ELSEVIER

Journal of Organometallic Chemistry 526 (1996) 85–97

Journal of Organo metallic Chemistry

Reactions of $Ru_3(\mu\text{-dppm})(CO)_{10}$ with unsaturated hydrocarbons Cycloocta-1,3,5,7-tetraene X-ray structures of $Ru_3(\mu\text{-dppm})(\mu\text{-}C_8H_8)(CO)_6$, $Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(\mu_3\text{-}C_8H_8)(Ph)(CO)_5$, $Ru_3\{\mu_3\text{-}PPhCH_2PPh(C_6H_4)\}(\mu\text{-}C_8H_8)(\mu\text{-}CO)(CO)_4$, and $Ru_3(\mu\text{-}H)\{\mu_3\text{-}PPh_2CHPPh(C_6H_4)\}(\mu\text{-}C_8H_9)(\mu\text{-}CO)(CO)_4$

Michael I. Bruce [a,*], Paul A. Humphrey [a], Brian W. Skelton [b], Allan H. White [b]

[a] *Department of Chemistry, University of Adelaide, Adelaide, S.A. 5005, Australia*
[b] *Department of Chemistry, University of Western Australia, Nedlands, W.A. 6907, Australia*

Received 4 April 1996; revised 20 May 1996

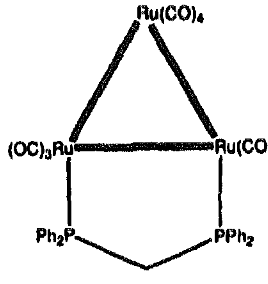
Abstract

Reactions between $Ru_3(\mu\text{-dppm})(CO)_{10}$ and cycloocta-1,3,5,7-tetraene (cot) in refluxing thf afford the four complexes $Ru_3(\mu\text{-dppm})(\mu\text{-}C_8H_8)(CO)_6$ (**2**), $Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(\mu_3\text{-}C_8H_8)(Ph)(CO)_5$ (**3**), $Ru_3\{\mu_3\text{-}PPhCH_2PPh(C_6H_4)\}(\mu\text{-}C_8H_8)(\mu\text{-}CO)(CO)_4$ (**4**) and $Ru_3(\mu\text{-}H)\{\mu_3\text{-}PPh_2CHPPh(C_6H_4)\}(\mu\text{-}C_8H_9)(\mu\text{-}CO)(CO)_4$ (**5**) which have been structurally characterised by means of X-ray crystallography. Complex **3** is the first example of an Ru_3 cluster containing a cot ligand capping the Ru_3 face. In **2** and **4**, the cot ligand is found bridging an Ru–Ru edge; in **2**, only one Ru of this edge is bonded to a P atom. In **3**, a P–C bond of the dppm ligand has oxidatively added to one Ru atom to give an unusual example of a cluster-bonded σ-phenyl group. Complex **5** contains a C_8H_9 ligand and dppm unusually dimetallated at the methylene carbon and at a phenyl group.

Keywords: Ruthenium; Crystal structure; Cluster; Phosphine; Metallation; Cyclooctatetraene

1. Introduction

The chemistry of the bis-tertiary phosphine-substituted cluster $Ru_3(\mu\text{-dppm})(CO)_{10}$ (**1**) has been found to encompass a wide range of reactions [1], some of which emulate those of the parent carbonyl, others being specific to this cluster [2]. The latter include transformations of the dppm ligand and reactions between either the dppm ligand, or ones derived from it, with other reactant molecules. One feature of the chemistry has been the expected stabilisation of the Ru_3 core towards fragmentation to mono- or bi-nuclear species, but in some reactions concomitant core expansion to Ru_4 or higher nuclearity complexes has also been observed [3].



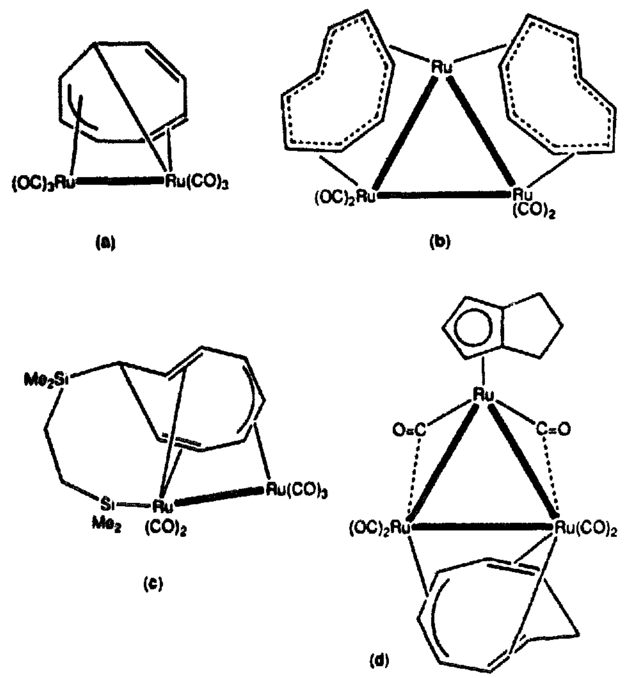
(1)

Continuing our studies of reactions between **1** and unsaturated hydrocarbons, of which we have described those with alkynes [4], norbornadiene [5], and with pentamethylcyclopentadiene [6], we have examined some reactions between **1** and cycloocta-1,3,5,7-tetraene (cot). Reactions between $Ru_3(CO)_{12}$ and cot have been

---

[*] Corresponding author.

PII S0022-328X(96)06519-9

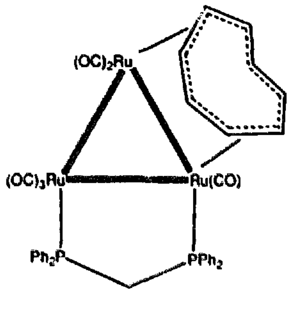


Scheme 1. Some ruthenium complexes derived from cot with structures related to those of complexes described herein: (a) $Ru_2(\mu-\eta^1,\eta^2:\eta^3-C_8H_8)(CO)_3$; (b) $Ru_3(\mu-\eta^4:\eta^4-C_8H_8)_2(CO)_4$; (c) $Ru_2(\mu-\eta^3:2\eta^2,Si-C_8H_8SiMe_2C_2H_4SiMe_2)(CO)_5$; (d) $Ru_3(\mu-2\eta^2:\eta^3-C_8H_9)(\mu-CO)_2(CO)_4(\eta^5-C_8H_9)$.

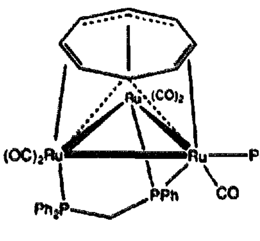
studied for over 30 years [7,8]. Simple thermal reactions have given the complexes $Ru(CO)_3(\eta^4-C_8H_8)$ [7–9], $Ru_2(\mu-C_8H_8)(CO)_6$ [7,8,10], $Ru_2(\mu-C_8H_8)(\mu-CO)(CO)_4$ [7,8] and $Ru_3(\mu-C_8H_8)_2(CO)_4$ [8,11]. In the latter two complexes, the mode of attachment of the cot ligand to the metal atoms cannot be described simply in terms of the η^n terminology. In solution many of these complexes are fluxional [12]. Further studies have encompassed a variety of substituted cyclooctatetraenes [13], some of the most interesting results relating to the formation and stabilisation of pentalene on ruthenium clusters [14]. Some of the monocyclic cyclooctatetraene complexes that are related to those obtained from **1** are collected in Scheme 1. This paper describes four trinuclear complexes which have been isolated and characterised crystallographically.

