Cluster chemistry XCVIII [*]. Formation of an Ru$_5$-dicarbon complex: X-ray structures of Ru$_5$(μ_5-C$_2$)(μ-PPh$_2$)$_2$(μ-Cl)$_2$(CO)$_{11}$ and Ru$_5$(μ-H){μ_5-CC(PPh$_2$)}(μ-Cl)(μ-PPh$_2$)(CO)$_{12}$

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Abstract

Reaction of Ru$_5$(μ_5-C$_2$PPh$_2$)(μ-PPh$_2$)(CO)$_{13}$ (1) with 5-chloro-4-chloromethyl-2,4-dimethylpent-1-ene in refluxing CHCl$_3$ affords Ru$_5$(μ_5-C$_2$)(μ-PPh$_2$)$_2$(μ-Cl)$_2$(CO)$_{11}$ (3) and Ru$_5$(μ-H){μ_5-CC(PPh$_2$)}(μ-Cl)(μ-PPh$_2$)(CO)$_{12}$ (4). The crystal structures of 3 and 4 were determined by X-ray crystallography. Complex 3 is the second example of a cluster containing a C$_2$ ligand sitting on top of a partially disordered puckered pentagonal Ru$_5$ cluster, with one carbon strongly bonded (σ) to one Ru atom (Ru-C, 1.937 (9) Å) with the C$_2$ moiety interacting in π fashion with the other four metal atoms. Complex 4 retains the C$_2$PPh$_2$ ligand of the precursor, sitting on an "open-envelope" Ru$_5$ cluster; one carbon is strongly bonded to four Ru atoms of a pseudosquare Ru$_4$ array.

Keywords: Ruthenium; Cluster; Dicarbon complex; Crystal structure

1. Introduction

We have described the addition of dimethyl disulphide to Ru$_5$(μ_5-C$_2$PPh$_2$)(μ-PPh$_2$)(CO)$_{13}$ (1) (Scheme 1) which results in a complex reaction sequence ending with the formation of the unusual complex 2, in which a C$_2$ ligands sits atop an Ru$_5$ pentagon; two PPh$_2$ and two SMe ligands bridge various edges and a face of the pentagon, which has a puckered conformation [2]. The C$_2$ cluster 2 is a source of many unusual complexes [3], but the presence of the PPh$_2$ and SMe groups sometimes masks the reactivity of the dicarbon fragment.

In the course of studies of reactions between 1 and unsaturated hydrocarbons and related molecules, we looked at the reactions of allyl halides. Part of this work has already been published, describing unusual coupling products involving the allyl group, while the halogen atom also adds to the cluster, bridging an Ru–Ru bond [4]. Initially, we could not obtain chloro complexes analogous to those obtained from the bromide; we subsequently found that our sample of "allyl chloride"

contained largely its photo-dimer, 5-chloro-4-chloromethyl-2,4-dimethylpent-1-ene [5]. This molecule reacts with 1 to give 3, which is an analogue of 2 containing Cl groups in place of SMe, as described below. We have also isolated a monochloro complex 4 in which the C–P bond in the original C$_2$PPh$_2$ ligand is retained.

2. Results

The reaction between 5-chloro-4-chloromethyl-2,4-dimethylpent-1-ene and 1 was carried out in refluxing chloroform for 30 h. Purification by preparative thin layer chromatography (TLC) afforded two major fractions, from which black crystals of 3 and orange crystals of 4 were obtained with 31% and 23% yields respectively. Their molecular structures were determined by single-crystal X-ray diffractometry.

2.1. Molecular structure of Ru$_5$(μ_5-C$_2$)(μ-PPh$_2$)$_2$(μ-Cl)$_2$(CO)$_{11}$ (3)

A molecule of 3 is depicted in Fig. 1. As can be seen, the cluster is a direct analogue of 2 and related

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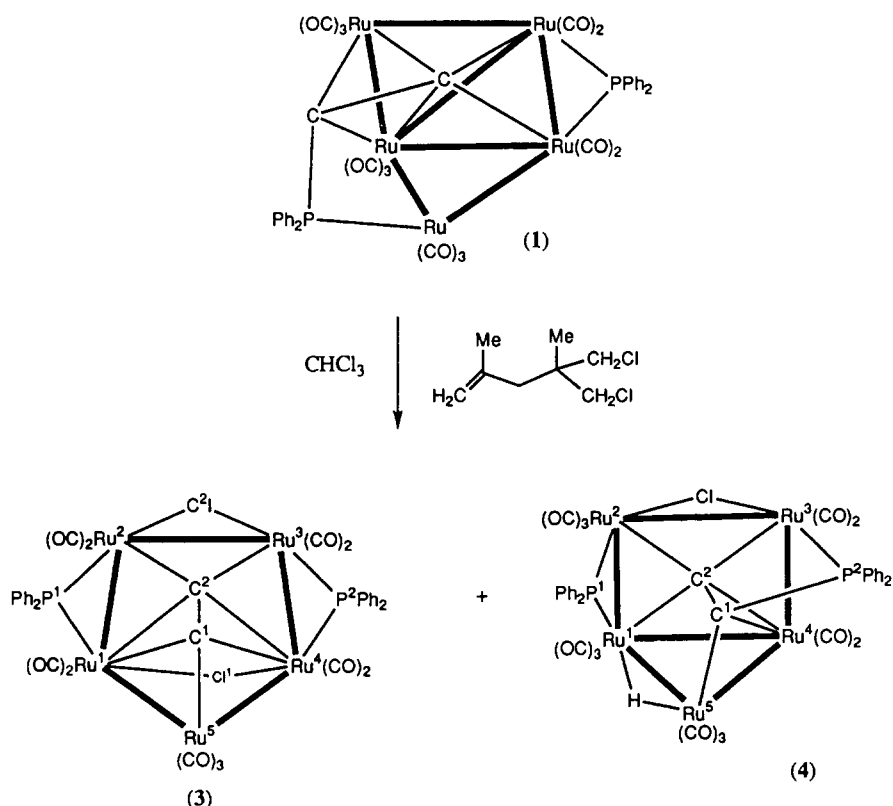
Scheme 1.

