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Cluster chemistry

LXXXIV *. Reactions of $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ with alkenes: attack at the C_2PPh_2 ligand without cleavage of the C–P bond. X-Ray structures of $Ru_5(\mu_5\text{-}C)(\mu\text{-}PPh_2)(\mu\text{-}RC_3H_3PPh_2)(CO)_{11}$ (R = Me, Ph) and $Ru_5(\mu_5\text{-}C)(\mu\text{-}PPh_2)(\mu\text{-}PhC_3H_3PPh_2)(CO)_{11-n}\{P(OMe)_3\}$ ($n = 0, 1$)

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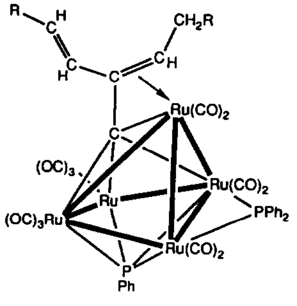
Abstract

Reactions of terminal alkenes ($CH_2{=}CHR$; R = Me, Ph) with $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ resulted in addition of the alkene to C_α of the Ph_2PC_2 ligand and the cleavage of the C_α–C_β bond to give complexes containing the $\mu\text{-}\eta^3,P\text{-}(CHRCHCH)PPh_2$ ligand attached to a square pyramidal Ru_5C core. Both complexes were characterized by single crystal X-ray studies. Addition of $P(OMe)_3$ to the styrene derivative resulted in Ru–Ru bond cleavage and CO substitution reactions. The product from the former reaction contains a basket-like (or wing-tip-bridged butterfly) Ru_5 cluster retaining the central carbido C atom. When this is heated, it is converted into a square pyramidal Ru_5C cluster, with migration of the tertiary phosphine ligand. The structures of both of the complexes $Ru_5(\mu_5\text{-}C)(\mu\text{-}PPh_2)(\mu\text{-}PhC_3H_3PPh_2)(CO)_{10}\{P(OMe)_3\}$ and $Ru_5(\mu_5\text{-}C)(\mu\text{-}PPh_2)(\mu\text{-}PhC_3H_3PPh_2)(CO)_{11}\{P(OMe)_3\}$ have been determined by X-ray diffraction studies. Probable routes to these clusters are discussed.

1. Introduction

In exploring the reactivity of $Ru_5(\mu_5\text{-}C_\alpha C_\beta PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**1**; Scheme 1) [2], we have noted the main types of reaction at the C_2PPh_2 ligand to be (a) addition at C_β preserving the C–C and C–P bonds [3]; (b) addition at C_β with associated cleavage of the C–P bond (**2**, **3**) [1]; (c) cycloaddition to the C_2 unit with C–P bond cleavage [3]; (d) reaction to give cluster-bound C_2 [4]; (e) alteration of the PPh_2 group by elimination of PPh to the cluster [5]; (f) cleavage of the C–C and C–P bonds [6].



R = H (**2**), Me (**3**)

We have already described reactions between **1** and ethene or 1,3-butadiene to give Ru_4 complexes containing three-component adducts of the C_2PPh_2 group, the alkene and CO which remain attached to a ruthenium cluster [7]. Extension of these studies to the reactions between **1** and other mono-alkenes has en-

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* For Part LXXXIII, see ref. 1.

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abled us to characterize two further types of products: those formed by addition of the alkene to C_β with cleavage of the C_α–C_β bond while preserving the C–P bond, discussed below, and addition to the C_2 unit with associated migration of the PPh_2 group to the cluster, described in the previous paper [1].

2. Results and discussion

From various reactions between **1** and ethene, complexes **2**, **4–6** have been isolated [1,3]. With propene and styrene, however, we have found that derivatives of the well-known $Ru_5(\mu_5\text{-}C)(CO)_{15}$ cluster are also formed. These contain novel tertiary phosphine ligands formed by addition of the alkene to C_β followed by hydrogen migration and C–C bond cleavage to give substituted allyl groups which also interact with the cluster. In one case, attempted derivatization with $P(OMe)_3$, carried out to prepare a better material for X-ray crystallography, resulted in isomerization and cluster-opening reactions. These reactions are discussed in turn.

2.1. Reactions between 1 and propene

This reaction was carried out in toluene for 4 days at 90°C and gave four products which were readily separated by preparative TLC on silica gel. Of these, complexes **3** and **7**, isolated in 42 and 21% yield, respectively, have been described elsewhere [1], while the third was identified as the cycloadduct **8** and was obtained in 14% yield as a red powder. The IR ν(CO) and FAB mass spectra resemble those of the analogous complex, **2**, formed with ethene and it is likely that the same formal cycloaddition of alkene and CO to the coordinated C_2PPh_2 group has occurred to give a cyclopentenonyl ligand attached to a metallated triangular Ru_4 cluster. The fourth product was obtained as red crystals in 8% yield and was fully characterized by an X-ray study as the cluster $Ru_5(\mu_5\text{-}C)(\mu\text{-}PPh_2)(\mu\text{-}MeC_3H_3PPh_2)(CO)_{11}$ (**9**), as described below.

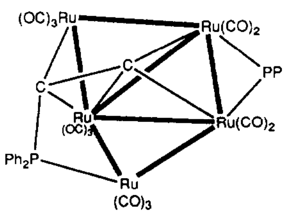
2.2. Reactions between 1 and styrene

Only one product, **10**, was isolated from the reaction between **1** and styrene carried out in benzene for 3 days at 90°C. Inferior quality crystals resulted in a poor quality X-ray study so it was treated with a slight excess of $P(OMe)_3$ to give two derivatives of composition $Ru_5(\mu_5\text{-}C)(\mu\text{-}PPh_2)(\mu\text{-}PhC_3H_3PPh_2)(CO)_{11-n}\{P(OMe)_3\}$ [n = 1(**11**) (black), 0 (**12**) (orange)] both of which were fully characterized by X-ray studies.

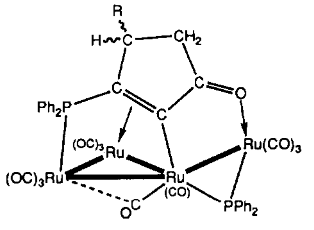
2.3. Structures of $Ru_5(\mu_5\text{-}C)(\mu\text{-}PPh_2)(\mu\text{-}RC_3H_3PPh_2)(CO)_{11-n}\{P(OMe)_3\}_n$ [R = Me, n = 0 (9); R = Ph, n = 0 (10); R = Ph, n = 1 (11)]

Figures 1, 2 and 3 are plots of single molecules of **9**, **10** and **11**, respectively, while selected bond parameters are listed in Table 1. Since the quality of **10** was poor, only **9** and **11** are discussed in any detail. Complexes **9–11** each contain an almost square-pyramidal Ru_5C cluster, to the apical Ru of which is attached a $P(\eta^3\text{-}CHCHCHR)Ph_2$ ligand [R = Me (**9**), Ph (**11**)] [Ru(1)–P(1) 2.287(2), 2.270(2) Å, respectively]; a basal edge of the cluster is symmetrically bridged by the μ-PPh_2 group [Ru(2)–P(2) 2.290(2), 2.293(2); Ru(3)–P(2), 2.294(2), 2.299(2) Å]. Four ruthenium atoms bear two CO groups each; in **9**, Ru(5) is attached to a third CO, while in **11**, the $P(OMe)_3$ ligand occupies the axial site [Ru(5)–P(3) 2.259(2) Å]. The allylic substituent of the tertiary phosphine is η^3-bonded to Ru(4); the outer carbons are further away (av. 2.343, 2.372 Å) than the central ones (2.224(7), 2.209(4) Å).