2. Results and discussion

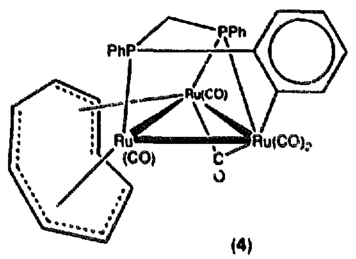
Reactions between **1** and cot were carried out in refluxing thf for extended periods, this being necessary to ensure that no **1** remained; a typical example is described in Section 4. The products were separated by preparative thin-layer chromatography on silica gel. Four complexes were isolated in yields ranging from 4 to 30%, with total conversions of around 50%, and were structurally characterised by X-ray crystallographic studies as (a) $Ru_3(\mu-dppm)(\mu-C_8H_8)(CO)_6$ (**2**), (b) $Ru_3(\mu_3-PPhCH_2PPh_2)(\mu_3-C_8H_8)(Ph)(CO)_5$ (**3**), (c) $Ru_3\{\mu_3-PPhCH_2PPh(C_6H_4)\}(\mu-C_8H_9)(\mu-CO)(CO)_4$ (**4**) and (d) $Ru_3(\mu-H)\{\mu_3-PPh_2CHPPh(C_6H_4)\}(\mu-C_8H_9)(\mu-CO)(CO)_4$ (**5**).



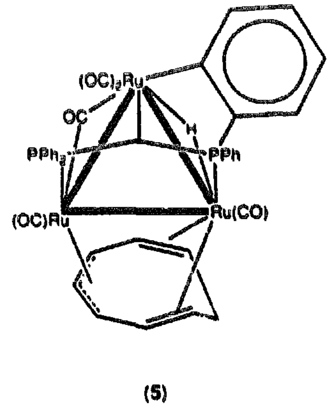
(2)



(3)



(4)



(5)

All four complexes contain a closed triangular array of three ruthenium atoms with inter-metallic distances which are dependent on the nature of the other ligands bridging the Ru–Ru vectors. As there are distinct structural features in each complex, each will be discussed separately. Plots of their molecular structures are given in Figs. 1–4 and selected structural parameters are collected in Tables 1–4.

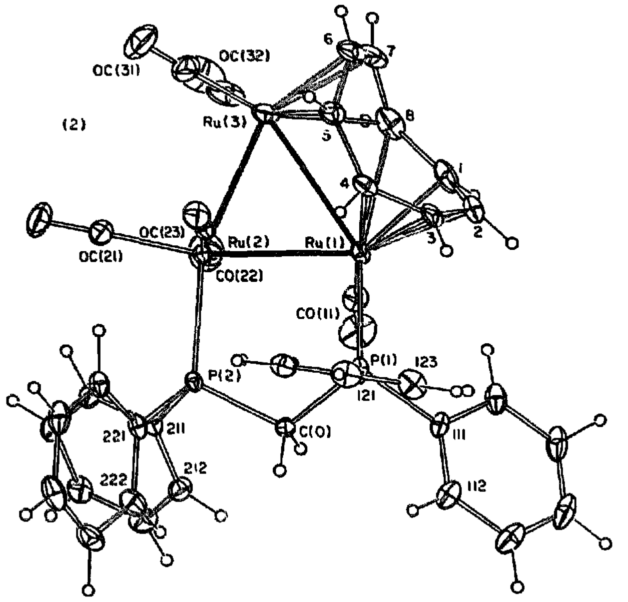


Fig. 1. Plot of a molecule of $Ru_3(\mu\text{-dppm})(\mu\text{-}C_8H_8)(CO)_6$ (2), showing the atom numbering scheme. In this and subsequent figures, non-hydrogen atoms are shown with 20% thermal envelopes; hydrogen atoms have arbitrary radii of 0.1 Å.

2.1. $Ru_3(\mu\text{-dppm})(\mu\text{-}C_8H_8)(CO)_6$ (2)

This red-brown complex was isolated in about 30% yield and is directly related to 1 by the replacement of two CO groups on each of two Ru atoms by one molecule of cot. An unaltered dppm ligand bridges one of the two ruthenium atoms bridged by the cot ligand and the third metal atom. The Ru–Ru separations range between 2.7784(99) and 3.023(1) Å. In 1, the Ru–Ru separations are 2.834(1), 2.841(1) and 2.860(1) Å, the shortest being that bridged by the dppm ligand [15]; it is not significantly different from the value of 2.839(1) Å found in 2. The longest bond found here is that bridged by the cot ligand and can be compared with values of 2.992(1) Å found in $Ru_3(\mu\text{-}C_8H_7C_8H_7)(CO)_6$ [13] and 2.928, 2.947(2) Å for the two cot-bridged Ru–Ru bonds in $Ru_3(\mu\text{-}C_8H_8)_2(CO)_4$ [11]. The unbridged Ru–Ru bond in 2 is considerably shorter than the similar bonds found in 1. Attachment of the dppm ligand is similar to that found in 1, although the Ru(1)–P(1) distance (2.281(2) Å) is shorter than Ru(2)–P(2) (2.326(1) Å) and similar bonds in 1, because of competition for electron density between the phosphine and cot ligands on Ru(1).

The cot ligand in 2 is attached in the $\eta^4:\eta^4$ mode to Ru(1) (through C(1–4)) and Ru(3) (through C(5–8)). The Ru–C separations fall into three sets: Ru(1)–C(1) and Ru(3)–C(6,7) (2.197(7), 2.206(6), 2.187(7) Å), Ru(1)–C(2,3) and Ru(3)–C(5) (2.253(7), 2.262(6), 2.253(6) Å) and two longer interactions, Ru(1)–C(4) (2.406(6) Å) and Ru(3)–C(8) (2.444(7) Å). Around the ring, only C(3)–C(4) and C(6)–C(7) are short (1.378(8), 1.385(9) Å), the other six C–C bonds averaging 1.42_5 Å (range 1.418–1.443(8) Å). The ring is non-planar, there being three mean planes through (i) C(1,2,3,4) (χ^2 0.2), (ii) C(1,4,5,8) (χ^2 123) and (iii) C(5,6,7,8) (χ^2 26) (dihedrals (i)/(ii, iii) 26(1)°, 59(2)°, and (ii)/(iii) 32(1)° respectively).