structural parameters of both complexes are collected in Table 1 to emphasize this point. Unlike 2, however, atoms Ru(3) and Ru(4) are disordered; the attached ligand atoms can only be modelled disposed in unique positions, albeit with high thermal motion, perhaps a foil for disorder among them also. The pentagon of Ru atoms (Ru–Ru separations range between 2.816(3) and 2.942(6) Å) adopts the open-envelope conformation, with Ru(1)–Ru(4)–Ru(5) forming the flap and Ru(1–4) forming the body of the envelope. Description of the two disordered components as distinct planes Ru(1,4,2A/B,3A/B) is possible (χ^2 (plane A) and χ^2 (plane B) being 175 and 0.8 respectively, with no atom deviant from its plane by more than 0.02 Å) but these two planes make quite different dihedral angles with Ru(1,4,5) (142.30(4) and 130.25(4)° respectively). The separation Ru(1) · · · Ru(4), at 3.422(2) Å, may be considered as non-bonding and is bridged by Cl(1) (Ru(1,4)–Cl(1), 2.473(3) and 2.447(3) Å), while Cl(2) bridges the Ru(2)–Ru(3) vector (Ru(2,3)–Cl(2) range between 2.155(4) and 2.618(4) Å). The pairs designated as A are short (Ru(2,3A)–Cl(2), 2.167(3) and 2.155(4) Å) and the B pairs are long (2.613(3) and 2.618(4) Å), suggesting that the seductively planar arrays with symmetrically bridging Cl(2) atoms may not be the appro-

priate model. Bonds Ru(1)–Ru(2) and Ru(3)–Ru(4) are bridged by the PPh$_2$ groups (Ru–P range between 2.075(4) and 2.478(3) Å). Both Ru–Cl and Ru–P distances are thus obviously affected by the disorder and "sensible" values (about 2.45 and 2.33 Å respectively), suggesting that the five-membered Ru$_5$ ring is puckered and probably undergoing some fluxional process, as found in other five-membered cyclic systems [6].

The C$_2$ ligand sits on the "open" side of the Ru$_5$ ring, being most closely attached to Ru(5) (Ru(5)–C(1), 1.931(9) Å) and Ru(2) and Ru(3) (separation from C(2), 2.07–2.29(1) Å), both carbon atoms also interacting with Ru(1) and Ru(4) (Ru(1)–C(1,2), 2.22 and 2.40(1) Å; Ru(4)–C(1,2), 2.246(9) and 2.42(1) Å). The C(1)–C(2) separation is 1.32(1) Å. 11 terminal CO ligands complete the coordination about the five metal atoms. The cluster contains 80 valence electrons as expected for an M$_5$ cluster with five M–M bonds.

2.2. Molecular structure of Ru$_5$H{μ$_5$-CC(PPh$_2$)}(μ-Cl)(μ-PPh$_2$)(CO)$_{12}$ (4)

A molecule of 4 is depicted in Fig. 2 and selected bond parameters are given in Table 2. In this cluster, the Ru$_5$ core also adopts an open-envelope conformation,

Fig. 1. (a) Plot of a molecule of Ru$_5$(μ$_5$-C$_2$)(μ-PPh$_2$)$_2$(μ-Cl)$_2$(CO)$_{11}$ (3) showing the atom-numbering scheme. (b) Plot of a molecule of Ru$_5$(μ$_4$-CCH(PPh$_2$))(μCl)(μ-PPh$_2$)(CO)$_{12}$ (4) similarly. Both projections are normal to the Ru$_4$ plane. Non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

(a)

(b)
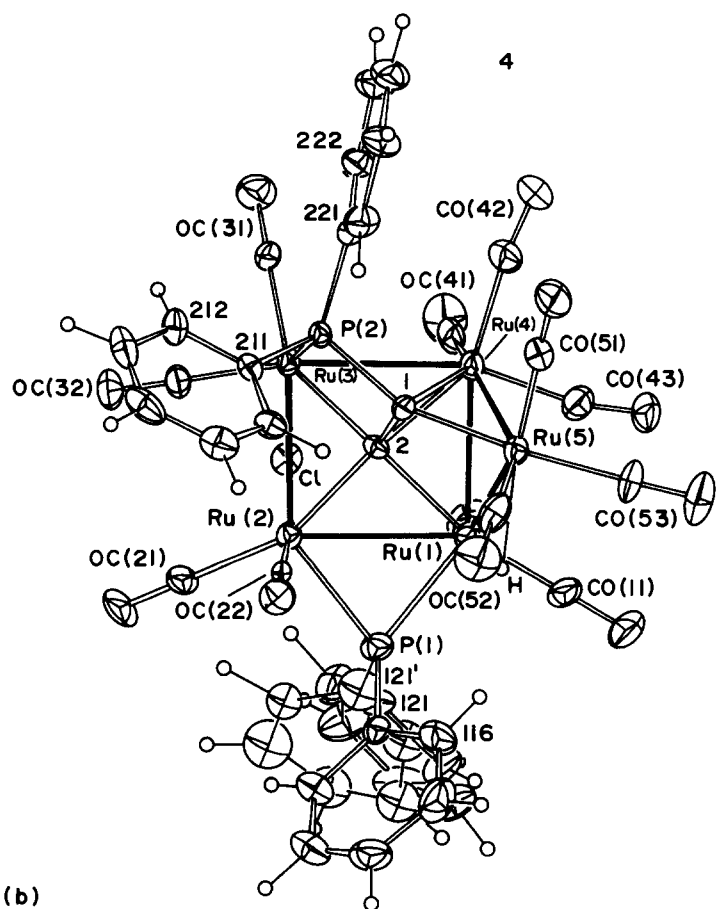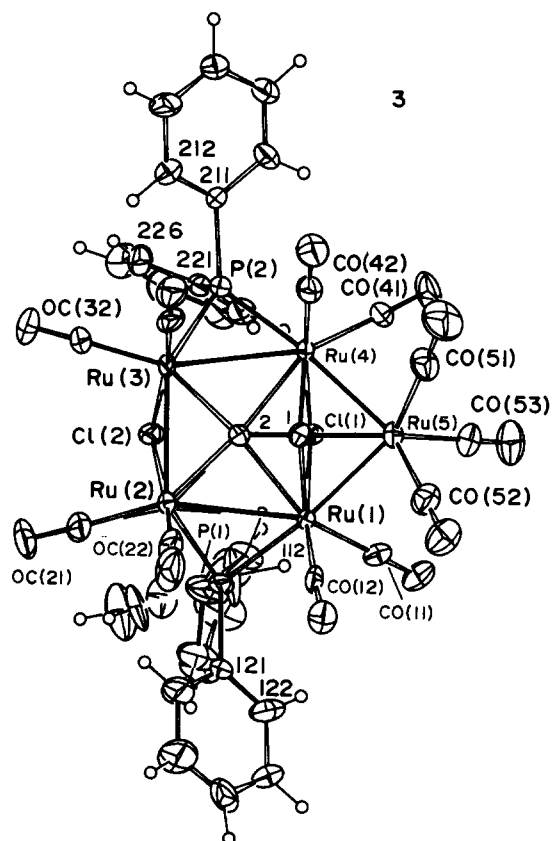
but with the two Ru atoms which form the hinge now within bonding distance (Ru(1)–Ru(4), 2.789(2) Å). Atoms Ru(1)–Ru(4)–Ru(5) form the flap while the body is formed from atoms Ru(1–4) (Ru–Ru distances range between 2.789(2) and 3.029(2) Å); the dihedral between the flap and the body is 107.63(4)°. Edges Ru(1)–Ru(2) and Ru(2)–Ru(3) are bridged symmetrically by PPh_2 (of which Ph(2) is rotationally disordered) and Cl respectively (Ru(1,2)–P(1), 2.290 and 2.295(3) Å; Ru(2,3)–Cl 2.482, 2.489(3) Å). The longest Ru–Ru vector is bridged by an H atom, which was suggested by difference map residues between Ru(1) and Ru(5) (see Section 4).