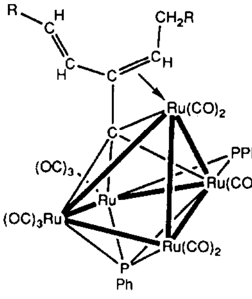
In the central Ru_5C cores, the carbido C atoms are 0.075(7), 0.096(5) Å below the almost square Ru_4 planes. The Ru–Ru distances range between 2.835–2.903(1), 2.826–2.897(1) (apical-basal) and 2.748–2.953(1), 2.746–2.966(1) Å (basal) for **9** and **11**, respec-



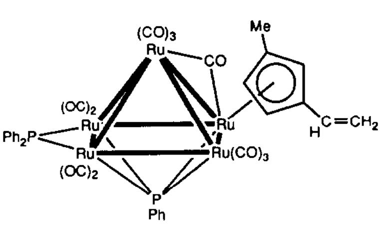
(**1**)



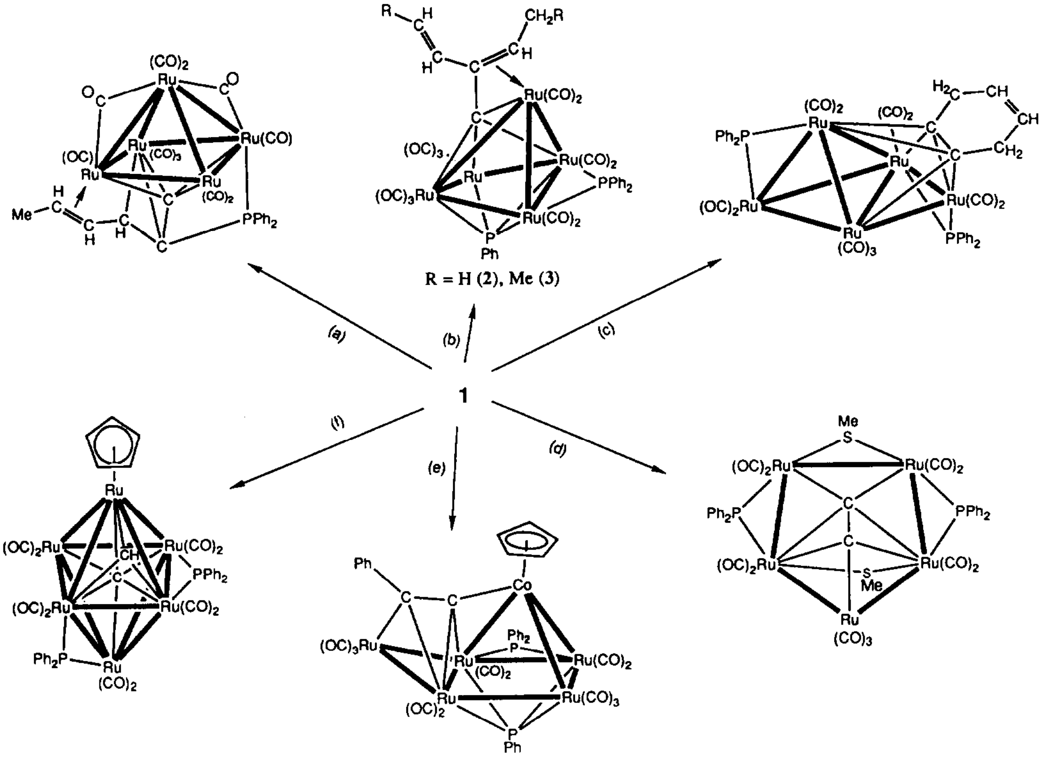
R = H (**4**), Me (**8**)



R = H (**6**), Me (**7**)



(**5**)

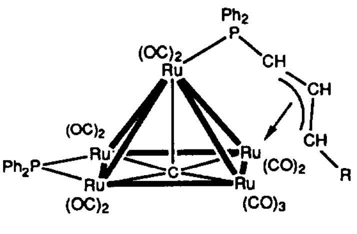


Scheme 1.

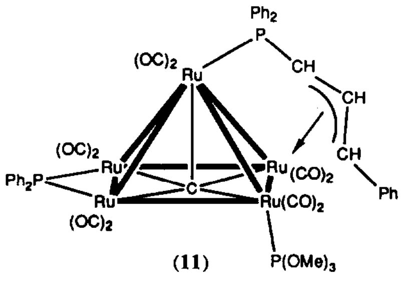
tively, both average lengths being 2.864 Å. In $Ru_5(\mu_5\text{-}C)(CO)_{15}$ [8] the basal Ru–Ru bonds average 2.855 Å and the apical-basal bonds 2.822 Å. The shortest bonds in **9** and **11** are those bridged by the PPh_2 groups, as found in $Ru_5C(\mu\text{-}H)_3(\mu\text{-}PPh_2)(CO)_{11}(PMePh_2)$ [2.7705(6) Å] [9] while the longest are basal vectors from Ru(4), bearing the allyl group, perhaps because of steric interference with a CO group [CO(53) in **9**, CO(51) in **11**]. The Ru–C distances (ranges 2.008–2.099(7), 1.978–2.123(5), av. 2.042, 2.047 Å, respectively) are also similar to those in the hydrido complex (av. 2.04 Å) [9].

2.4. Structure of $Ru_5(\mu_5\text{-}C)(\mu\text{-}PPh_2)(\mu\text{-}PhC_3H_3PPh_2)(CO)_{11}\{P(OMe)_3\}$ (12)

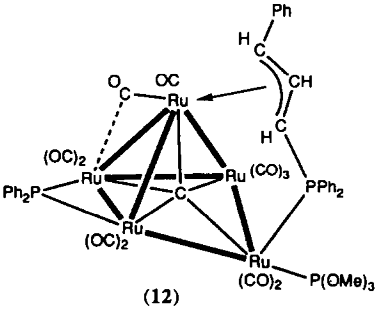
The molecular structure of **12** is shown in Fig. 4; selected bond parameters are collected in Table 1. The Ru_5C core in **12** is related to that found in **9** by the opening of one Ru–Ru bond, so that Ru(5) is below the CRu(1)Ru(2)Ru(3) plane. The geometry can be described as an *arachno*-pentagonal bipyramid. The carbido C atom remains attached to all five Ru atoms, but the C–Ru(5) vector [2.17(1) Å] is considerably longer than the other four (av. 2.03 Å). The eleven CO groups are distributed two to each Ru except Ru(1),



R = Me (**9**), Ph (**10**)



(**11**)



(**12**)

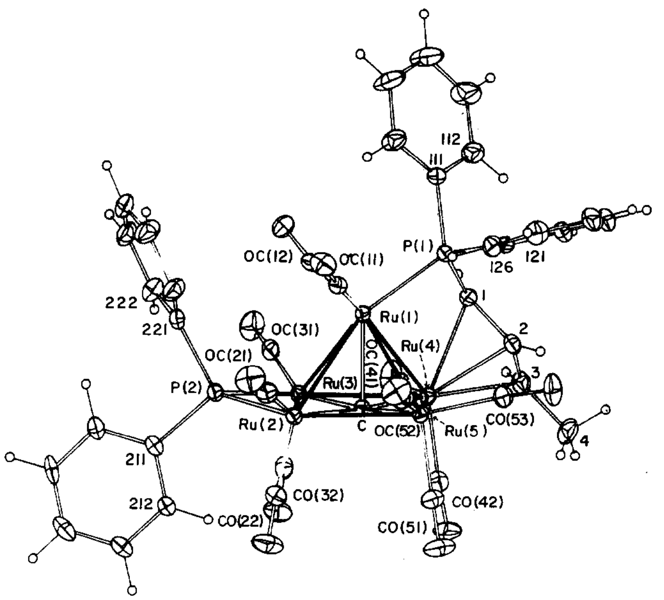


Fig. 1. Plot of a molecule of $Ru_5(\mu_5\text{-}C)(\mu\text{-}PPh_2)(\mu\text{-}MeC_3H_3PPh_2)(CO)_{11}$ (**9**), showing atom numbering scheme. Non-hydrogen atoms shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

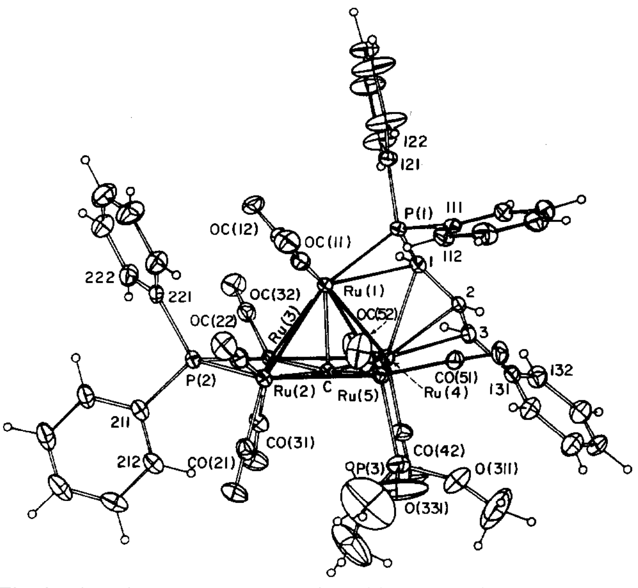


Fig. 3. Plot of a molecule of $Ru_5(\mu_5\text{-}C)(\mu\text{-}PPh_2)(\mu\text{-}PhC_3H_3PPh_2)(CO)_{10}\{P(OMe)_3\}$ (**11**), showing atom numbering scheme. Non-hydrogen atoms shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

which has three; CO(41) semi-bridges the Ru(4)–Ru(2) vector. The $P(OMe)_3$ ligand is attached equatorially to Ru(5) [Ru(5)–P(3) 2.288(4) Å]. The remaining ligand is the same tertiary phosphine as found in **11** and is bridging the non-bonding Ru(1) ··· Ru(5) vector, being attached to the basal Ru(5) by P(1) [Ru(5)–P(1) 2.426(3) Å] and to the apical Ru(4) by C(1)C(2)C(3) of the phenylallyl substituent [Ru(4)–C(outer) 2.20, 2.35(1); Ru(4)–C(inner) 2.22(1) Å]. Of the Ru–Ru bonds not involving Ru(5), that symmetrically bridged by the PPh_2 group is the shortest [Ru(2)–Ru(3) 2.735(2) Å], the four others ranging between 2.831 and 2.933(2) Å. The bonds from Ru(5) to Ru(1) and Ru(3) are somewhat longer [2.996(2), 2.989(2) Å, respectively].