The spectroscopic properties are in accord with the solid-state structure. There are four strong to very strong ν(CO) bands in the infrared spectrum, while the ^1H NMR spectrum contains a sharp singlet at δ 4.12 (intensity 8) for the cot ligand, showing that the complex is fluxional, probably by the usual circumambulatory process (1,2-shifts) that brings all ring protons into equivalence. A single triplet is found for the dppm CH_2 protons at δ 4.51, showing that they too are undergoing a fluxional process, probably by the oscillation of the

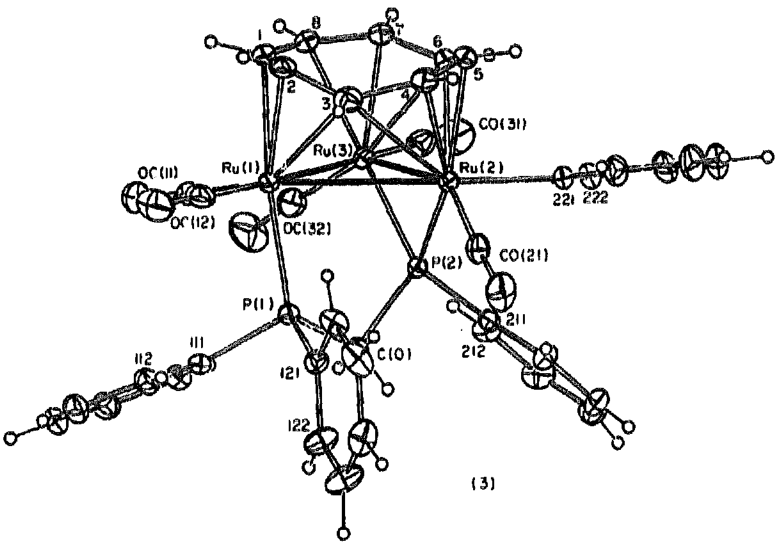


Fig. 2. Plot of a molecule of $Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(\mu_3\text{-}C_8H_8)(Ph)(CO)_5$ (3), showing the atom numbering scheme.

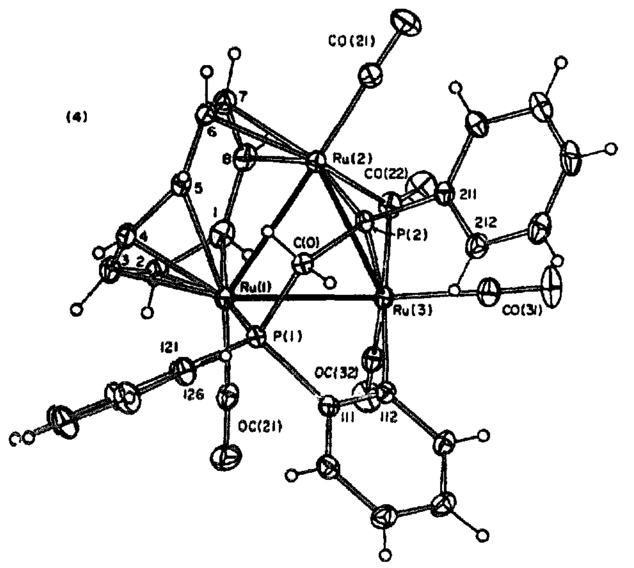


Fig. 3. Plot of a molecule of $Ru_3(\mu_3\text{-}PPhCH_2PPh(C_6H_4))(\mu\text{-}C_8H_9)(\mu\text{-}CO)(CO)_4$ (4), showing the atom numbering scheme.

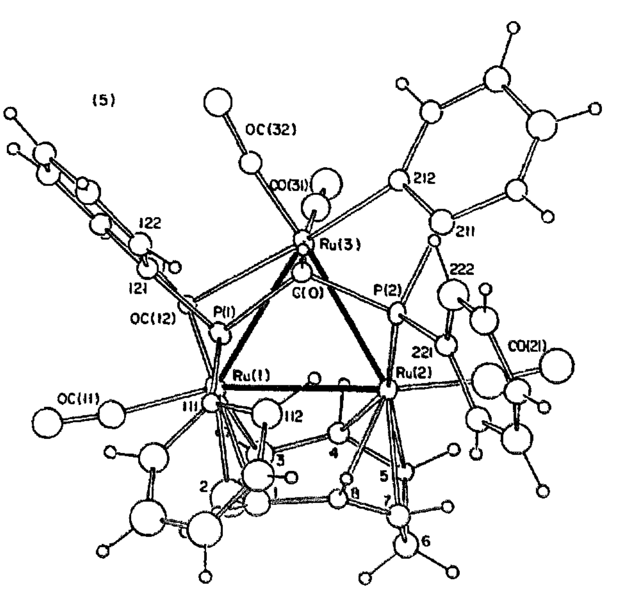


Fig. 4. Plot of a molecule of $Ru_3(\mu\text{-}H)(\mu_3\text{-}PPh_2CHPPh(C_6H_4))(\mu\text{-}C_8H_9)(\mu\text{-}CO)(CO)_4$ (5), showing the atom numbering scheme.

CH_2 group. The fast atom bombardment mass spectrum (FAB MS) contains a molecular ion at m/z 961 and fragment ions formed by the loss of up to six CO ligands.

2.2. $Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(\mu_3\text{-}C_8H_8)(Ph)(CO)_5$ (3)

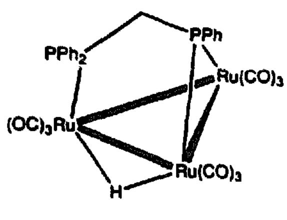
Only small amounts of this compound were found and characterisation was by X-ray crystallography. In 3, the cot ligand is attached to all three ruthenium atoms, sitting across the cluster. To our knowledge, there is no analogous complex derived from ruthenium carbonyl itself. The ring is attached by three C=C double bonds, one of which is somewhat further away from the metal atoms than the others. There are also long interactions with the other two ring carbons which are in incipient bridging modes. The dppm ligand has undergone the common dephenylation reaction, but in 3, for the first time to our knowledge, the phenyl group has not been eliminated but trapped by σ-bonding to one of the ruthenium atoms bridged by the phosphido group. The isolated σ-bonded phenyl group is rare in ruthenium clusters, although the participation of C_6H_4 ligands as part of metallated phenylphosphines (as in 4 below) is more common. The Ru(2)–C(221) distance (2.096(3) Å) is normal for an Ru–C(aryl) σ bond. The dihedral between the Ru(1,2,3) and C(221–226) planes is 12.4(1)°.

In 3, the Ru_3 triangle is considerably enlarged, with Ru–Ru separations ranging between 2.8581(9) and 3.1989(6) Å. The shortest distance is that bridged by phosphido P(2), the longest being trans to the Ph group on Ru(2). The dephenylated dppm ligand has been structurally characterised before in $Ru_3(\mu\text{-}H)(\mu_3\text{-}$

Table 1
Selected bond lengths (Å) and angles (deg) for $Ru_3(\mu\text{-}dppm)(\mu\text{-}C_8H_8)(CO)_6$ (2)

Bond lengths			
Ru(1)–Ru(2)	2.839(1)	Ru(3)–C(6)	2.206(7)
Ru(1)–Ru(3)	3.023(1)	Ru(3)–C(7)	2.187(7)
Ru(2)–Ru(3)	2.7784(9)	Ru(3)–C(8)	2.444(7)
Ru(1)–P(1)	2.281(2)	C(1)–C(2)	1.41(1)
Ru(2)–P(2)	2.326(1)	C(1)–C(8)	1.42(1)
P(1)–C(0)	1.850(5)	C(2)–C(3)	1.421(9)
P(2)–C(0)	1.849(5)	C(3)–C(4)	1.378(8)
Ru(1)–C(1)	2.197(7)	C(4)–C(5)	1.443(8)
Ru(1)–C(2)	2.253(6)	C(5)–C(6)	1.418(8)
Ru(1)–C(3)	2.262(6)	C(6)–C(7)	1.385(9)
Ru(1)–C(4)	2.406(6)	C(7)–C(8)	1.44(1)
Ru(3)–C(5)	2.253(6)		
Bond angles			
Ru(1)–P(1)–C(0)	113.8(2)	P(1)–C(0)–P(2)	114.2(3)
Ru(2)–P(2)–C(0)	113.2(4)		

$PPhCH_2PPh_2)(CO)_9$ (6) [2], in which the phosphido-bridged Ru–Ru separation is 2.820(1) Å. The Ru–P distances in this complex (2.306–2.384(1) Å) are considerably longer than those found in **3** (2.264–2.337(1) Å), again reflecting the presence of the cot ligand in this complex.