The remaining ligand is attached through P(2) to Ru(3) (Ru(3)–P(2), 2.291(3) Å) and the C_2 moiety interacts strongly with Ru(1–4) via C(2) (Ru(1–4)–C(2), 2.19, 2.10, 2.11 and 2.11(2) Å) and C(1), which bridges the Ru(4)–Ru(5) vector (Ru(4,5)–C(1), 2.20 and 2.04(1) Å). Approximately, the interaction of the C_2 unit with the cluster can be described as similar to the usual $2\sigma,\pi(\|)$ alkyne interaction with an Ru_3 cluster. However, the C(1) substituent is strongly bent back (C(2)–C(1)–P(2), 99.5(7)°) by virtue of coordination of P(2) to Ru(3). Consequently, we have considered whether the ligand is best described as a vinylidene [$CCH(PPh_2)$] or as a distorted acetylide [$C_2(PPh_2)$].

The geometry of the Ru_4–C_2PPh_2 part of this complex strongly resembles that found in the complex $Ru_5(\mu\text{-}H)\{\mu_5\text{-}CC(PPh_2)\}(\mu\text{-}SPh)(\mu\text{-}PPh_2)(CO)_{12}$ (5), described earlier [7], as is clearly shown by the compar-

Table 1
Selected bond parameters for $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu\text{-}X)_2(CO)_{11}$ (X = Cl (3) or SMe (1) [2])

	Bond length (Å)			Bond length (Å)	
	3	1		3	1
Ru(1)–Ru(5)	2.845(1)	2.890(1)	Ru(2B)–Cl(2)	2.613(3)	
Ru(4)–Ru(5)	2.860(1)	2.898(1)	Ru(3A)–Cl(2)	2.155(4)	2.387(1) (S)
Ru(1)–Ru(2A)	2.816(2)	2.882(1)	Ru(3B)–Cl(2)	2.618(4)	
Ru(1)–Ru(2B)	2.939(2)		Ru(5)–C(1)	1.931(9)	1.938(4)
Ru(2A)–Ru(2B)	0.641(2)		Ru(1)–C(1)	2.22(1)	2.261(4)
Ru(2A)–Ru(3A)	2.873(3)	2.855(2)	Ru(4)–C(1)	2.246(9)	2.232(4)
Ru(2A)–Ru(3B)	2.942(3)		Ru(1)–C(2)	2.40(1)	2.410(4)
Ru(2B)–Ru(3A)	2.859(2)		Ru(2A)–C(2)	2.29(1)	2.134(4)
Ru(2B)–Ru(3B)	2.798(2)		Ru(2B)–C(2)	2.07(1)	
Ru(3A)–Ru(3B)	0.583(2)		Ru(3A)–C(2)	2.25(1)	2.132(4)
Ru(3A)–Ru(4)	2.855(2)	2.898(1)	Ru(3B)–C(2)	2.07(1)	
Ru(3B)–Ru(4)	2.921(2)		Ru(4)–C(2)	2.42(1)	2.471(3)
Ru(1)–P(1)	2.332(3)	2.341(1)	C(1)–C(2)	1.32(1)	1.305(5)
Ru(2A)–P(1)	2.075(4)	2.294(1)	Ru(2A)–C(21)	1.93(2)	
Ru(2B)–P(1)	2.472(4)		Ru(2B)–C(21)	1.92(2)	
Ru(3A)–P(2)	2.161(4)	2.290(1)	Ru(2A)–C(22)	2.13(1)	
Ru(3B)–P(2)	2.478(3)		Ru(2B)–C(22)	1.60(1)	
Ru(4)–P(2)	2.345(3)	2.341(1)	Ru(3A)–C(31)	2.13(1)	
Ru(1)–Cl(1)	2.473(3)	2.449(2) (S)	Ru(3B)–C(31)	1.63(1)	
Ru(4)–Cl(1)	2.447(3)	2.454(1) (S)	Ru(3A)–C(32)	1.89(1)	
Ru(2A)–Cl(2)	2.167(3)	2.392(2) (S)	Ru(3B)–C(32)	1.92(1)	

	Range (Å) for 3
Ru–CO	1.86–1.92(1), average 1.88 (excluding CO groups attached to disordered Ru atoms)
C–O	1.12–1.15(2), average 1.14
P–C(Ph)	1.75–1.83(1), average 1.80

	Bond angle (°)			Bond angle (°)	
	3	1		3	1
Ru(5)–Ru(1)–Ru(2A)	125.92(5)	119.29(2)	Ru(1)–Ru(2A)–Ru(3A)	95.40(7)	95.38(2)
Ru(5)–Ru(1)–Ru(2B)	116.87(4)		Ru(1)–Ru(2B)–Ru(3B)	95.71(5)	
Ru(5)–Ru(4)–Ru(3A)	123.88(4)	117.51(2)	Ru(2A)–Ru(3A)–Ru(4)	95.69(6)	96.39(2)
Ru(5)–Ru(4)–Ru(3B)	116.64(4)		Ru(2B)–Ru(3B)–Ru(4)	96.51(5)	
Ru(1)–Ru(5)–Ru(4)	73.71(4)	73.14(4)			