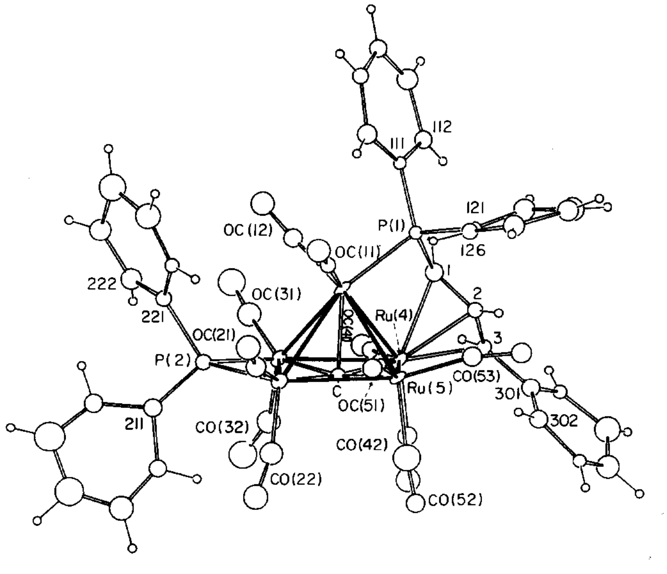


Fig. 2. Plot of a molecule of $Ru_5(\mu_5\text{-}C)(\mu\text{-}PPh_2)(\mu\text{-}PhC_3H_3PPh_2)(CO)_{11}$ (**10**), showing atom numbering scheme. Non-hydrogen atoms have 20% thermal envelopes; hydrogen atoms have arbitrary radii of 0.1 Å.

The ^1H NMR spectra of complexes **9**–**12** are consistent with the solid-state molecular structures. Of most interest are the resonances associated with the allylic side-chains of the new tertiary phosphine ligands. In all cases standard 2D COSY NMR spectra were recorded to assist the assignments. In **9**, resonances at δ 0.19, 3.83 and 4.81 were assigned to H(1), H(2) and H(3), respectively. A resonance at δ 2.30 was assigned to the Me protons. The corresponding protons in **10** (and **11**) were assigned to resonances at δ 0.29 (0.22), 4.72 (4.79) and 5.46 (5.44). In **11**, a resonance at δ 3.32 was assigned to the $P(OMe)_3$ protons. The different structure of **12** is reflected in its ^1H NMR spectrum. Resonances at δ 2.74, 3.82, 3.99 and 6.31 were assigned to H(3), $P(OMe)_3$, H(1) and H(2). In the spectrum of **12**, lower intensity peaks reveal the presence of a second minor complex, probably an isomer. The mixture proved to be inseparable, although the crystal used for the structural determination contained only one form;

TABLE 1. Selected bond distance (Å) in complexes **9**–**12**

Bond	**9** [a]	**10** [b]	**11** [c]	**12** [d]
Ru(1)–Ru(2)	2.903(1)	2.897(7)	2.881(1)	2.831(2)
Ru(1)–Ru(3)	2.835(2)	2.837(7)	2.8255(7)	–
Ru(1)–Ru(4)	2.874(2)	2.869(5)	2.8970(8)	2.933(2)
Ru(1)–Ru(5)	2.840(1)	2.799(6)	2.853(1)	2.996(2)
Ru(2)–Ru(3)	2.748(1)	2.745(6)	2.746(1)	2.735(1)
Ru(2)–Ru(4)	–	–	–	2.831(2)
Ru(2)–Ru(5)	2.858(1)	2.840(7)	2.8703(9)	–
Ru(3)–Ru(4)	2.901(1)	2.888(7)	2.8698(8)	2.892(2)
Ru(3)–Ru(5)	–	–	–	2.989(2)
Ru(4)–Ru(5)	2.953(1)	2.979(6)	2.966(1)	–
Ru(1)–P(1)	2.287(2)	2.23(1)	2.270(2)	–
Ru(5)–P(1)	–	–	–	2.426(3)
Ru(2)–P(2)	2.290(2)	2.30(2)	2.293(2)	2.290(4)
Ru(3)–P(2)	2.294(2)	2.28(1)	2.299(2)	2.286(4)
Ru(5)–P(3)	–	–	2.259(2)	2.288(4)
Ru(1)–C	2.099(8)	2.14(5)	2.123(5)	1.99(1)
Ru(2)–C	2.015(6)	1.92(4)	2.027(5)	2.07(1)
Ru(3)–C	2.035(7)	2.04(5)	2.045(4)	2.00(1)
Ru(4)–C	2.053(7)	2.14(5)	2.061(5)	2.06(1)
Ru(5)–C	2.008(7)	2.01(6)	1.978(4)	2.17(1)
Ru(4)–C(1)	2.360(9)	2.30(5)	2.402(5)	2.20(1)
Ru(4)–C(2)	2.224(7)	2.21(5)	2.209(4)	2.22(1)
Ru(4)–C(3)	2.325(6)	2.35(5)	2.341(5)	2.35(1)
P(1)–C(1)	1.783(9)	1.77(5)	1.758(5)	1.83(1)
C(1)–C(2)	1.42(1)	1.35(7)	1.425(7)	1.41(1)
C(2)–C(3)	1.40(1)	1.51(6)	1.407(7)	1.42(2)
C(3)–C(Me, Ph)	1.50(1)	1.51(7)	1.469(7)	1.46(2)

[a] For **9**: Ru–CO, range 1.870(9)–1.93(1), av. 1.894; C–O, range 1.11–1.16(1), av. 1.14; P–C(Ph), range 1.825–1.835(9), av. 1.829.
[b] For **10**: Ru–CO, range 1.85(6)–2.23(4), av. 1.94; C–O, range 1.10(7)–1.20(5), av. 1.15; P–C(Ph), range 1.65(6)–1.83(4), av. 1.78.
[c] For **11**: Ru–CO, range 1.851(7)–1.916(6), av. 1.884; C–O, range 1.120–1.154(8), av. 1.137; P–C(Ph), range 1.809(7)–1.832(5), av. 1.823.
[d] For **12**: Ru–CO, range 1.83–1.92(1), av. 1.87; C–O, range 1.12–1.19(2), av. 1.15; P–C(Ph), range 1.81(1)–1.87(2), av. 1.84.

we are not able to say whether it is the major or minor isomer. The overall similarities in properties, including their spectra, suggest that isomerism may occur by different coordination sites for the $P(OMe)_3$ ligand at Ru(5). It is interesting that decarbonylation of the mixture gives only a single isomer of **11**. The ^1H NMR spectrum of the minor isomer of **12** has been assigned as follows: δ 2.69 (H(3)), 3.62 ($P(OMe)_3$), 4.09 (H(1)) and *ca.* 7.15 (H(2)) (partially obscured by Ph peaks).

All three clusters are electron precise, although individual Ru atoms may not have an 18-electron configuration; for **9** and **11**, the 50 electrons required come from the Ru–Ru bonds (16), the CO and phosphine ligands (24), the μ-PR_2 and the allylic groups (3 each) and the cluster-bound carbon atom (4). For **12**, addition of the $P(OMe)_3$ ligand is compensated by cleavage of one Ru–Ru bond.