(6)

The Ru–C(cot) separations lie between 2.182(6) and 2.702(4) Å. Careful examination of the shorter distances suggests that the ring is attached in an $\eta^2:\eta^2:\eta^2$ mode to Ru(1,2,3) respectively, although (a) the Ru(3)–C(7,8) distances (2.218, 2.375(5) Å) are longer than found for Ru(1)–C(2,3) (2.292, 2.182(5) Å) and Ru(2)–C(4,5) (2.229, 2.186(5) Å) and (b) the remaining ring carbons are only weakly interacting, at best (Ru(1,2)–C(3) 2.471, 2.702(5) Å; Ru(2,3)–C(6) 2.434, 2.536(5) Å). Within the ring, C–C distances again fall into two groups, three between 1.373(6) and 1.388(7) Å and five between 1.424(6) and 1.441(5) Å. The cot ring is non-planar (χ^2 5218; δ C(1–8) 0.032(6), 0.127(6), −0.262(6), 0.051(6), 0.181(5), −0.187(5), 0.063(5), −0.016(6) Å). Atoms C(2,5,7) which, in projection, lie most nearly above the ruthenium atoms are the furthest from them, while the closest atoms above the ruthenium atoms are C(1,2), C(4,5) and C(7,8).

This is this first occasion in which an Ru_3 cluster containing the cot ligand attached to all three Ru atoms has been structurally characterised. The related complex $Ru_3(\mu_3\text{-S}^t\text{Bu})(\mu_3\text{-C}_7H_7)(CO)_6$, in which the C_7H_7 ring caps an Ru_3 core in the $\eta^2:\eta^2:\eta^3$ mode, is known [16], as are many similar μ_3-$\eta^2:\eta^2:\eta^2$-arene clusters [17]. The Ru–C(ring) distances range between 2.084 and 2.533(6) Å, the latter being to an outer carbon of a π-allyl system. The C–C distances fall between 1.400 and 1.435(8) Å.

Although we were not able to get a ^1H NMR spectrum to prove the point, it is likely that in this complex, as in others, the ring is fluxional by rotation around the Ru_3 core. The solid-state structure probably represents an intermediate position of the ring frozen by crystal forces, so that all eight π electrons are probably involved in ring–metal bonding, as required for a precise electron count. We note that long Ru–ring carbon distances have previously been considered to indicate at least partial bonding interactions, as found in $Ru_3(\mu\text{-C}_8H_9)(\mu\text{-CO})_2(CO)_4(\eta^5\text{-C}_8H_9)$ (long Ru–C distances of 2.525, 2.710 Å) [18].

2.3. $Ru_3\{\mu_3\text{-PPhCH}_2PPh(C_6H_4)\}(\mu\text{-C}_8H_8)(\mu\text{-CO})(CO)_4$ (4)

In the third complex, isolated in only 4% yield, the cot ligand is again found bridging an Ru–Ru bond, but this time the interaction is of the $\eta^2,\eta^2:\eta^3$ type, as found in $Ru_2(\mu\text{-C}_8H_8)(CO)_6$ [10]. The Ru–Ru distances range between 2.7567(6) and 2.9366(4) Å. The

Table 2
Selected bond lengths (Å) and angles (deg) for $Ru_3(\mu_3\text{-PPhCH}_2PPh_2)(\mu_3\text{-C}_8H_8)(Ph)(CO)_5$ (3)

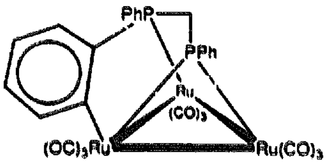
Bond lengths			
Ru(1)–Ru(2)	3.1989(6)	Ru(2)–C(6)	2.434(3)
Ru(1)–Ru(3)	2.9682(6)	Ru(3)–C(6)	2.536(5)
Ru(2)–Ru(3)	2.8581(9)	Ru(3)–C(7)	2.218(5)
Ru(1)–P(1)	2.337(1)	Ru(3)–C(8)	2.375(4)
Ru(2)–P(2)	2.264(1)	Ru(2)–C(221)	2.096(3)
Ru(3)–P(2)	2.2833(8)	C(1)–C(2)	1.388(7)
P(1)–C(0)	1.820(4)	C(1)–C(8)	1.440(6)
P(2)–C(0)	1.832(4)	C(2)–C(3)	1.424(6)
Ru(1)–C(1)	2.292(4)	C(3)–C(4)	1.436(6)
Ru(1)–C(2)	2.182(6)	C(4)–C(5)	1.373(6)
Ru(1)–C(3)	2.471(6)	C(5)–C(6)	1.435(6)
Ru(2)–C(3)	2.702(5)	C(6)–C(7)	1.441(5)
Ru(2)–C(4)	2.229(5)	C(7)–C(8)	1.384(6)
Ru(2)–C(5)	2.186(5)		
Bond angles			
Ru(1)–P(1)–C(0)	114.8(1)	Ru(1)–Ru(2)–C(221)	167.9(1)
Ru(2)–P(2)–C(0)	119.5(2)		
Ru(3)–P(2)–C(0)	118.5(1)		
Ru(2)–P(2)–Ru(3)	77.87(4)	P(1)–C(0)–P(2)	107.3(2)

Table 3
Selected bond lengths (Å) and angles (deg) for Ru$_3${μ_3-PPhCH$_2$(C$_6$H$_4$)}(μ-C$_8$H$_8$)(μ-CO)(CO)$_4$ (4)

Bond lengths			
Ru(1)–Ru(2)	2.9365(5)	Ru(2)–C(7)	2.195(5)
Ru(1)–Ru(3)	2.8781(6)	Ru(2)–C(8)	2.277(3)
Ru(2)–Ru(3)	2.7567(6)	Ru(3)–C(112)	2.122(3)
Ru(1)–P(1)	2.2936(8)	Ru(2)–C(22)	2.066(4)
Ru(2)–P(2)	2.3294(9)	Ru(3)–C(22)	2.133(4)
Ru(3)–P(2)	2.3409(9)		
P(1)–C(0)	1.831(3)	C(1)–C(2)	1.392(6)
P(2)–C(0)	1.836(3)	C(1)–C(8)	1.450(5)
Ru(1)–C(1)	2.344(3)	C(2)–C(3)	1.422(6)
Ru(1)–C(2)	2.216(4)	C(3)–C(4)	1.386(5)
Ru(1)–C(3)	2.250(5)	C(4)–C(5)	1.436(4)
Ru(1)–C(4)	2.207(5)	C(5)–C(6)	1.443(5)
Ru(1)–C(5)	2.401(5)	C(6)–C(7)	1.410(4)
Ru(2)–C(6)	2.174(5)	C(7)–C(8)	1.389(6)
Bond angles			
Ru(1)–P(1)–C(0)	111.9(1)	Ru(3)–C(22)–O(22)	139.6(4)
Ru(2)–P(2)–C(0)	118.9(1)	Ru(2)–C(22)–O(22)	138.3(4)
Ru(3)–P(2)–C(0)	112.2(1)		
Ru(2)–P(2)–Ru(3)	72.35(3)	P(1)–C(0)–P(2)	103.1(1)

shortest, Ru(2)–Ru(3), is bridged both by phosphido P(2) and a CO group, while the longest is bridged by the cot ligand and is comparable with the values mentioned above.

