 mg, 2.2%); (5), yellow-brown crystals (<0.5%); (6), yellow crystals (110 mg, 5%). Microanalyses of compounds (2), (4), and (6) gave the following results, with expected values given in parentheses: (2), C, 43.3 (43.65); H, 2.45 (2.40); P, 7.30 (8.25); (4) C, 53.55 (53.6); H, 3.50 (3.55); Cl, 3.85 (4.00); (6), C, 55.3 (55.4); H, 3.45 (3.45)%.

Crystal Structure Determinations.—Complex (2). A suitable crystal of complex (2), as the chloroform solvate, was grown from chloroform–heptane; it had dimensions *ca.* $0.6 \times 0.2 \times 0.2$ mm. Intensity data were recorded on a Nonius CAD4 diffractometer.

Crystal data. $C_{41}H_{26}Cl_3O_9P_3Ru_3$, $M = 1\ 164.5$, ortho-rhombic, $a = 17.296(3)$, $b = 14.804(5)$, $c = 16.938(5)$ Å, $U = 4\ 337$ Å^3, $D_m = 1.8$ g cm^{-3} (by flotation in CCl_4–MeI), $Z = 4$, $D_c = 1.72$ g cm^{-3}, $F(000) = 2\ 288$, space group *Pnma*, Mo-K_α radiation, $\lambda = 0.710\ 69$ Å, $\mu(Mo-K_\alpha) = 3.23$ cm^{-1}.

For the structure solution and refinement, 2 119 independent reflections with $F_o > 3\sigma(F_o)$ were used. The structure was solved by Patterson and Fourier methods (using the program SHELX[21]) and was refined by least squares, with anisotropic thermal parameters for all non-hydrogen atoms. Each phenyl ring was treated as a regular hexagon (C–C 1.395 Å) and the phenyl-hydrogen atoms were included at calculated positions

(C–H 1.080 Å). The final electron-density difference map showed no peaks >0.76 e Å^{-3}. The weighting scheme $w = 1/[\sigma^2(F_o) + 0.0145F_o^2]$ gave satisfactory agreement analyses. Refinement led to $R\ 0.054$ ($R'\ 0.048$). Scattering factors were from ref. 22.

Complex (4). Yellow crystals of complex (4) were grown from dichloromethane–hexane. That chosen for study was a *plate*-like crystal of dimensions *ca.* $1.5 \times 0.8 \times 0.2$ mm.

Crystal data. $C_{41}H_{32}ClO_4P_3Ru_2$, $M = 919.2$, triclinic, $a = 9.867(1)$, $b = 15.650(2)$, $c = 12.818(2)$ Å, $\alpha = 90.00(1)$, $\beta = 103.58(1)$, $\gamma = 92.12(1)°$, $U = 1\ 923$ Å^3, $D_m = 1.61$ g cm^{-3} (by flotation in CCl_4–hexane), $Z = 2$, $D_c = 1.58$ g cm^{-3}, $F(000) = 920$, space group $P\bar{1}$, $\mu(Mo-K_\alpha) = 2.21$ cm^{-1}.

The structure solution and refinement were similar to that described above for complex (2), using 6 227 unique reflections with $F_o > 6\sigma(F_o)$. Convergence was reached at $R\ 0.051$ ($R'\ 0.059$) with a final electron-density difference map showing no remaining peaks >1.1 e Å^{-3}. The weighting scheme was $w = 1[\sigma^2(F_o) + 0.000035F_o^2]$. Scattering factors were from ref. 22.

Complex (6). Yellow crystals were grown from dichloro-methane–hexane. That used was a rectangular plate-like crystal of dimensions *ca.* $0.9 \times 0.9 \times 0.2$ mm.

Crystal data. $C_{42}H_{31}O_5P_3Ru_2$, $M = 910$, monoclinic, $a = 9.866(1)$, $b = 17.507(4)$, $c = 22.639(5)$ Å, $\beta = 96.31(2)°$, $U = 3\ 887$ Å^3, $D_m = 1.55$ g cm^{-3} (by flotation in CCl_4–hexane), $Z = 4$, $D_c = 1.56$ g cm^{-3}, $F(000) = 1\ 824$, space group $P2_1/n$, $\mu(Mo-K_\alpha) = 1.56$ cm^{-1}.