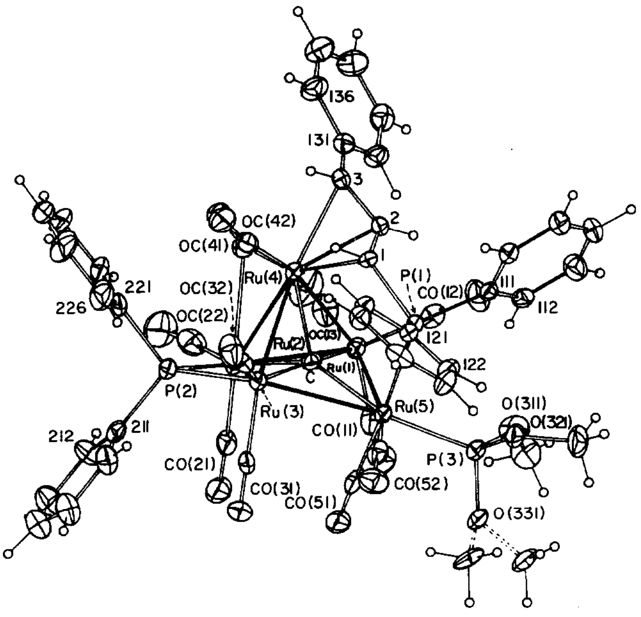
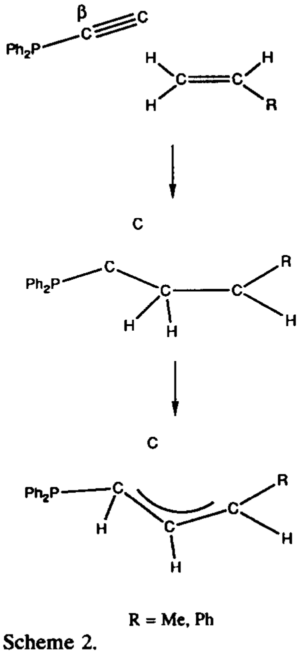


Fig. 4. Plot of a molecule of $Ru_5(\mu_5\text{-}C)(\mu\text{-}PPh_2)(\mu\text{-}PhC_3H_3PPh_2)(CO)_{11}\{P(OMe)_3\}$ (**12**), showing atom numbering scheme. Non-hydrogen atoms shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

The formation of the allylic ligand is of interest, involving cleavage of the C_α–C_β bond in the C_2PPh_2 ligand of **1**, addition of the alkene to C_β and a 1,2-H shift from the CH_2 group of the alkene to C_β. The

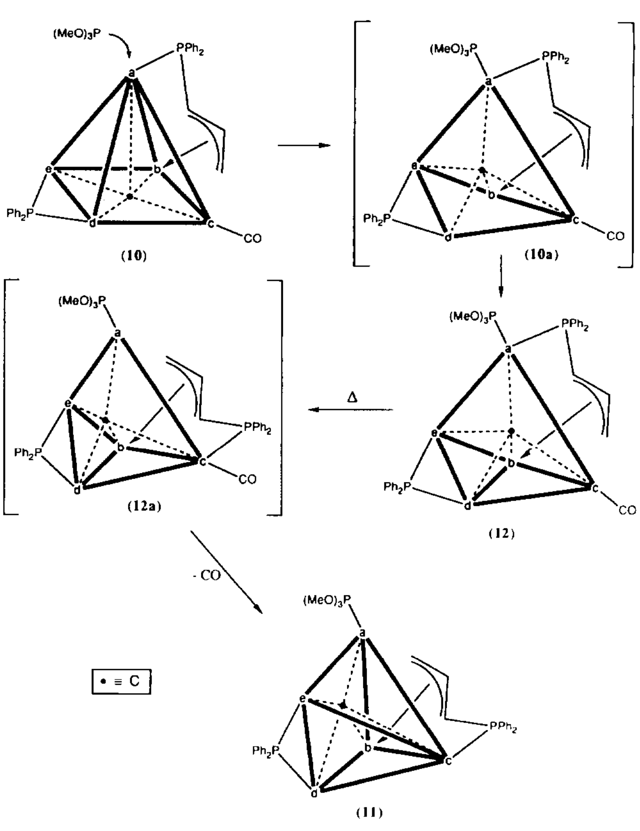


Scheme 2.

resulting allyl group coordinates to an Ru atom to give a bridging group across an Ru(ap)–Ru(bas) bond, with loss of 2 CO molecules. Scheme 2 summarizes the net transformation. It is not possible to determine the order of these reactions.

Addition of $P(OMe)_3$, originally intended to provide a crystallizable derivative of **10** by substitution of a CO ligand has, in addition, resulted in a skeletal change and apparent isomerization by addition to the cluster with a concomitant cleavage of one of the Ru–Ru bonds. The two complexes **11** and **12** are related by a thermal decarbonylation reaction which involves a facile closing of the cluster along one edge of the Ru_5C core with concomitant loss of CO. There are two interesting features of these reactions. First, in **12**, the phosphorus atoms of the $P(CHCHCHPh)Ph_2$ and $P(OMe)_3$ ligands are both attached to the same Ru atom, whereas in **11**, they are bound to adjacent metal atoms. Second, the positions of the PPh_2 and CHCHCHPh groups on the cluster, relative to the μ-PPh_2 group, are reversed.

The substitution of CO by *P*-donor ligands in $Ru_5C(CO)_{15}$ has been studied [8] and a possible reaction sequence leading to the formation of the opened cluster found in **12** has been related to their electron-acceptor powers and ease of rearrangement of the Ru_5C cluster. In our case, addition of $P(OMe)_3$ occurs at the apical Ru(a) (Scheme 3), also bearing the PPh_2 group of the $P(CHCHCHPh)Ph_2$ ligand in a precursor of similar structure to **9**. This initiates cleavage of two Ru–Ru bonds [Ru(a)–Ru(b) and Ru(a)–Ru(d)] (**10a**) and formation of a new bond [Ru(b)–Ru(d)], to give **12**. On heating, migration of the allylic PPh_2 group from Ru(a) to Ru(c) (**12a**) is accompanied by bond rearrangement [Ru(b)–Ru(e) → Ru(b)–Ru(a)], bond formation [Ru(c)–Ru(e)] and loss of CO to give **11**. The conversion of **12** to **11**, which necessarily involves migration of a tertiary phosphine from one Ru to the next, is the first example, to our knowledge, to be found for a ruthenium cluster; previous examples include migration of chelating dppm ligands around a Pt_3 cluster [10] and the recently described isomerizations of Re_2Pt clusters [11].



Scheme 3.

3. Conclusions

We have described reactions between **1** and the alkenes propene and styrene which proceed by addition of the alkene to C_β of the C_2PPh_2 ligand in **1** with concomitant cleavage of the C_α–C_β bond. The second carbon of the C_2 fragment is incorporated into the Ru_5 square pyramid to give the well-known Ru_5C core; a similar cleavage of the C_α–C_β bond occurred in the reaction of **1** with dihydrogen to give $Ru_5C(\mu\text{-}H)_3(\mu\text{-}PPh_2)(CO)_{11}(PMePh_2)$ [9]. Related reactions occur with 1,3-butadiene, but in this case the C_α–C_β bond is preserved, one C atom of the resulting alkylidyne ligand interacting with all four basal Ru atoms. We have also found an interesting opening of the Ru_5C core on reaction with $P(OMe)_3$; subsequent closing to regenerate the Ru_5C cluster involves migration of a *P*-donor ligand between adjacent Ru atoms.

A striking conclusion that is apparent from all of our studies of the chemistry of **1** [1,2] is that the final geometry and conformation of the Ru_5 skeleton is dependent on the coordination of the organic ligand. In other words, after formation of the organic moiety, the metal skeleton adopts the lowest energy arrangement consistent with the bonding requirements of the ligand. This observation has important implications in relation to the predictability of organic reactions on medium-sized metal clusters, where facile conformational changes and *M–M* bond making/breaking result in non-ideal polyhedra being formed. Although this "softness" of metal clusters, at least insofar as *M–M* separations are concerned, is well known, it is only with the medium-sized clusters ($M_{\geq 5}$) where a much larger range of geometries is available (compared with M_3 and M_4 systems) that this conclusion is emphasized.

4. Experimental details

General experimental conditions and instrumentation have been described earlier [12]. Complex **1** was prepared as described in ref. 12. Propene (J.T. Baker) and styrene (Aldrich) were commercial products; the latter was distilled under vacuum before use.