The dppm ligand has undergone both dephenylation and metallation to give the μ_3-PPhCH$_2$PPh(C$_6$H$_4$) ligand, first structurally characterised in Ru$_3${μ_3-PPhCH$_2$PPh(C$_6$H$_4$)}(CO)$_9$ (7) [2], in which the Ru–Ru bond bridged by the phosphido group (2.888(1) Å) is also semi-bridged by a CO group. The Ru–P distances are similar to **4**, with Ru(1)–P(1) (2.2937(8) Å; the phosphine) being shorter than the Ru–P(2) (phosphido) separations. The C$_6$H$_4$ group bridges P(1) and Ru(3), i.e. one of the phosphido-bridged Ru atoms, in both cases, with Ru(3)–C(212) 2.122(3) Å in **4**, compared with 2.158(3) Å in **7** [2].



(**7**)

Table 4
Selected bond lengths (Å) and angles (deg) for Ru$_3$(μ-H){μ_3-PPh$_2$CHPPh(C$_6$H$_4$)}(μ-C$_8$H$_9$)(μ-CO)(CO)$_4$ (5)

Bond lengths			
Ru(1)–Ru(2)	2.967(5)	Ru(2)–C(8)	2.34(4)
Ru(1)–Ru(3)	2.935(6)	Ru(3)–C(212)	2.03(4)
Ru(2)–Ru(3)	2.937(5)	Ru(1)–C(12)	1.85(4)
Ru(1)–P(1)	2.34(1)	Ru(3)–C(12)	2.51(4)
Ru(2)–P(2)	2.30(1)	C(1)–C(2)	1.30(8)
P(1)–C(0)	1.75(4)	C(1)–C(8)	1.45(6)
P(2)–C(0)	1.84(4)	C(2)–C(3)	1.44(8)
Ru(1)–C(1)	2.19(5)	C(3)–C(4)	1.42(7)
Ru(1)–C(2)	2.04(7)	C(4)–C(5)	1.37(6)
Ru(1)–C(3)	2.22(4)	C(5)–C(6)	1.48(6)
Ru(2)–C(4)	2.37(4)	C(6)–C(7)	1.47(6)
Ru(2)–C(5)	2.33(4)	C(7)–C(8)	1.31(5)
Ru(2)–C(7)	2.22(5)		
Bond angles			
Ru(1)–P(1)–C(0)	107(1)	Ru(3)–C(0)–P(2)	85(1)
Ru(2)–P(2)–C(0)	107(1)	P(1)–C(0)–P(2)	119(2)
Ru(2)–P(2)–Ru(3)	69.7(8)	Ru(1)–C(12)–O(12)	160(3)
Ru(3)–C(0)–P(1)	97(2)	Ru(13)–C(12)–O(12)	116(3)

Table 5
Non-hydrogen positional and isotropic displacement parameters for $Ru_3(\mu\text{-dppm})(\mu\text{-}C_8H_8)(CO)_6$ (**2**)

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.65706(2)	0.24169(3)	0.19778(4)	0.0324(1)
Ru(2)	0.69654(2)	0.22178(3)	−0.05807(4)	0.0304(1)
Ru(3)	0.78458(2)	0.17975(3)	0.12404(5)	0.0479(2)
C(11)	0.5991(3)	0.1587(4)	0.1643(6)	0.048(2)
O(11)	0.5586(2)	0.1120(3)	0.1497(6)	0.081(2)
C(21)	0.7383(3)	0.1976(4)	−0.2108(6)	0.047(2)
O(21)	0.7637(2)	0.1857(4)	−0.3039(5)	0.086(2)
C(22)	0.6657(3)	0.1068(4)	−0.0457(6)	0.050(2)
O(22)	0.6501(3)	0.0374(3)	−0.0495(5)	0.083(2)
C(23)	0.7428(2)	0.3249(4)	−0.0404(5)	0.035(2)
O(23)	0.7725(2)	0.3857(3)	−0.0467(4)	0.055(2)
C(31)	0.8520(3)	0.2075(6)	0.0203(7)	0.080(3)
O(31)	0.8937(2)	0.2307(5)	−0.0389(6)	0.119(3)
C(32)	0.7840(4)	0.0669(5)	0.0720([illegible])	0.082(3)
O(32)	0.7891(3)	−0.0033(4)	0.0425(7)	0.142(3)
P(1)	0.58418(6)	0.33665(9)	0.1304(1)	0.0279(4)
C(111)	0.5146(2)	0.3449(3)	0.2282(5)	0.035(2)
C(112)	0.4689(3)	0.4050(4)	0.2015(7)	0.050(2)
C(113)	0.4158(3)	0.4101(4)	0.2756(8)	0.065(3)
C(114)	0.4082(3)	0.3562(5)	0.3777(7)	0.069(3)
C(115)	0.4523(3)	0.2966(5)	0.4048(6)	0.064(3)
C(116)	0.5063(3)	0.2910(4)	0.3319(5)	0.049(2)
C(121)	0.6086(2)	0.4493(3)	0.1167(5)	0.029(2)
C(122)	0.5969(3)	0.5063(4)	0.2120(6)	0.043(2)
C(123)	0.6193(3)	0.5894(4)	0.2047(7)	0.055(2)
C(124)	0.6539(3)	0.6140(4)	0.1024(7)	0.052(2)
C(125)	0.6651(3)	0.5582(4)	0.0062(6)	0.042(2)
C(126)	0.6427(2)	0.4749(3)	0.0130(5)	0.034(2)
C(0)	0.5485(2)	0.3085(3)	−0.0240(5)	0.030(2)
P(2)	0.60411(6)	0.27046(9)	−0.1450(1)	0.0267(4)
C(211)	0.5598(2)	0.1914(3)	−0.2350(5)	0.031(2)
C(212)	0.4955(3)	0.1821(4)	−0.2280(6)	0.044(2)
C(213)	0.4655(3)	0.1241(4)	−0.3050(7)	0.052(2)
C(214)	0.4975(3)	0.0759(4)	−0.3906(6)	0.049(2)
C(215)	0.5603(3)	0.0836(4)	−0.3978(7)	0.059(3)
C(216)	0.5904(3)	0.1406(4)	−0.3207(6)	0.051(2)
C(221)	0.6057(3)	0.3581(3)	−0.2624(5)	0.034(2)
C(222)	0.5508(3)	0.3892(4)	−0.3142(6)	0.051(2)
C(223)	0.5514(3)	0.4555(4)	−0.4026(6)	0.059(3)
C(224)	0.6082(3)	0.4903(4)	−0.4373(6)	0.058(2)
C(225)	0.6619(3)	0.4589(4)	−0.3862(6)	0.054(2)
C(226)	0.6611(3)	0.3930(4)	−0.3019(5)	0.039(2)
C(1)	0.6809(3)	0.1848(5)	0.3824(6)	0.067(3)
C(2)	0.6677(3)	0.2712(5)	0.4064(5)	0.058(2)
C(3)	0.6924(3)	0.3407(4)	0.3363(5)	0.045(2)
C(4)	0.7375(3)	0.3431(4)	0.2437(5)	0.040(2)
C(5)	0.7973(3)	0.3032(4)	0.2299(6)	0.045(2)
C(6)	0.8254(3)	0.2353(4)	0.2976(6)	0.057(2)
C(7)	0.7962(3)	0.1595(4)	0.3285(7)	0.065(3)
C(8)	0.7307(4)	0.1432(4)	0.3211(7)	0.066(3)