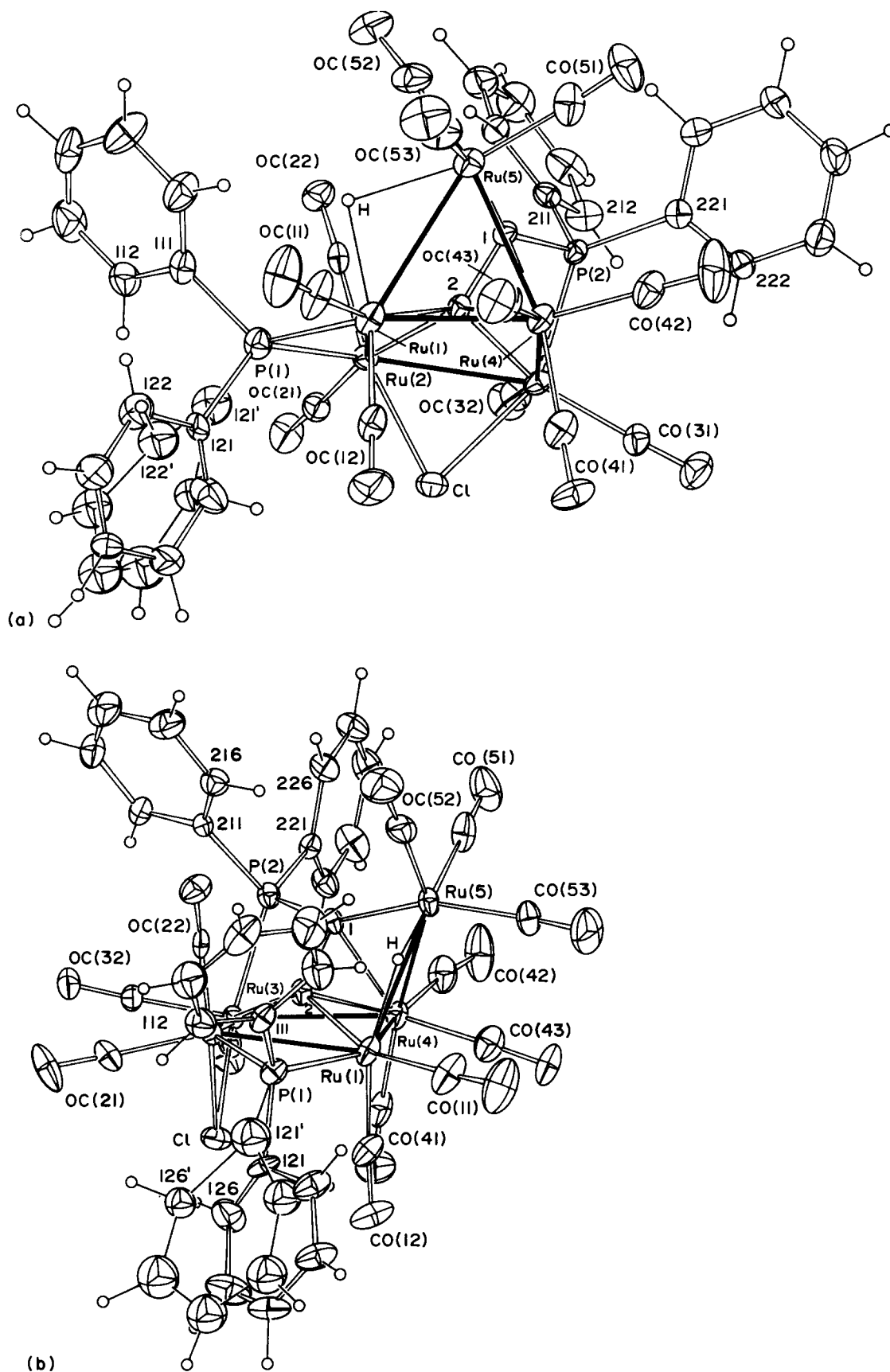|	Dihedral angle (°)	
	3	1
(Ru(1)–Ru(4)–Ru(5))–(Ru(1)–Ru(2A)–Ru(3A)–Ru(4))	142.30(4)	132.21(1)
(Ru(1)–Ru(4)–Ru(5))–(Ru(1)–Ru(2B)–Ru(3B)–Ru(4))	130.25(4)	

Fig. 2. (a) A projection of **4**, normal to the Ru$_3$ plane. (b) A projection of **4**, oblique. Both (a) and (b) show the putative hydrogen location and its environment.

Table 2
Selected bond parameters) for Ru$_5$(μ-H)(μ$_5$-CC(PPh$_2$))(μ-X)(μ-PPh$_2$)(CO)$_{12}$(X = Cl (4) in SPh (5) [7])

	Bond lengths (Å)			Bond length (Å)	
	4	**5**		**4**	**5**
Ru(1)–Ru(2)	2.860(2)	2.900(1)	Ru(3)–P(2)	2.291(3)	2.337(3)
Ru(1)–Ru(4)	2.789(2)	2.806(2)	Ru(1)–C(2)	2.194(8)	2.209(9)
Ru(1)–Ru(5)	3.029(2)	2.992(2)	Ru(2)–C(2)	2.10(1)	2.129(9)
Ru(2)–Ru(3)	2.831(2)	2.821(2)	Ru(3)–C(2)	2.112(9)	2.103(9)
Ru(3)–Ru(4)	2.956(2)	2.940(1)	Ru(4)–C(1)	2.20(1)	2.207(9)
Ru(4)–Ru(5)	2.829(2)	2.807(1)	Ru(4)–C(2)	2.11(1)	2.155(9)
Ru(2)–Cl	2.482(3)	2.447(3) (S)	Ru(5)–C(1)	2.04(1)	2.032(9)
Ru(3)–Cl	2.489(3)	2.402(3) (S)	Ru(1)–H	1.97(9)	
Ru(1)–P(1)	2.290(4)	2.296(3)	Ru(5)–H	2.07(9)	
Ru(2)–P(1)	2.295(3)	2.293(3)	C(1)–C(2)	1.44(2)	1.44(1)

	Range (Å)
Ru–CO	1.82(1)–1.93(1), average 1.87
C–O	1.11(2)–1.18(2), average 1.15
P–C(Ph)	1.80(2)–1.83(1), average 1.81