4.1. Reaction of 1 with propene

A mixture of **1** (200 mg, 0.158 mmol) and propene (2.6 g, 61.8 mmol) in toluene (10 ml) was heated in a Carius tube at 90°C for 4 days. The solvent was removed and the residue purified by preparative TLC (petroleum ether/acetone 4 : 1) to give six major bands. A brown band (R_f 0.7) was recrystallized (CH_2Cl_2/MeOH) to give **3** (24 mg, 12%) [1], a red band (R_f 0.6) was recrystallized (CH_2Cl_2/MeOH) to yield **7** (42 mg, 21%) [1], a second red band (R_f 0.45) was recrystallized (CH_2Cl_2/MeOH) to yield **8** (26 mg, 14%), and a third red band (R_f 0.35) was recrystallized (CH_2Cl_2/MeOH) to yield **9** (15 mg, 8%), m.p. 216–219°C (dec.). Anal. Found: C, 38.26; H, 2.18; M^+, 1251 (mass spectrometry). $C_{40}H_{26}O_{11}P_2Ru_5$ calc.: C, 38.43; H, 2.10%; M, 1251. IR (cyclohexane): ν(CO) 2052m, 2023vs, 2013s, 2002m, 1989s, 1977m, 1962m, 1949w, 1937vw cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.19 (1H, dd, $J(HP) = 13.3$, $J(HH) = 10.7$ Hz, H(1)); 2.30 (3H, d, $J(HH) = 6.0$ Hz, Me); 3.83 (1H, ddd, $J(HP) = 8.2$, $J(HH) = 10.6$, 10.6 Hz, H(2)); 4.81 (1H, dq, $J(HH) = 10.7$, 6.0 Hz, H(3)); 7.24–7.78 (20H, m, Ph). FAB MS: m/z 1251, M^+; loss of 11 CO groups. Some starting material (R_f 0.5) was also recovered (41 mg, 21%). A brown band (R_f 0.4; 8 mg) has not been identified.

4.2. Reaction of 1 with styrene

A solution of **1** (100 mg, 0.079 mmol) and styrene (0.5 g, 4.8 mmol) in benzene (20 ml) in a Carius tube was heated for 3 days at 90°C (tube oven), then allowed to cool to room temperature. The solvent was removed and the residue purified by preparative TLC (petroleum ether/acetone 5 : 1). The major red band (R_f 0.25) was recrystallized (CH_2Cl_2/MeOH) to yield **10** (33 mg, 32%), m.p. 211–212°C (dec.). Anal. Found: C,

TABLE 2. Crystal data and refinement details for **9–12** [a]

Compound	**9**	**10**	**11**	**12**
Formula	$C_{40}H_{26}O_{11}P_2Ru_5$	$C_{45}H_{28}O_{11}P_2Ru_5 \cdot$ "solvent"	$C_{47}H_{37}O_{13}P_3Ru_5$	$C_{48}H_{37}O_{14}P_3Ru_5 \cdot 0.3CH_2Cl_2$
MW	1249.9	1312.0	1408.1	1461.6
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$; No 2	$P\bar{1}$; No 2	$P2_1/c$; No 14	$P2_1/c$; No 14
a (Å)	19.535(8)	15.67(2)	11.053(3)	12.060(4)
b (Å)	11.789(6)	13.241(8)	20.359(4)	14.793(5)
c (Å)	10.373(6)	11.472(10)	24.450(13)	31.319(11)
α (°)	112.42(4)	90.93(6)	–	–
β (°)	97.04(4)	100.44(8)	114.08(3)	98.35(3)
γ (°)	100.56(4)	99.33(7)	–	–
U (Å^3)	2122	2307	5023	5528
Z	2	2	4	4
D (g cm^{-3})	1.96	1.89	1.86	1.76
F(000)	1208	1272	2752	2858.4
Crystal size (mm)	0.14 × 0.21 × 0.30	0.17 × 0.06 × 0.33	0.35 × 0.32 × 0.18	0.33 × 0.10 × 0.24
A^* (min, max)	1.20, 1.45	1.18, 1.62	1.25, 1.32	1.13, 1.31
μ (cm^{-1})	16.9	15.6	14.7	14.3
$2\theta_{max}$ (°)	50	48	50	50
Unique data, N	7147	7152	8494	9803
Obs. data, N_o	5326	2738	6575	5203
R	0.038	0.123	0.031	0.054
R_w	0.042	0.129	0.034	0.052

[a] Abnormal features/variations in procedure: **9**, H(1, 2, 3) were located in difference maps. **10**, Only after prolonged perseverance was a data set of marginal usefulness obtained from crystallographically inferior material. Thermal parameters of all atoms except Ru were refined using the isotropic form. Major difference artefacts were modelled as fully weighted C, O atoms ("solvent") without any neighbouring connectivity. (Note that the crystals were grown from toluene/hexane.) **11**, H(1, 2, 3) were located in difference maps. **12**, H(1, 2, 3) were estimated; solvent population and probable identity were established by refinement after consideration of difference map residues. One methyl group in the $P(OMe)_3$ ligand is disordered equally between two sites.

TABLE 3. Non-hydrogen atom positional and isotropic displacement parameters for **9**

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.25251(3)	0.33882(5)	0.41250(6)	0.0310(2)
Ru(2)	0.20076(3)	0.55795(5)	0.56499(6)	0.0342(3)
Ru(3)	0.28993(3)	0.57025(5)	0.38277(6)	0.0331(2)
Ru(4)	0.19664(3)	0.34788(5)	0.14801(6)	0.0345(2)
Ru(5)	0.10561(3)	0.33140(5)	0.35070(6)	0.0352(3)
C	0.1942(4)	0.4522(6)	0.3567(7)	0.033(3)
C(11)	0.2428(4)	0.3223(7)	0.5821(8)	0.047(4)
O(11)	0.2396(4)	0.3070(5)	0.6836(6)	0.068(3)
C(12)	0.3543(4)	0.3858(7)	0.4545(9)	0.047(4)
O(12)	0.4147(3)	0.4030(6)	0.4876(7)	0.070(3)
C(21)	0.1868(4)	0.5501(8)	0.7404(9)	0.051(4)
O(21)	0.1786(4)	0.5463(7)	0.8448(6)	0.082(4)
C(22)	0.1456(5)	0.6750(7)	0.5924(9)	0.055(4)
O(22)	0.1093(4)	0.7424(6)	0.6061(8)	0.092(4)
C(31)	0.3838(4)	0.5936(7)	0.3500(7)	0.048(4)
O(31)	0.4405(3)	0.6137(6)	0.3296(7)	0.079(3)
C(32)	0.2732(4)	0.6946(7)	0.3203(8)	0.054(4)
O(32)	0.2620(4)	0.7657(6)	0.2784(7)	0.090(4)
C(41)	0.2746(4)	0.4121(8)	0.0828(8)	0.053(4)
O(41)	0.3177(3)	0.4388(6)	0.0265(6)	0.086(3)
C(42)	0.1317(4)	0.4294(7)	0.0870(8)	0.050(4)
O(42)	0.0918(3)	0.4726(6)	0.0463(7)	0.077(4)
C(51)	0.0326(4)	0.4082(8)	0.3053(9)	0.057(4)
O(51)	−0.0097(4)	0.4516(7)	0.2782(8)	0.093(4)
C(52)	0.0772(4)	0.3153(8)	0.5115(9)	0.055(4)
O(52)	0.0551(3)	0.2996(7)	0.6034(7)	0.079(4)
C(53)	0.0526(4)	0.1646(7)	0.2259(9)	0.053(4)
O(53)	0.0165(3)	0.0672(6)	0.1517(7)	0.087(4)
C(1)	0.2363(4)	0.1635(7)	0.1161(8)	0.042(3)
C(2)	0.1700(4)	0.1389(6)	0.0238(8)	0.042(3)
C(3)	0.1681(4)	0.1865(7)	−0.0808(8)	0.048(4)
C(4)	0.0997(6)	0.1611(9)	−0.182(1)	0.083(5)
P(1)	0.2440(1)	0.1310(2)	0.2709(2)	0.0368(8)
C(111)	0.3226(4)	0.0670(7)	0.2767(8)	0.042(3)
C(112)	0.3412(5)	−0.0071(9)	0.1538(9)	0.067(5)
C(113)	0.3989(6)	−0.057(1)	0.166(1)	0.093(6)
C(114)	0.4357(6)	−0.040(1)	0.292(1)	0.101(7)
C(115)	0.4188(6)	0.036(1)	0.413(1)	0.101(7)
C(116)	0.3622(5)	0.0899(9)	0.4066(9)	0.066(5)
C(121)	0.1728(4)	−0.0038(7)	0.2469(8)	0.043(3)
C(122)	0.1528(4)	−0.1120(7)	0.1196(9)	0.052(4)
C(123)	0.1044(5)	−0.2169(7)	0.107(1)	0.068(5)
C(124)	0.0757(5)	−0.2153(8)	0.226(1)	0.071(5)
C(125)	0.0942(5)	−0.1100(9)	0.348(1)	0.066(5)
C(126)	0.1423(4)	−0.0023(7)	0.3601(9)	0.053(4)
P(2)	0.3121(1)	0.6905(2)	0.6240(2)	0.0371(8)
C(211)	0.3261(4)	0.8629(7)	0.6932(8)	0.044(4)
C(212)	0.2778(4)	0.9135(7)	0.6379(9)	0.054(4)
C(213)	0.2868(5)	1.0428(7)	0.688(1)	0.065(5)
C(214)	0.3434(6)	1.1230(8)	0.790(1)	0.077(5)
C(215)	0.3913(5)	1.0744(8)	0.846(1)	0.079(5)
C(216)	0.3834(5)	0.9457(7)	0.7987(9)	0.059(4)
C(221)	0.3857(4)	0.6705(7)	0.7332(8)	0.046(3)
C(222)	0.4559(4)	0.6987(9)	0.7129(9)	0.059(4)
C(223)	0.5103(5)	0.6776(9)	0.792(1)	0.075(5)
C(224)	0.4976(5)	0.6289(9)	0.8892(9)	0.072(5)
C(225)	0.4318(5)	0.6005(9)	0.909(1)	0.083(5)
C(226)	0.3751(5)	0.6237(9)	0.831(1)	0.068(5)