In **4**, the cot ring appears to be η^3-bonded to Ru(1) (2.207–2.250(5) Å) and η^2-bonded to Ru(2) (2.174, 2.195(5) Å); the Ru(2)–C(8) distance (2.277(3) Å) is again longer than expected for an η^1 (σ) bond. In $Ru_2(\mu\text{-}C_8H_8)(CO)_6$, similar distances are 2.19–2.30(1.5) Å (for the η^3 carbons), 2.30 and 2.32(1.5) Å (for the η^2 carbons), and 2.14(1.5) Å for the η^1 carbon [11]. Around the ring, C–C distances are grouped into ranges between 1.386(5) and 1.409(4) Å (four), 1.422(6) and 1.450(5) Å (four), although the e.s.d.s do not allow a definitive separation between them. The C_8 ring is folded across the C(1) ··· C(5) vector (dihedral 43.2(2)°). The ^{1}H NMR spectrum contains only a sharp singlet, at δ 4.38, showing that the ring is also fluxional in **4**.

The electronic requirements of the cluster are com-

Table 6
Non-hydrogen positional and isotropic displacement parameters for $Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(\mu_3\text{-}C_8H_8)(Ph)(CO)_5$ (3)

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.21305(3)	0.79957(1)	0.51880(2)	0.0407(1)
Ru(2)	−0.05971(3)	0.70498(1)	0.42147(2)	0.0335(1)
Ru(3)	0.25284(3)	0.66906(1)	0.50356(2)	0.0384(1)
C(11)	0.4194(5)	0.8051(2)	0.5560(2)	0.068(2)
O(11)	0.5459(4)	0.8119(2)	0.5837(2)	0.109(2)
C(12)	0.2040(6)	0.8829(2)	0.5341(3)	0.071(3)
O(12)	0.2064(5)	0.9335(1)	0.5451(2)	0.110(3)
C(21)	−0.2175(4)	0.7455(2)	0.3306(2)	0.050(2)
O(21)	−0.3210(3)	0.7672(1)	0.2704(2)	0.083(2)
C(31)	0.2861(4)	0.5864(2)	0.4942(2)	0.059(2)
O(31)	0.3086(4)	0.5378(2)	0.4869(2)	0.096(2)
C(32)	0.4309(5)	0.6845(2)	0.5033(3)	0.065(2)
O(32)	0.5387(4)	0.6909(2)	0.5000(3)	0.107(2)
P(1)	0.1469(1)	0.81950(4)	0.37425(5)	0.0356(4)
C(111)	0.2971(4)	0.8636(1)	0.3735(2)	0.040(1)
C(112)	0.2958(5)	0.9255(2)	0.3794(2)	0.052(2)
C(113)	0.4170(6)	0.9597(2)	0.3912(3)	0.066(2)
C(114)	0.5411(6)	0.9321(2)	0.3965(3)	0.066(2)
C(115)	0.5443(5)	0.8710(2)	0.3893(3)	0.062(2)
C(116)	0.4229(4)	0.8364(2)	0.3780(2)	0.049(2)
C(121)	−0.0223(4)	0.8644(2)	0.3038(2)	0.043(2)
C(122)	−0.0531(5)	0.8808(2)	0.2207(3)	0.063(2)
C(123)	−0.1834(6)	0.9129(2)	0.1637(3)	0.077(2)
C(124)	−0.2841(5)	0.9281(2)	0.1890(3)	0.070(2)
C(125)	−0.2538(5)	0.9130(2)	0.2716(4)	0.070(3)
C(126)	−0.1247(5)	0.8818(2)	0.3280(3)	0.054(2)
C(0)	0.1231(4)	0.7532(2)	0.3084(2)	0.039(2)
P(2)	0.08296(9)	0.68997(4)	0.35926(5)	0.0313(3)
C(211)	0.0314(4)	0.6361(1)	0.2706(2)	0.036(1)
C(212)	0.1341(5)	0.5968(2)	0.2694(3)	0.050(2)
C(213)	0.0917(6)	0.5602(2)	0.1986(3)	0.064(3)
C(214)	−0.0543(6)	0.5613(2)	0.1280(3)	0.068(3)
C(215)	−0.1575(5)	0.5996(2)	0.1280(3)	0.060(2)
C(216)	−0.1153(4)	0.6369(2)	0.1991(2)	0.049(2)
C(221)	−0.2013(4)	0.6302(2)	0.3636(2)	0.042(1)
C(222)	−0.1450(5)	0.5752(2)	0.3572(2)	0.051(2)
C(223)	−0.2343(6)	0.5236(2)	0.3260(3)	0.072(3)
C(224)	−0.3848(7)	0.5271(3)	0.2991(3)	0.088(3)
C(225)	−0.4458(6)	0.5803(3)	0.3043(4)	0.086(3)
C(226)	−0.3556(5)	0.6321(2)	0.3365(3)	0.061(2)
C(1)	0.2920(5)	0.7570(2)	0.6530(2)	0.055(2)
C(2)	0.1619(5)	0.7918(2)	0.6234(2)	0.055(2)
C(3)	0.0092(5)	0.7838(2)	0.5523(3)	0.055(2)
C(4)	−0.0949(5)	0.7344(2)	0.5296(2)	0.052(2)
C(5)	−0.0669(4)	0.6738(2)	0.5359(2)	0.051(2)
C(6)	0.0657(4)	0.6412(2)	0.5511(2)	0.047(2)
C(7)	0.2262(4)	0.6448(2)	0.6160(2)	0.050(2)
C(8)	0.3215(5)	0.6942(2)	0.6493(2)	0.053(2)

pleted by five CO groups, one of which more-or-less symmetrically bridges an Ru–Ru bond. Other spectral features are in accord with this structure. In the infrared spectrum, only four terminal ν(CO) bands are found, together with a weak absorption at 1861 cm^{-1}, assigned to the μ-CO ligand. Apart from the cot resonance, multiplets centred at δ 3.18 and between δ 5.79 and 7.85 can be assigned to the CH_2 and aromatic protons respectively. A molecular ion is found at m/z 855 in the FAB MS and shows the usual loss of CO groups.

2.4. $Ru_3(\mu\text{-}H)\{\mu_3\text{-}PPh_2CHPPh(C_6H_4)\}(\mu\text{-}C_8H_9)(\mu\text{-}CO)(CO)_4$ (5)

Complex 5 differs from the previous three products in containing a C_8H_9 ligand and a dppm ligand which is metallated at both a phenyl group and the central

Table 7
Non-hydrogen positional and isotropic displacement parameters for $Ru_3\{\mu_3\text{-}PPhCH_2PPh(C_6H_4)\}(\mu\text{-}C_8H_8)(\mu\text{-}CO)(CO)_4$ (4)