	Bond angle (°)			Bond angle (°)	
	4	**5**		**4**	**5**
Ru(2)–Ru(1)–Ru(4)	91.55(4)	91.34(4)	Ru(2)–Ru(3)–Ru(4)	88.73(4)	90.22(4)
Ru(2)–Ru(1)–Ru(5)	102.17(4)		Ru(1)–Ru(4)–Ru(3)	88.72(5)	88.70(4)
Ru(4)–Ru(1)–Ru(5)	58.02(4)	57.80(4)	Ru(1)–Ru(4)–Ru(5)	65.26(4)	64.43(5)
Ru(1)–Ru(2)–Ru(3)	89.86(4)	89.22(4)	Ru(1)–Ru(5)–Ru(4)	56.73(4)	57.77(4)

	Dihedral (°)
Ru(1, 2, 3, 4)–Ru(1, 4, 5)	107.63(4)

ative data listed in Table 2. Complex **5** was obtained from reactions between **1** and PhSH, which also afforded the related vinylidene complex Ru$_5${μ$_4$-

CCH(PPh$_2$)}(μ-SPh)(μ-PPh$_2$)(CO)$_{12}$ (**6**), so that a direct comparison between the two is possible (Scheme 2). Apart from the obvious change in conformation, the

(2)

(5)

(6)

(7)
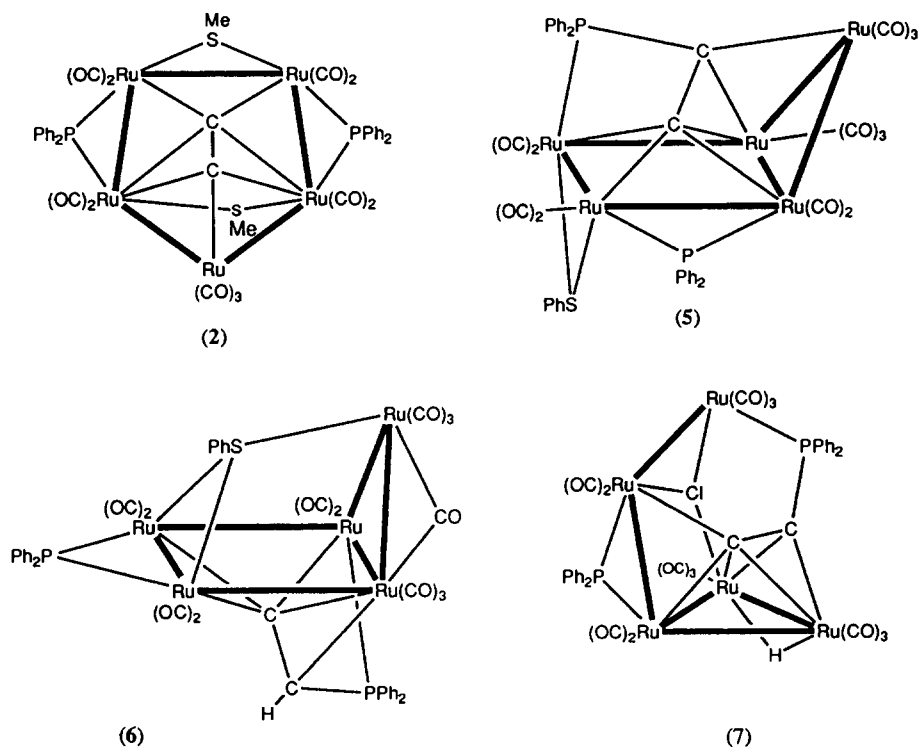
Scheme 2.