TABLE 4. Non-hydrogen positional and isotropic displacement parameters for **10**

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.3111(3)	0.2700(3)	0.3171(4)	0.033(2)
Ru(2)	0.2913(3)	0.2276(3)	0.5585(4)	0.037(2)
Ru(3)	0.1445(3)	0.2176(3)	0.3842(4)	0.036(2)
Ru(4)	0.2058(3)	0.0744(3)	0.2393(4)	0.034(2)
Ru(5)	0.3691(3)	0.0985(3)	0.4238(4)	0.033(2)
C(11)	0.416(3)	0.348(3)	0.403(4)	0.03(1)
O(11)	0.479(3)	0.395(3)	0.454(3)	0.08(1)
C(12)	0.251(4)	0.382(4)	0.262(5)	0.05(2)
O(12)	0.233(3)	0.461(3)	0.242(4)	0.08(1)
C(21)	0.385(4)	0.304(4)	0.663(5)	0.06(2)
O(21)	0.450(3)	0.357(3)	0.706(4)	0.09(1)
C(22)	0.279(4)	0.141(5)	0.681(6)	0.08(2)
O(22)	0.269(3)	0.102(3)	0.771(4)	0.09(1)
C(31)	0.064(4)	0.291(5)	0.287(6)	0.08(2)
O(31)	0.028(3)	0.345(3)	0.230(4)	0.10(2)
C(32)	0.034(4)	0.118(5)	0.403(6)	0.08(2)
O(32)	−0.028(3)	0.092(4)	0.444(4)	0.11(2)
C(41)	0.093(3)	0.094(3)	0.164(4)	0.04(1)
O(41)	0.026(3)	0.093(3)	0.108(3)	0.07(1)
C(42)	0.170(4)	−0.044(4)	0.318(5)	0.05(2)
O(42)	0.143(3)	−0.111(3)	0.365(4)	0.08(1)
C(51)	0.343(5)	−0.025(5)	0.518(6)	0.10(3)
O(51)	0.327(2)	−0.099(2)	0.563(3)	0.05(1)
C(52)	0.491(3)	0.173(3)	0.547(4)	0.02(1)
O(52)	0.554(2)	0.196(2)	0.625(3)	0.05(1)
C(53)	0.430(4)	0.045(4)	0.317(5)	0.05(2)
O(53)	0.468(2)	−0.005(3)	0.263(3)	0.06(1)
C	0.253(3)	0.148(3)	0.412(4)	0.03(1)
P(1)	0.3601(9)	0.2587(9)	0.147(1)	0.025(3)
C(111)	0.351(3)	0.366(3)	0.051(4)	0.02(1)
C(112)	0.310(4)	0.353(4)	−0.065(4)	0.05(1)
C(113)	0.316(4)	0.452(4)	−0.130(5)	0.06(2)
C(114)	0.364(3)	0.543(4)	−0.085(4)	0.04(1)
C(115)	0.407(3)	0.543(3)	0.030(4)	0.03(1)
C(116)	0.398(4)	0.459(4)	0.105(5)	0.05(2)
C(121)	0.460(3)	0.213(3)	0.132(4)	0.02(1)
C(122)	0.467(4)	0.174(4)	0.022(5)	0.06(2)
C(123)	0.546(4)	0.133(5)	0.014(6)	0.08(2)
C(124)	0.614(4)	0.156(4)	0.088(5)	0.06(2)
C(125)	0.622(4)	0.210(4)	0.212(5)	0.06(2)
C(126)	0.538(3)	0.237(3)	0.218(4)	0.04(1)
P(2)	0.180(1)	0.322(1)	0.552(1)	0.035(4)
C(211)	0.126(4)	0.313(4)	0.664(5)	0.05(2)
C(212)	0.095(4)	0.389(4)	0.729(5)	0.05(2)
C(213)	0.055(6)	0.391(6)	0.822(7)	0.13(3)
C(214)	0.036(5)	0.289(6)	0.862(7)	0.12(3)
C(215)	0.048(5)	0.203(5)	0.811(6)	0.09(2)
C(216)	0.082(3)	0.215(4)	0.715(4)	0.04(1)
C(221)	0.197(3)	0.460(3)	0.531(4)	0.03(1)
C(222)	0.279(3)	0.514(3)	0.541(4)	0.03(1)
C(223)	0.285(5)	0.610(5)	0.506(6)	0.09(2)
C(224)	0.222(5)	0.676(5)	0.461(6)	0.10(3)
C(225)	0.127(4)	0.611(4)	0.462(5)	0.07(2)
C(226)	0.123(4)	0.507(4)	0.486(5)	0.06(2)
C(1)	0.271(4)	0.159(4)	0.096(5)	0.05(2)
C(2)	0.279(3)	0.059(3)	0.095(4)	0.03(1)
C(3)	0.199(3)	−0.023(3)	0.064(4)	0.03(1)

TABLE 4 (continued)

Atom	x	y	z	U_{eq} (Å^2)
C(301)	0.211(4)	−0.134(4)	0.064(5)	0.05(1)
C(302)	0.263(4)	−0.171(4)	0.151(4)	0.05(2)
C(303)	0.265(3)	−0.279(3)	0.154(4)	0.03(1)
C(304)	0.209(4)	−0.340(5)	0.062(6)	0.08(2)
C(305)	0.162(5)	−0.303(5)	−0.044(6)	0.10(2)
C(306)	0.161(3)	−0.191(3)	−0.026(4)	0.03(1)
O(01)	0.584(2)	0.226(2)	0.423(3)	0.05(1)
C(01)	0.089(6)	0.539(6)	0.229(7)	0.13(3)

41.04; H, 2.47; M$^+$, 1313 (mass spectrometry). $C_{45}H_{28}O_{11}P_2Ru_5$ calc.: C, 41.19; H, 215%; M, 1313. IR (cyclohexane): ν(CO) 2053m, 2025vs, 2017s, 2004m, 1990s, 1978m, 1962m, 1951w, 1939w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.29 (1H, dd, J(HP) = 12.9, J(HH) = 10.2 Hz, H(1)); 4.72 (1H, ddd, J(HP) = 7.3, J(HH) = 10.4, 10.4 Hz, H(2)); 5.46 (1H, d, J(HH) = 10.7 Hz, H(3)); 7.25–7.85 (25H, m, Ph). FAB MS: m/z 1313 [M]$^+$; 1285–1005 [M − nCO]$^+$(n = 1–11); 928 [M − 11CO − Ph]$^+$; 851 [M − 11CO − 2Ph]$^+$; 774 [M − 11CO − 3Ph]$^+$.