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.71700(2)	0.70596(1)	0.72395(2)	0.0298(1)
Ru(2)	0.49275(2)	0.71729(1)	0.52797(2)	0.0315(1)
Ru(3)	0.42268(2)	0.70522(1)	0.64924(2)	0.0297(1)
C(11)	0.7539(3)	0.7269(2)	0.8368(2)	0.041(2)
O(11)	0.7843(3)	0.7378(2)	0.9084(2)	0.067(2)
C(21)	0.3526(3)	0.7195(2)	0.4043(2)	0.043(2)
O(21)	0.2636(3)	0.7232(2)	0.3279(2)	0.065(1)
C(22)	0.3742(3)	0.7902(2)	0.5490(2)	0.043(2)
O(22)	0.3106(3)	0.8472(1)	0.5188(2)	0.063(2)
C(31)	0.2282(4)	0.7005(2)	0.5940(2)	0.047(2)
O(31)	0.1100(3)	0.6987(2)	0.5588(2)	0.084(2)
C(32)	0.4728(3)	0.7898(2)	0.7328(2)	0.041(2)
O(32)	0.4999(3)	0.8386(1)	0.7822(2)	0.065(2)
P(1)	0.67373(7)	0.58073(4)	0.74332(5)	0.0298(3)
C(111)	0.5699(3)	0.5740(2)	0.7884(2)	0.032(1)
C(112)	0.4577(3)	0.6256(2)	0.7501(2)	0.032(1)
C(113)	0.3718(3)	0.6198(2)	0.7807(2)	0.040(2)
C(114)	0.4001(4)	0.5665(2)	0.8467(2)	0.047(2)
C(115)	0.5124(4)	0.5168(2)	0.8837(2)	0.047(2)
C(116)	0.5966(3)	0.5198(2)	0.8540(2)	0.040(2)
C(121)	0.8263(3)	0.5172(2)	0.8117(2)	0.035(1)
C(122)	0.9570(3)	0.5498(2)	0.8734(2)	0.045(2)
C(123)	1.0740(4)	0.5032(2)	0.9246(3)	0.058(2)
C(124)	1.0619(4)	0.4245(2)	0.9165(3)	0.063(2)
C(125)	0.9331(4)	0.3913(2)	0.8562(3)	0.056(2)
C(126)	0.8156(4)	0.4372(2)	0.8035(2)	0.045(2)
C(0)	0.5567(3)	0.5308(2)	0.6342(2)	0.031(1)
P(2)	0.42373(7)	0.60457(4)	0.56274(5)	0.0296(3)
C(211)	0.2626(3)	0.5483(2)	0.4891(2)	0.034(1)
C(212)	0.2247(4)	0.4947(2)	0.5287(2)	0.045(2)
C(213)	0.1009(4)	0.4537(2)	0.4762(3)	0.056(2)
C(214)	0.0128(4)	0.4668(2)	0.3838(3)	0.059(2)
C(215)	0.0475(4)	0.5190(2)	0.3441(3)	0.052(2)
C(216)	0.1733(3)	0.5600(2)	0.3962(2)	0.041(2)
C(1)	0.6986(4)	0.8293(2)	0.6635(3)	0.045(2)
C(2)	0.8356(4)	0.8110(2)	0.7359(3)	0.046(2)
C(3)	0.9196(4)	0.7458(2)	0.7488(3)	0.049(2)
C(4)	0.8742(3)	0.6784(2)	0.6975(2)	0.043(2)
C(5)	0.7465(3)	0.6619(2)	0.6099(2)	0.038(2)
C(6)	0.6726(3)	0.7013(2)	0.5233(2)	0.039(2)
C(7)	0.6352(3)	0.7803(2)	0.5076(2)	0.043(2)
C(8)	0.6230(3)	0.8272(2)	0.5652(2)	0.042(2)

carbon. While the latter feature is common with mononuclear complexes, it is rare with metal clusters because the phenyl groups, with sp^2-hybridised carbons, are usually more readily metallated than alkyl carbons (sp^3).

The Ru_3 cluster is an isosceles triangle with Ru–Ru separations of 2.936 Å (two edges) and 2.967(5) Å. As with **2** and **4**, the longer bond is that bridged by the C_8 ligand. Although of the same separations, Ru(1)–Ru(3) is asymmetrically bridged by CO(12), while Ru(2)–Ru(3) is probably bridged by the H atom, which was not located in the X-ray study. There is some bending away of ligands about this bond: C(6)–Ru(2)–Ru(3) 126.8(9)°, C(21)–Ru(2)–Ru(3) 115(1)°, C(31)–Ru(3)–Ru(2) 101(1)°. The hydrocarbon is η^3-bonded to Ru(1) and η^4-bonded to Ru(2).

The Ru(3)–C(0) and –C(212) distances are 2.25 and 2.03(4) Å; the former, rather imprecise, value may be compared with that for the similar bond found in $Ru_3(\mu\text{-}H)\{\mu_3\text{-}(PMe_2)_2CH\}(CO)_9$ (2.266(4) Å) [19]. The Ru(1,2)–P(1,2) distances are 2.34, 2.30(1) Å, while the Ru(3)–C(0)–P(1,2) angles are strained at 97, 85(2)° respectively; the P(1)–C(0)–P(2) angle is 119(2)°.

A characteristic resonance at δ −15.91 can be assigned to a hydrogen on the cluster (not refined in the X-ray study), probably derived from the dppm ligand. Different couplings to ^{31}P nuclei suggest that it is located on the Ru(2)–Ru(3) vector, which carries no other bridging group. The other H atom has added to the C_8 ligand, which is attached to Ru(1) in an η^3-allylic fashion from C(1,2,3) (Ru(1)–C(1,2,3) 2.04(7)–2.22(4) Å) and to Ru(2) by two isolated double bonds

Table 8
Non-hydrogen positional and isotropic displacement parameters for $Ru_3(\mu\text{-}H)\{\mu_3\text{-}PPh_2CHPPh(C_6H_4)\}(\mu\text{-}C_8H_9)(\mu\text{-}CO)(CO)_4$ (5)