Table 3
Non-hydrogen positional and isotropic displacement parameters for **3**

Atom	x/a	y/b	z/c	U_{eq} (Å^{-2})
Ru(1)	0.28806(4)	0.90083(5)	0.41711(5)	0.0449(3)
Ru(2A) [a]	0.20769(9)	1.0540(1)	0.3792(1)	0.0612(7)
Ru(2B) [a]	0.23369(7)	1.07904(7)	0.39722(9)	0.0334(5)
Ru(3A) [a]	0.25073(9)	1.09464(9)	0.21139(9)	0.0543(6)
Ru(3B) [a]	0.27489(7)	1.11441(8)	0.2324(1)	0.0412(5)
Ru(4)	0.33817(4)	0.94543(5)	0.21562(5)	0.0474(3)
Ru(5)	0.42429(4)	0.87273(5)	0.38252(6)	0.0495(3)
Cl(1)	0.2434(1)	0.8580(2)	0.2524(2)	0.063(1)
Cl(2)	0.1541(2)	1.0397(2)	0.2336(2)	0.103(1)
C(11)	0.2862(5)	0.7831(6)	0.4425(6)	0.062(4)
O(11)	0.2796(4)	0.7102(4)	0.4518(5)	0.095(4)
C(12)	0.3324(5)	0.9225(6)	0.5408(6)	0.066(4)
O(12)	0.3598(4)	0.9318(5)	0.6169(5)	0.100(4)
C(21)	0.1572(9)	1.1573(9)	0.3975(8)	0.154(9)
O(21)	0.1179(7)	1.2112(7)	0.3996(7)	0.205(7)
C(22)	0.2793(8)	1.1080(7)	0.4975(8)	0.120(7)
O(22)	0.3158(6)	1.1382(6)	0.5636(6)	0.173(6)
C(31)	0.3460(7)	1.1683(6)	0.2284(7)	0.098(6)
O(31)	0.3973(5)	1.2086(5)	0.2319(6)	0.123(5)
C(32)	0.2123(8)	1.2046(9)	0.173(1)	0.142(8)
O(32)	0.1825(6)	1.2656(7)	0.1451(8)	0.200(7)
C(41)	0.3693(5)	0.8464(6)	0.1631(6)	0.063(4)
O(41)	0.3886(4)	0.7892(5)	0.1283(5)	0.108(4)
C(42)	0.4160(6)	1.0047(6)	0.1934(7)	0.078(5)
O(42)	0.4641(4)	1.0391(5)	0.1797(6)	0.121(5)
C(51)	0.5064(5)	0.8899(7)	0.3381(8)	0.091(5)
O(51)	0.5569(4)	0.9036(6)	0.3120(8)	0.151(6)
C(52)	0.4746(6)	0.8606(7)	0.5076(8)	0.086(5)
O(52)	0.5056(4)	0.8571(6)	0.5841(5)	0.119(4)
C(53)	0.4240(6)	0.7504(6)	0.3620(8)	0.082(5)
O(53)	0.4160(5)	0.6783(5)	0.3450(7)	0.137(5)
C(1)	0.3686(5)	0.9776(5)	0.3680(6)	0.060(4)
C(2)	0.3138(6)	1.0303(6)	0.3417(6)	0.069(4)
P(1)	0.1826(2)	0.9475(2)	0.4504(2)	0.082(1)
C(111)	0.0991(6)	0.9067(9)	0.3917(8)	0.110(6)
C(112A) [a]	0.085(1)	0.829(1)	0.315(2)	0.08(1)
C(113A) [a]	0.0195(9)	0.788(2)	0.271(2)	0.12(1)
C(114A) [a]	−0.026(2)	0.778(3)	0.306(2)	0.19(2)
C(115A) [a]	−0.024(1)	0.805(3)	0.396(2)	0.17(2)
C(116A) [a]	0.036(1)	0.863(2)	0.438(2)	0.14(2)
C(112B) [a]	0.089(1)	0.853(1)	0.352(2)	0.12(1)
C(113B) [a]	0.036(1)	0.814(2)	0.303(2)	0.12(1)
C(114B) [a]	−0.033(1)	0.866(2)	0.305(2)	0.11(1)
C(115B) [a]	−0.025(1)	0.939(2)	0.346(3)	0.17(2)
C(116B)	0.041(1)	0.967(2)	0.393(2)	0.12(1)
C(121)	0.1775(6)	0.9408(7)	0.5711(7)	0.083(5)
C(122)	0.1763(9)	0.8662(9)	0.6143(9)	0.148(9)
C(123)	0.177(1)	0.864(1)	0.709(1)	0.18(1)
C(124)	0.181(1)	0.937(1)	0.7569(9)	0.23(1)
C(125)	0.178(2)	1.010(1)	0.715(1)	0.33(2)
C(126)	0.182(1)	1.014(1)	0.623(1)	0.24(1)
P(2)	0.2663(2)	1.0233(2)	0.0923(2)	0.077(1)
C(211)	0.3090(6)	1.0661(7)	0.0047(7)	0.089(5)
C(212)	0.3180(8)	1.1530(8)	−0.0071(9)	0.135(8)
C(213)	0.351(1)	1.1834(9)	−0.073(1)	0.19(1)
C(214)	0.3780(9)	1.1269(9)	−0.124(1)	0.17(1)
C(215)	0.372(1)	1.0422(9)	−0.112(1)	0.18(1)
C(216)	0.3369(9)	1.0096(8)	−0.049(1)	0.142(8)
C(221)	0.1805(5)	0.9849(7)	0.0226(6)	0.084(5)

Table 3 (continued)

Atom	x/a	y/b	z/c	U_{eq} (Å^2)
C(222)	0.1583(6)	0.9010(8)	0.0254(6)	0.092(5)
C(223)	0.0908(7)	0.876(1)	−0.0267(7)	0.124(7)
C(224)	0.0472(7)	0.936(1)	−0.0771(8)	0.147(8)
C(225)	0.0656(7)	1.017(1)	−0.0832(9)	0.162(9)
C(226)	0.1335(7)	1.0445(9)	−0.0317(9)	0.128(7)

[a] Site occupancy factor, 0.5.

major points of difference are found in the interaction of the C_2 unit with the cluster. In **4** and **5**, C(2) is strongly interacting with the pseudo-square Ru_4 part of the cluster and C(1) is attached to Ru(4) and Ru(5). In **6**, however, while there is a similar close attachment of C(2) to four of the Ru atoms, C(1) only interacts with Ru(4). Atom P(1) is bonded to Ru(1) rather than to Ru(3) as found in **4** and **5**, and the P(1)–C(1) distance in **6** (1.68(6) Å) is considerably shorter than those found in **4** and **5** (about 1.83 Å). Whereas a resonance for the cluster-bound proton in **5** was found in the ^{1}H NMR spectrum, this atom was not located in the structural study. In contrast, we have been able to refine the H atom bridging the long Ru(1)–Ru(5) vector in **4**, although we were unable to obtain a ^{1}H NMR spectrum. All these data strongly support formulation of the ligand in **4** as the C_2PPh_2 ligand, unchanged from that in precursor **1**. 12 terminal CO ligands complete the coordination about the five metal atoms.

The spectroscopic properties of the two complexes are in accord with their solid state structures. In their IR spectra, both complexes show ν(CO) absorptions in the terminal region only, that for **3** being somewhat simpler (six bands) than that found for **4** (11 bands), as might be intuitively expected. In the ^{13}C NMR spectrum of **3**, we could only locate the resonance for C_α (a triplet at $\delta = 227.54$ ppm); that for C_β is probably obscured by the phenyl resonances. Only seven CO resonances were found, probably as a result of fluxional processes at individual Ru atoms. The fast atom bombardment (FAB) mass spectra of both complexes contained molecular ions, which fragmented by successive loss of CO groups.

3. Discussion

The formation of **3** and **4** requires transfer of Cl atoms from the chloro compound to the cluster, control experiments showed that **1** is unaffected by the chloroform solvent. Unsaturated organochlorine compounds of this type are known to react with metal carbonyls, usually to give metal chlorides and organometallics containing the dechlorinated organic residue. For exam-

ple, metal–trimethylenemethane complexes have been obtained by dechlorination of chloromethallyl chloride, $CH_2=C(CH_2Cl)_2$, a molecule closely related to the dichloropentene used here [8]. In the reaction under discussion, **1** serves as the Cl acceptor, to give eventually **3**; in this conversion, one C–P and two Ru–Ru bonds are broken and two CO groups are lost; additional electrons are donated by the two Cl atoms (three each), the new PPh_2 group (three) and the C_2 ligand (six).

In the formation of **4** from **1** and the chlorocarbon, the elements of HCl have been added to **2** with cleavage of one Ru–Ru bond and loss of a CO ligand. We have previously shown that HCl adds directly to **2** to give the scorpion cluster **7**, containing only five Ru–Ru bonds [9]. We have been unable to show whether **4** is an intermediate in the formation of **3** or a competing side product and we have no evidence that **4** and **7** are interconvertible. As mentioned above, the structures of **4** and **5** are directly comparable and the structural and spectroscopic results both support their formulations as hydrido-acetylide clusters rather than the isomeric vinylidene derivatives [7]. Both clusters contain 78 valence electrons as expected for an M_5 cluster with six M–M bonds.