The structure solution and refinement were similar to that described above for complex (2), using 5 386 unique reflections with $F_o > 4\sigma(F_o)$. Convergence was reached at $R\ 0.047$ ($R'\ 0.047$) with a final electron-density difference synthesis showing no peaks >1.00 e Å^{-3}. The weighting scheme was $w = 1/[\sigma^2(F_o) + 0.00032F_o^2]$.

Acknowledgements

References

1 R. Whyman, *J. Chem. Soc., Dalton Trans.*, 1972, 1375.
2 S. D. Jackson, P. B. Wells, R. Whyman, and P. Worthington, in 'Catalysis,' eds. C. Kemball and D. A. Dowden, Royal Society of Chemistry, 1981, vol. 4, p. 75.
3 J. J. de Boer, J. A. van Doorn, and C. Masters, *J. Chem. Soc., Chem. Commun.*, 1978, 1005.
4 A. A. Arduini, A. A. Bahsoun, J. A. Osborn, and C. Voelker, *Angew. Chem., Int. Ed. Engl.*, 1980, 19, 1024; A. A. Bahsoun, J. A. Osborn, C. Voelker, J. J. Bonnet, and G. Lavigne, *Organometallics*, 1982, 1, 1114.
5 G. Lavigne, N. Lugan, and J. Bonnet, *Nouv. J. Chim.*, 1981, 5, 423; G. Lavigne and J. J. Bonnet, *Inorg. Chem.*, 1981, 20, 2713; A. W. Coleman, D. F. Jones, P. H. Dixneuf, C. Brisson, J. J. Bonnet, and G. Lavigne, *ibid.*, 1984, 23, 952.
6 R. C. Ryan, C. U. Pittman, and J. P. O'Connor, *J. Am. Chem. Soc.*, 1977, 99, 1986.
7 F. Iwasaki, M. J. Mays, P. R. Raithby, P. L. Taylor, and P. J. Wheatley, *J. Organomet. Chem.*, 1981, 213, 185.
8 G. Lavigne, N. Lugan, and J. J. Bonnet, *Organometallics*, 1982, 1, 1040.
9 P. Chini and B. T. Heaton, *Top. Curr. Chem.*, 1977, 71, 53.
10 D. F. Foster, B. S. Nicholls, and A. K. Smith, *J. Organomet. Chem.*, 1982, 236, 395.

11 D. F. Foster, B. S. Nicholls, and A. K. Smith, *J. Organomet. Chem.*, 1983, **244**, 159.
12 D. F. Foster, J. Harrison, B. S. Nicholls, and A. K. Smith, *J. Organomet. Chem.*, 1983, **248**, C29.
13 M. M. Harding, B. S. Nicholls, and A. K. Smith, *J. Chem. Soc., Dalton Trans.*, 1983, 1479.
14 J. A. Clucas, M. M. Harding, B. S. Nicholls, and A. K. Smith, *J. Chem. Soc., Chem. Commun.*, 1984, 319.
15 J. A. Clucas, D. F. Foster, M. M. Harding, and A. K. Smith, *J. Chem. Soc., Chem. Commun.*, 1984, 949.
16 M. M. Harding, B. S. Nicholls, and A. K. Smith, *J. Organomet. Chem.*, 1982, **226**, C17.
17 C. W. Bradford, R. S. Nyholm, G. J. Gainsford, J. M. Guss, P. R. Ireland, and R. Mason, *J. Chem. Soc., Chem. Commun.*, 1972, 87.
18 G. M. Dawkins, M. Green, J. C. Jeffery, C. Sambale, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1983, 499.
19 W. R. Roper, G. E. Taylor, J. M. Waters, and L. J. Wright, *J. Organomet. Chem.*, 1979, **182**, C46.
20 A. Mantovani and S. Cenini, *Inorg. Synth.*, 1975, **16**, 47.
21 G. M. Sheldrick, SHELX program for crystal structure determination, University Chemical Laboratory, Cambridge, 1976.
22 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.