4.3. Reaction of 10 with P(OMe)$_3$

A solution of **10** (50 mg, 0.038 mmol) and P(OMe)$_3$ (150 ml of a 0.355 M solution in tetrahydrofuran, 0.053 mmol) in tetrahydrofuran (20 ml) was heated for 3.5 h at 40°C. The solvent was removed and the residue purified by preparative TLC (petroleum ether/acetone 2:1) to yield three major bands. A dark brown band (R_f 0.50) was recrystallized (CH_2Cl_2/MeOH) to yield black crystals of **11** (13 mg, 24%), m.p. 211–214°C (dec.). Anal. Found: C, 39.76; H, 2.72; M$^+$, 1409 (mass spectrometry). $C_{47}H_{37}O_{13}P_3Ru_5$ calc.: C, 40.14; H, 2.60%; M, 1409. IR (cyclohexane): ν(CO) 2035m, 2011vs, 2004s, 1982s, 1969m, 1945m, 1939w, 1927m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.22 (1H, dd, J(HP) = 12.9, J(HH) = 10.1 Hz, H(1)); 3.32 (9H, d, J(HP) = 11.8 Hz, P(OMe)$_3$); 4.79 (1H, ddd, J(HP) = 7.0, J(HH) = 10.3, 10.3 Hz, H(2)); 5.44 (1H, d, J(HH) = 10.6 Hz, H(3)); 7.23–7.91 (25H, m, Ph). FAB MS: m/z 1409, [M]$^+$; loss of 10 CO groups. A yellow band (R_f 0.45) was recrystallized (CH_2Cl_2/MeOH) to yield orange crystals of **12** (34 mg, 64%), m.p. 192–198°C (dec.). Anal. Found: C, 39.84; H, 2.63%; M$^+$, 1437 (mass spectrometry). $C_{48}H_{37}O_{14}P_3Ru_5 \cdot 0.3CH_2Cl_2$ calc.: C, 40.09; H, 2.65%; M, 1437. IR (cyclohexane): ν(CO) 2050m, 2024s, 2001vs, 1995sh, 1981m, 1967m, 1947m, 1924vw cm^{-1}. ^{1}H NMR ($CDCl_3$): Isomer 1: δ 2.74 (1H, d, J(HH) = 8.8 Hz, H(3)); 3.82 (9H, d, J(HP) = 11.3 Hz, P(OMe)$_3$);

TABLE 5. Non-hydrogen atom positional and isotropic displacement parameters for **11**

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.64822(4)	0.78802(2)	0.42511(2)	0.0357(2)
Ru(2)	0.88798(4)	0.74993(2)	0.41374(2)	0.0390(2)
Ru(3)	0.82245(4)	0.69187(2)	0.49937(2)	0.0365(2)
Ru(4)	0.56623(4)	0.65172(2)	0.41369(2)	0.0367(2)
Ru(5)	0.63359(4)	0.71780(2)	0.32163(2)	0.0382(2)
C(11)	0.6967(6)	0.8644(3)	0.3978(3)	0.054(3)
O(11)	0.7173(5)	0.9147(2)	0.3815(2)	0.081(2)
C(12)	0.6840(5)	0.8216(3)	0.5034(3)	0.052(3)
O(12)	0.7022(4)	0.8472(2)	0.5472(2)	0.076(2)
C(21)	1.0070(6)	0.7008(3)	0.3951(3)	0.062(3)
O(21)	1.0791(5)	0.6715(3)	0.3823(2)	0.098(3)
C(22)	0.9424(6)	0.8248(3)	0.3838(3)	0.056(3)
O(22)	0.9751(5)	0.8695(2)	0.3657(2)	0.089(3)
C(31)	0.9005(6)	0.6089(3)	0.5212(3)	0.055(3)
O(31)	0.9421(5)	0.5575(2)	0.5338(2)	0.087(3)
C(32)	0.8088(5)	0.7034(3)	0.5736(3)	0.053(3)
O(32)	0.7989(5)	0.7099(2)	0.6179(2)	0.080(2)
C(41)	0.5921(5)	0.6194(3)	0.4902(3)	0.055(3)
O(41)	0.5943(4)	0.5919(3)	0.5313(2)	0.086(2)
C(42)	0.6090(6)	0.5695(3)	0.3907(3)	0.061(3)
O(42)	0.6286(6)	0.5187(2)	0.3786(3)	0.107(3)
C(51)	0.4555(6)	0.7094(3)	0.2655(2)	0.049(2)
O(51)	0.3496(4)	0.7025(2)	0.2308(2)	0.068(2)
C(52)	0.6720(6)	0.7863(3)	0.2794(3)	0.064(3)
O(52)	0.6910(6)	0.8277(3)	0.2526(2)	0.108(3)
C	0.7261(4)	0.6987(2)	0.4082(2)	0.036(2)
C(1)	0.4049(5)	0.7327(3)	0.4098(2)	0.042(2)
C(2)	0.3551(4)	0.6795(2)	0.3688(2)	0.038(2)
C(3)	0.3495(5)	0.6162(3)	0.3907(2)	0.045(2)
P(1)	0.4292(1)	0.81282(7)	0.38955(6)	0.0400(5)
C(111)	0.3192(5)	0.8290(3)	0.3120(2)	0.045(2)
C(112)	0.3673(6)	0.8582(3)	0.2735(3)	0.059(3)
C(113)	0.2828(8)	0.8710(3)	0.2151(3)	0.078(4)
C(114)	0.1517(8)	0.8531(4)	0.1947(3)	0.085(4)
C(115)	0.1047(7)	0.8246(4)	0.2322(3)	0.079(3)
C(116)	0.1877(6)	0.8121(3)	0.2911(3)	0.060(3)
C(121)	0.3738(5)	0.8708(3)	0.4305(3)	0.049(2)
C(122)	0.3583(9)	0.8565(4)	0.4802(4)	0.099(5)
C(123)	0.324(1)	0.9057(5)	0.5121(4)	0.116(6)
C(124)	0.3070(9)	0.9667(5)	0.4938(4)	0.101(5)
C(125)	0.320(1)	0.9820(4)	0.4435(5)	0.155(8)
C(126)	0.351(1)	0.9330(4)	0.4110(4)	0.129(7)
C(131)	0.2917(5)	0.5591(3)	0.3521(3)	0.047(2)
C(132)	0.2247(6)	0.5134(3)	0.3718(3)	0.063(3)
C(133)	0.1634(7)	0.4600(3)	0.3366(4)	0.086(4)
C(134)	0.1736(7)	0.4496(3)	0.2836(4)	0.078(4)
C(135)	0.2430(8)	0.4925(4)	0.2648(3)	0.083(4)
C(136)	0.2996(7)	0.5477(3)	0.2984(3)	0.066(3)
P(2)	1.0078(1)	0.75385(7)	0.51548(6)	0.0433(6)
C(211)	1.1751(5)	0.7190(3)	0.5492(3)	0.052(2)
C(212)	1.1971(6)	0.6563(3)	0.5330(3)	0.061(3)
C(213)	1.3230(8)	0.6295(4)	0.5560(3)	0.080(4)
C(214)	1.4273(7)	0.6659(5)	0.5962(3)	0.096(4)
C(215)	1.4081(7)	0.7263(5)	0.6125(3)	0.087(4)
C(216)	1.2810(6)	0.7546(4)	0.5890(3)	0.069(3)
C(221)	1.0235(5)	0.8296(3)	0.5583(3)	0.049(2)
C(222)	1.0514(6)	0.8264(3)	0.6186(3)	0.064(3)
C(223)	1.0578(7)	0.8829(4)	0.6508(3)	0.084(4)
C(224)	1.0366(9)	0.9421(4)	0.6234(4)	0.096(4)

TABLE 5 (continued)

Atom	x	y	z	U_{eq} (Å^2)
C(225)	1.0108(9)	0.9458(3)	0.5651(4)	0.102(5)
C(226)	1.0035(7)	0.8899(3)	0.5314(3)	0.073(3)
P(3)	0.6902(2)	0.63462(9)	0.27560(8)	0.0670(8)
O(311)	0.5719(8)	0.5869(4)	0.2409(4)	0.200(5)
C(311)	0.519(2)	0.5535(7)	0.1955(7)	0.26(1)
O(321)	0.7932(7)	0.5868(3)	0.3181(3)	0.145(4)
C(321)	0.863(1)	0.5409(6)	0.3274(9)	0.29(1)
O(331)	0.739(1)	0.6485(4)	0.2288(5)	0.27(1)
C(331)	0.825(2)	0.671(1)	0.2167(9)	0.33(2)

3.99 (1H, d, J(HH) = 11.4 Hz, H(1)); 6.31 (1H, ddd, J(HH) = 8.7, 11.3 Hz, J(HP) = 8.5 Hz, H(2)); 7.12–8.07 (m, Ph); Isomer 2: 2.69 (0.3H, dd, J(HH) = 9.0 Hz, J(HP) = 3.1 Hz, H(3)); 3.62 (2.7H, d, J(HP) = 10.6 Hz, $P(OMe)_3$); 4.09 (0.3H, d, J(HH) = 10.4 Hz, H(1)); 7.12–7.18 (m, H(2) + Ph); 7.21–8.07 (m, Ph). FAB MS: m/z 1436, M^+; loss of 11 CO groups.