We had hoped that the availability of a chlorine-containing pentagonal Ru_5C_2 cluster, analogous to **2**, might offer avenues to the preparation of other mixed-metal systems or hydrido complexes. The unusual nature and limited availability of the chlorinating agent (a previously observed dimerization product of allyl chloride) renders this approach of limited value. So far, we have not succeeded in finding an alternative source of Cl atoms to effect the transformation of **1** into **3**.

4. Experimental details

General experimental conditions and instrumentation were similar to those described earlier [10]. Complex **1** was prepared by the published method [11]. 5-Chloro-4-chloromethyl-2,4-dimethylpent-1-ene was prepared by photolysis of allyl chloride [5].

Table 4
Non-hydrogen positional and isotropic displacement parameters for **4**

Atom	x/a	y/b	z/c	U_{eq} (Å^2)
Ru(1)	0.22738(8)	0.88281(5)	0.17160(5)	0.0538(4)
Ru(2)	0.25304(7)	0.86243(5)	0.32259(5)	0.0407(4)
Ru(3)	0.48176(8)	0.90889(5)	0.38379(5)	0.0402(4)
Ru(4)	0.45971(8)	0.90814(5)	0.22745(5)	0.0499(4)
Ru(5)	0.38681(8)	0.77061(5)	0.16312(5)	0.0506(4)
Cl	0.3149(3)	0.9894(2)	0.3479(2)	0.061(1)
C(11)	0.137(1)	0.8857(8)	0.0677(7)	0.089(7)
O(11)	0.0795(9)	0.8843(7)	0.0013(5)	0.142(7)
C(12)	0.205(1)	0.9802(7)	0.1718(6)	0.068(6)
O(12)	0.1861(9)	1.0422(5)	0.1666(6)	0.116(6)
C(21)	0.2004(9)	0.8676(7)	0.3983(7)	0.060(6)
O(21)	0.1678(8)	0.8684(6)	0.4422(5)	0.108(6)
C(22)	0.2409(8)	0.7651(6)	0.3201(5)	0.041(4)
O(22)	0.2305(7)	0.7037(4)	0.3172(4)	0.066(4)
C(31)	0.6117(9)	0.9688(7)	0.4377(6)	0.062(6)
O(31)	0.6882(8)	1.0025(5)	0.4683(5)	0.098(6)
C(32)	0.4771(9)	0.8824(6)	0.4730(6)	0.054(6)
O(32)	0.4787(7)	0.8653(5)	0.5291(4)	0.073(4)
C(41)	0.466(1)	1.0071(7)	0.2523(7)	0.074(7)
O(41)	0.468(1)	1.0680(5)	0.2616(6)	0.109(7)
C(42)	0.609(1)	0.9074(7)	0.2368(7)	0.074(7)
O(42)	0.6938(9)	0.9089(8)	0.2331(6)	0.135(7)
C(43)	0.388(1)	0.9237(7)	0.1214(7)	0.078(7)
O(43)	0.3609(8)	0.9415(5)	0.0594(5)	0.095(5)
C(51)	0.532(1)	0.7394(8)	0.1793(7)	0.076(7)
O(51)	0.6167(8)	0.7187(7)	0.1873(5)	0.114(6)
C(52)	0.333(1)	0.6798(7)	0.1629(7)	0.076(7)
O(52)	0.293(1)	0.6241(5)	0.1631(6)	0.120(7)
C(53)	0.328(1)	0.7766(8)	0.0535(6)	0.084(7)
O(53)	0.294(1)	0.7837(6)	−0.0110(5)	0.132(7)
C(1)	0.4475(8)	0.8033(5)	0.2740(5)	0.039(4)
C(2)	0.3735(8)	0.8562(5)	0.2810(5)	0.040(5)
P(1)	0.0893(3)	0.8623(2)	0.2089(2)	0.056(1)
C(111)	0.0031(9)	0.7821(6)	0.1824(6)	0.055(5)
C(112)	−0.066(1)	0.7660(7)	0.2147(8)	0.077(8)
C(113)	−0.127(1)	0.7042(8)	0.1989(9)	0.095(9)
C(114)	−0.126(1)	0.6593(8)	0.1473(8)	0.099(8)
C(115)	−0.061(1)	0.6720(9)	0.1111(8)	0.11(1)
C(116)	0.003(1)	0.7339(8)	0.1298(8)	0.091(8)
C(121) [a]	−0.015(1)	0.9324(8)	0.1872(9)	0.052(7)
C(122) [a]	−0.110(2)	0.929(1)	0.111(1)	0.08(1)
C(123) [a]	−0.184(2)	0.984(1)	0.086(1)	0.09(1)
C(124) [a]	−0.172(2)	1.0387(9)	0.136(1)	0.09(1)
C(125) [a]	−0.081(2)	1.042(1)	0.205(1)	0.11(1)
C(126) [a]	−0.006(2)	0.985(1)	0.226(1)	0.09(1)
C(121') [a]	0.014(5)	0.909(3)	0.207(3)	0.11(2)
C(122') [a]	−0.078(4)	0.949(3)	0.150(3)	0.10(2)
C(123') [a]	−0.182(4)	1.001(3)	0.132(3)	0.11(2)
C(124') [a]	−0.171(5)	1.041(3)	0.193(3)	0.11(2)
C(125') [a]	−0.097(5)	1.021(4)	0.262(4)	0.14(2)
C(126') [a]	−0.017(4)	0.966(2)	0.265(3)	0.08(1)
P(2)	0.5596(2)	0.8034(1)	0.3704(1)	0.039(1)
C(211)	0.5491(9)	0.7250(6)	0.4215(6)	0.045(5)
C(212)	0.614(1)	0.7246(6)	0.5005(6)	0.064(6)
C(213)	0.613(1)	0.6623(8)	0.5385(7)	0.086(8)
C(214)	0.552(1)	0.6039(7)	0.5022(8)	0.087(9)
C(215)	0.491(1)	0.6052(7)	0.4255(8)	0.079(8)
C(216)	0.489(1)	0.6657(6)	0.3853(7)	0.059(6)
C(221)	0.7037(8)	0.7924(6)	0.3819(5)	0.045(5)

Table 4 (continued)

Atom	x/a	y/b	z/c	U_{eq} ($\mathring{A}^{-2}$)
C(222)	0.775(1)	0.8498(6)	0.3968(6)	0.058(6)
C(223)	0.886(1)	0.8404(8)	0.4100(8)	0.083(8)
C(224)	0.922(1)	0.7740(8)	0.4034(7)	0.079(7)
C(225)	0.854(1)	0.7149(7)	0.3894(8)	0.072(7)
C(226)	0.743(1)	0.7242(7)	0.3777(7)	0.066(6)
H	0.216(7)	0.784(5)	0.133(5)	0.050(−)

^{a} site occupancy factors: C(121)–C(126), 0.705(9); C(121′)–C(126′), 1.0–0.705(9).

4.1. Reaction of 1 with 5-chloro-4-chloromethyl-2,4-di-methylpent-1-ene

A solution of **1** (200 mg, 0.16 mmol) and 5-chloro-4-chloromethyl-2,4-dimethylpent-1-ene (150 mg, 0.83 mmol) in $CHCl_3$ (20 cm^3) was refluxed for 30 h. The solvent was removed and the residue purified by preparative TLC (light petroleum : acetone, 10 : 3) to yield two major bands. A dark-red band ($R_f = 0.50$) was recrystallized (CH_2Cl_2–MeOH) to yield black crystals of $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu\text{-}Cl)_2(CO)_{11}$(**3**)(64 mg (31%)). Anal. Found: C, 34.70; H, 1.60%; $M = 1280$ (mass spectrometry (MS)). $C_{37}H_{20}Cl_2O_{11}P_2Ru_5$ Calc.: C, 34.75; H, 1.58%; $M = 1280$. IR: ν(CO) (cyclohexane) 2077s, 2042vs, 2026m, 2011s, 1988m, 1978m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.95–7.72 (m, Ph) ppm. ^{13}C NMR ($CDCl_3$): δ 127.72–131.88 (m, Ph), 139.69–139.93, 141.46–141.87 (m, ispo C), 190.02 (s(br), CO), 191.38 (t, $J_{CP} = 5.5$ Hz, C_β), 193.74 (s, CO), 194.34 (s, CO), 200.82 (s, CO), 203.91 (s, CO), 227.54 (t, $J_{CP} =$

9.8 Hz, C_α) ppm. FAB MS; m/z 1280, [M]$^+$; 1252–972 [M − nCO]$^+$($n = 1$–11). An orange band ($R_f = 0.40$) was recrystallized (CH_2Cl_2–MeOH) to yield $Ru_5\{\mu_4\text{-}CCH(PPh_2)\}(\mu\text{-}Cl)(\mu\text{-}PPh_2)(CO)_{12}$(**4**) (48 mg (23%)), Anal. Found: C, 35.16; H, 1.51%; $M = 1274$ (MS). $C_{38}H_{21}ClO_{12}P_2Ru_5$ Calc.: C, 34.75; H, 1.58%; $M = 1274$. IR: ν(CO) (cyclohexane) 2084m, 2050m, 2036vs, 2030s, 2021m, 2013m, 2000m, 1987m, 1981m, 1971w, 1956w cm^{-1}. FAB MS: m/z 1274, [M]$^+$; 1246–938 [M − nCO]$^+$($n = 1$–12).

5. Crystallography

Unique data sets were measured at about 295 K within the specified $2\theta_{max}$ limits using an Enraf–Nonius CAD4 diffractometer (2θ–θ scan mode; monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ $\mathring{A}$); N independent reflections were obtained, N_0 with $I > 3\sigma(I)$ being considered "observed" and used in the full-matrix

Table 5
Crystal data and refinement details for 3 and 4

Compound	$Ru_5(\mu_5\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu\text{-}Cl)_2(CO)_{11}$ (3)	$Ru_5(\mu\text{-}H)\{\mu\text{-}CC(PPh_2)\}(\mu\text{-}Cl)(\mu\text{-}PPh_2)(CO)_{12}$ (4)
Formula	$C_{37}H_{20}Cl_2O_{11}P_2Ru_5$	$C_{38}H_{21}ClO_{12}P_2Ru_5$
Molecular weight	1278.8	1272.3
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	19.410(6)	13.220(5)
b (Å)	15.453(6)	18.662(9)
c (Å)	14.802(7)	19.691(3)
β (°)	103.88(3)	117.22(2)
V (Å^3)	4311	4320
Z	4	4
D_c (g cm^{-3})	1.97	1.96
$F(000)$	2456	2448
Crystal size (mm)	0.07 × 0.26 × 0.35	0.18 × 0.07 × 0.57
A^*(min); A^*(max)	1.13; 1.60	1.14; 1.44
μ (cm^{-1})	17.8	19.0
$2\theta_{max}$ (°)	50	65
N	7596	14940
N_0	4500	5876
R	0.047	0.065
R_w	0.043	0.062

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 and 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 implemented by Hall and Stewart [12]; neutral atom complex scattering factors were employed. Pertinent results are given in the Figures and Tables.

5.1. Abnormal features / variations in procedure

5.1.1. Complex 3

As described above, disorder was evident in Ru(2,3), each atom being resolvable and refinable as two components A and B separated by about 0.6 Å, with site occupancies set at 0.5 after trial refinement. Further disorder was not resolvable in associated ligand atoms, apparent high thermal motion possibly being a foil for any static disorder here and throughout the structure more widely. Possibly uncorrelated disorder is also found in phenyl ring 11, two "rotationally" disordered components being observed.

5.1.2. Complex 4

Disorder is also evident in one of the phenyl ring components (12) of this structure, the two components having unequal occupancies of 0.705(9) and 1 − 0.705(9); the smaller component C(12n') was refined with isotropic parameter forms. Optimum definition of ligand hydrogen atoms in this structure became an operational desideratum, with the possibility of location on the C_2 ligand or on the cluster; in an initial refinement based on data to $2\theta_{max} = 50°$, the residual was high (about 0.07), possibly consequent upon disorder and/or poorly diffracting material, but difference map residues were indicative of a cluster-bound hydrogen located between Ru(1) and Ru(5) rather than on the C_2 ligand, being refinable in (x, y, z). An independent experiment on a different specimen using carefully mea-

sured albeit weak data to $2\theta_{max} = 65°$ supported this finding, as recorded herein.

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