4.4. Conversion of 12 into 11

A solution of **12** (12 mg, 0.0084 mmol) was heated in toluene (15 ml) at 90°C for 2.5 h with a nitrogen purge. The solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 10 : 3) to give black **11** (9.0 mg, 75%), identified by TLC, IR and FAB MS).

4.5. Reaction of 11 with CO

A solution of **11** (17 mg, 0.012 mmol) in toluene (15 ml) was heated at 90°C for 20 min with a CO purge. Apart from the formation of a minor red product (not **12**), which has not been otherwise identified, only starting material (9.4 mg, 55%) was recovered.

5. Crystallography

Unique data sets were measured at *ca.* 295 K within the limit $2\theta_{max} = 50°$ using Syntex $P2_1$ and Enraf–Nonius CAD4 diffractometers (2θ–θ scan mode; monochromatic Mo Kα radiation, λ 0.7107$_3$ Å); N independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered "observed" and used in the full matrix least squares refinement after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals R, R' on $|F|$ are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computation used the XTAL 2.6 program system [13] implemented by Hall; neutral atom complex scattering factors were employed. Pertinent results are given in the figures and tables. Structure factor amplitudes, thermal and hydrogen atom parameters and full

TABLE 6. Non-hydrogen atom positional and isotropic displacement parameters for **12**

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.28502(8)	0.86432(7)	0.69605(3)	0.0512(4)
Ru(2)	0.35953(9)	0.70799(7)	0.65651(3)	0.0581(4)
Ru(3)	0.16324(8)	0.69895(7)	0.60066(3)	0.0510(4)
Ru(4)	0.29959(8)	0.86026(7)	0.60341(3)	0.0484(4)
Ru(5)	0.04985(8)	0.80990(7)	0.66139(3)	0.0456(3)
C(11)	0.268(1)	0.8138(9)	0.7507(4)	0.077(6)
O(11)	0.263(1)	0.7844(9)	0.7839(3)	0.135(6)
C(12)	0.255(1)	0.9848(9)	0.7126(4)	0.073(6)
O(12)	0.2474(9)	1.0583(7)	0.7250(3)	0.109(5)
C(13)	0.438(1)	0.879(1)	0.7127(4)	0.091(7)
O(13)	0.5346(8)	0.8868(9)	0.7245(4)	0.134(6)
C(21)	0.332(1)	0.6228(9)	0.6958(4)	0.087(6)
O(21)	0.3182(9)	0.5666(7)	0.7193(3)	0.127(6)
C(22)	0.514(1)	0.693(1)	0.6769(4)	0.094(7)
O(22)	0.6099(9)	0.6771(9)	0.6869(4)	0.153(7)
C(31)	0.083(1)	0.6003(8)	0.6181(4)	0.075(6)
O(31)	0.0375(9)	0.5405(6)	0.6297(3)	0.111(5)
C(32)	0.089(1)	0.6897(8)	0.5455(4)	0.068(5)
O(32)	0.0442(9)	0.6802(7)	0.5094(3)	0.103(5)
C(41)	0.458(1)	0.8404(9)	0.6190(4)	0.076(6)
O(41)	0.5536(7)	0.8498(6)	0.6197(3)	0.090(4)
C(42)	0.287(1)	0.8283(8)	0.5453(4)	0.064(5)
O(42)	0.2782(8)	0.8180(7)	0.5080(3)	0.094(4)
C(51)	0.0758(9)	0.7130(9)	0.7023(3)	0.060(5)
O(51)	0.0874(8)	0.6570(6)	0.7264(3)	0.090(4)
C(52)	−0.077(1)	0.7525(9)	0.6323(3)	0.062(5)
O(52)	−0.1551(7)	0.7119(6)	0.6165(3)	0.094(4)
C	0.2184(9)	0.7892(8)	0.6463(3)	0.051(4)
C(1)	0.1521(8)	0.9459(7)	0.5828(3)	0.042(4)
C(2)	0.2386(9)	1.0015(7)	0.6033(3)	0.052(5)
C(3)	0.3364(9)	1.0090(7)	0.5835(4)	0.052(5)
P(1)	0.0254(3)	0.9292(2)	0.6077(1)	0.045(1)
C(111)	−0.0132(8)	1.0470(7)	0.6181(3)	0.044(4)
C(112)	0.015(1)	1.0863(8)	0.6583(3)	0.058(5)
C(113)	−0.005(1)	1.1774(9)	0.6639(4)	0.083(6)
C(114)	−0.049(1)	1.2288(8)	0.6302(4)	0.080(6)
C(115)	−0.077(1)	1.1913(9)	0.5898(4)	0.073(6)
C(116)	−0.060(1)	1.1016(8)	0.5840(4)	0.057(5)
C(121)	−0.0834(9)	0.9014(7)	0.5633(3)	0.049(4)
C(122)	−0.196(1)	0.9031(9)	0.5696(4)	0.067(5)
C(123)	−0.2818(9)	0.8776(9)	0.5396(4)	0.070(6)
C(124)	−0.258(1)	0.8487(8)	0.4990(4)	0.075(6)
C(125)	−0.148(1)	0.8477(8)	0.4915(4)	0.062(5)
C(126)	−0.0632(9)	0.8734(8)	0.5221(4)	0.058(5)
C(131)	0.437(1)	1.0578(8)	0.6018(4)	0.058(5)
C(132)	0.460(1)	1.0877(9)	0.6434(4)	0.068(5)
C(133)	0.553(1)	1.141(1)	0.6589(4)	0.080(6)
C(134)	0.625(1)	1.164(1)	0.6291(5)	0.095(7)
C(135)	0.606(1)	1.134(1)	0.5887(5)	0.097(7)
C(136)	0.514(1)	1.081(1)	0.5736(5)	0.086(6)
P(2)	0.3217(3)	0.6161(2)	0.5973(1)	0.066(1)
C(211)	0.313(1)	0.4940(9)	0.6031(3)	0.068(6)
C(212)	0.388(1)	0.449(1)	0.6317(5)	0.116(9)
C(213)	0.382(2)	0.355(1)	0.6380(6)	0.15(1)
C(214)	0.300(2)	0.310(1)	0.6135(7)	0.15(1)
C(215)	0.218(2)	0.351(1)	0.5876(6)	0.14(1)
C(216)	0.226(1)	0.446(1)	0.5806(5)	0.111(8)
C(221)	0.402(1)	0.6245(9)	0.5508(5)	0.100(7)
C(222)	0.515(1)	0.647(1)	0.5599(6)	0.121(9)

TABLE 6 (continued)

Atom	x	y	z	U_{eq} (Å^2)
C(223)	0.577(2)	0.652(1)	0.5249(6)	0.17(1)
C(224)	0.527(2)	0.634(1)	0.4855(7)	0.19(1)
C(225)	0.414(2)	0.612(1)	0.4762(5)	0.17(1)
C(226)	0.350(2)	0.606(1)	0.5101(5)	0.129(9)
P(3)	−0.0540(3)	0.8793(2)	0.7075(1)	0.060(1)
O(311)	−0.002(1)	0.9527(7)	0.7406(3)	0.110(5)
C(311)	0.037(1)	0.499(1)	0.7831(4)	0.104(8)
O(321)	−0.1478(7)	0.9293(6)	0.6794(3)	0.075(4)
C(321)	−0.231(1)	0.994(1)	0.6954(6)	0.126(9)
O(331)	−0.1054(7)	0.8101(6)	0.7380(3)	0.082(4)
C(331A) [a]	−0.187(2)	0.752(2)	0.726(1)	0.12(2)
C(331B) [a]	−0.197(2)	0.820(2)	0.7618(9)	0.10(1) [a]
Cl(1) [b]	−0.281(3)	0.441(3)	0.633(1)	0.42(3) [a]
Cl(2) [b]	−0.151(3)	0.475(3)	0.562(1)	0.41(3) [a]
C(0) [b]	−0.230(6)	0.509(8)	0.602(3)	0.34(8) [a]

[a] Site occupancy factor = 0.5. [b] site occupancy factor = 0.3. [c] Isotropic thermal parameter.

non-hydrogen geometries are available from the authors.

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