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.8365(2)	0.0921(3)	0.4194(4)	0.028(2)
Ru(2)	0.7761(2)	0.3412(3)	0.4889(4)	0.026(2)
Ru(3)	0.8709(2)	0.2695(3)	0.2424(4)	0.028(2)
C(11)	0.853(3)	−0.074(5)	0.408(5)	0.06(2)
O(11)	0.867(2)	−0.174(3)	0.391(4)	0.07(1)
C(12)	0.939(2)	0.109(3)	0.353(4)	0.02(1)
O(12)	1.010(2)	0.091(3)	0.331(3)	0.043(8)
C(21)	0.756(4)	0.500(6)	0.530(6)	0.09(2)
O(21)	0.737(2)	0.602(4)	0.533(4)	0.09(1)
C(31)	0.982(3)	0.351(5)	0.314(5)	0.06(2)
O(31)	1.037(2)	0.400(3)	0.341(4)	0.07(1)
C(32)	0.908(2)	0.214(4)	0.090(5)	0.04(1)
O(32)	0.927(2)	0.176(3)	−0.031(3)	0.06(1)
P(1)	0.7466(7)	0.059(1)	0.213(1)	0.030(5)
C(111)	0.652(2)	−0.013(4)	0.232(4)	0.03(1)
C(112)	0.576(3)	0.037(5)	0.210(5)	0.06(2)
C(113)	0.500(3)	−0.024(5)	0.236(5)	0.07(2)
C(114)	0.503(4)	−0.117(6)	0.303(6)	0.09(2)
C(115)	0.571(4)	−0.174(6)	0.312(6)	0.10(2)
C(116)	0.641(3)	−0.121(5)	0.282(5)	0.06(2)
C(121)	0.774(2)	−0.040(4)	0.058(4)	0.03(1)
C(122)	0.715(3)	−0.080(4)	−0.063(5)	0.04(1)
C(123)	0.736(3)	−0.149(4)	−0.182(5)	0.04(1)
C(124)	0.811(3)	−0.176(4)	−0.205(4)	0.04(1)
C(125)	0.873(3)	−0.140(4)	−0.091(5)	0.04(1)
C(126)	0.854(2)	−0.070(4)	0.028(4)	0.03(1)
C(0)	0.744(2)	0.196(4)	0.153(4)	0.03(1)
P(2)	0.7077(7)	0.330(1)	0.268(1)	0.028(5)
C(211)	0.753(3)	0.439(4)	0.179(5)	0.05(1)
C(212)	0.839(2)	0.418(4)	0.162(4)	0.03(1)
C(213)	0.879(3)	0.500(4)	0.103(5)	0.04(1)
C(214)	0.848(3)	0.596(4)	0.056(5)	0.05(1)
C(215)	0.768(3)	0.622(5)	0.088(5)	0.07(2)
C(216)	0.719(2)	0.548(4)	0.137(4)	0.03(1)
C(221)	0.593(2)	0.348(4)	0.238(5)	0.03(1)
C(222)	0.558(3)	0.348(5)	0.105(6)	0.07(2)
C(223)	0.472(3)	0.351(4)	0.079(5)	0.06(1)
C(224)	0.431(3)	0.375(4)	0.197(5)	0.05(1)
C(225)	0.461(3)	0.385(5)	0.324(6)	0.07(2)
C(226)	0.549(3)	0.370(4)	0.358(5)	0.04(1)
C(1)	0.741(3)	0.097(6)	0.568(5)	0.05(1)
C(2)	0.816(4)	0.091(6)	0.624(7)	0.10(2)
C(3)	0.882(3)	0.181(5)	0.639(5)	0.05(1)
C(4)	0.882(2)	0.310(4)	0.659(4)	0.03(1)
C(5)	0.828(2)	0.387(3)	0.726(4)	0.02(1)
C(6)	0.755(3)	0.342(4)	0.784(5)	0.05(1)
C(7)	0.699(3)	0.304(4)	0.656(5)	0.04(1)
C(8)	0.691(2)	0.200(4)	0.565(4)	0.03(1)

(Ru(2)–C(4,5) 2.37, 2.33(4) Å; Ru(2)–C(7,8) 2.22(5), 2.34(4) Å). Within the precision of this structure, these distances are similar to those found previously for similar systems. These include the complexes $Ru_3(\mu\text{-}C_8H_9)(CO)_6(\eta^5\text{-}C_8H_9)$ [18] and $Ru_2(\mu\text{-}\eta^3\text{:}\eta^2,\eta^2\text{-}\mathit{Si}\text{–}C_8H_8SiMe_2C_2H_4SiMe_2)(CO)_5$ [20]. In the former, the hydrocarbon-bridged Ru–Ru bond is 2.853(1) Å, while the Ru–C(ring) separations range between 2.194 and 2.275 Å. In the binuclear complex, the ring allylic carbons are between 2.187–2.263(7) Å from one ruthenium, while the two η^2 systems are separated by 2.302–2.357(5) Å from the other Ru atom. Atom C(6) is bent away from the cluster and, although H atoms were not refined, angle C(5)–C(6)–C(7) (101(4)°) is consistent with sp^3 hybridisation for this carbon, it bears two hydrogens in agreement with the electron counts and stoichiometry of the complex as a whole. Unfortunately, 5 was obtained in amounts too small for detailed NMR studies to confirm this point.

The spectroscopic properties of 5 also include five

Table 9
Crystal data and refinement details for complexes **2**, **3**, **4** and **5**

Compound	**2**	**3**	**4**	**5**
Formula	$C_{39}H_{30}O_6P_2Ru_3$	$C_{38}H_{30}O_5P_2Ru_3$	$C_{32}H_{24}O_5P_2Ru_3$	$C_{38}H_{30}O_5P_2Ru_3$
MW	959.8	931.8	853.7	931.8
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_12_12_1$; (No. 19)	$P2_1/c$; (No. 14)	$P2_1/c$; (No. 14)	$P\bar{1}$; (No. 2)
a (Å)	21.609(7)	10.224(3)	11.711(2)	16.306(7)
b (Å)	15.701(5)	22.282(3)	17.266(3)	11.243(5)
c (Å)	10.512(3)	17.774(2)	18.048(2)	9.659(6)
α (deg)				101.06(5)
β (deg)		121.07(2)	125.63(1)	94.52(4)
γ (deg)				91.67(3)
V (Å^3)	3568	3468	2966	1731
Z	4	4	4	2
D_c (g cm^{-3})	1.79	1.78	1.91	1.78
F(000)	1896	1840	1672	920
Crystal size (mm^3)	0.38 × 0.29 × 0.55	0.32 × 0.14 × 0.20	0.07 × 0.32 × 0.75	0.09 × 0.03 × 0.20
A^* (min, max)	1.30, 1.42	1.21, 1.41	1.13, 1.75	1.06, 1.15
μ (cm^{-1})	13.6	14.3	16.6	14.3
$2\theta_{max}$ (deg)	50	60	60	45
N	3534	9056	8283	4513
N_o	3175	6643	6367	1611
R	0.026	0.030	0.027	0.089
R_w	0.027	0.032	0.029	0.092

terminal ν(CO) bands and a μ-CO absorption at 1894 cm^{-1} in the infrared spectrum, while the CH proton appears as a triplet at δ 4.60 in the ^{1}H NMR spectrum. The individual ring protons of the C_8H_9 ligand were not resolved, a broad multiplet being found between δ 2.58 and 3.82. The FAB MS confirms the stoichiometry, with a molecular ion at m/z 933 and ions formed by stepwise loss of up to five CO groups.

3. Conclusions

The major difference found between the reactions of cot with $Ru_3(CO)_{12}$ and **1** is the preservation of the Ru_3 core in the complexes obtained from **1**. Complexes **2**–**5** contain monocyclic C_8 ligands, no evidence being found for the formation of pentalene or other bicyclic ligands. The bonding of the C_8 ligands to the Ru_3 core in **2**, **4** and **5** resembles that found in complexes derived from ruthenium carbonyl or other tertiary phosphine-free precursors, although these may be binuclear, rather than trinuclear, complexes. In all cases, the C_8H_8 ligand acts as an eight-electron donor, while the C_8H_9 ligand in **5** is a seven-electron donor. All complexes are electron-precise.

In the case of **3**, we have obtained the first example of an Ru_3 cluster containing a cot ligand attached to all three metal atoms. The detailed structural parameters are not easily interpreted in terms of a valence bond picture, extensive delocalisation occurring. Some Ru–C(ring) separations are longer than 2.5 Å; however, for the cot ligand to act as an eight-electron donor, atoms C(3) and C(6) should be involved in the ring–cluster bonding, if only weakly. Possibly the solid-state structure represents an intermediate stage in the fluxional process. In **2** and **4**, the cot ligand is fluxional, following the precedents set by the carbonyl analogues. Variable-temperature NMR experiments to determine the effect of the dppm ligand on the energy or mechanism of the fluxional processes will be described elsewhere.

As found previously, the dppm ligand is very prone to thermal alteration by reactions involving oxidative addition of C–H or C–P bonds to the cluster and elimination of the elements of benzene. Here, we have found examples of complexes containing the dephenylated dppm ligand (in **3**), the metallated dephenylated ligand (in **4**) and, unusually, dppm doubly metallated at the aryl and methylene carbons (in **5**). In the latter example, the two H atoms from the dppm ligand appear on the cluster and incorporated into the C_8H_9 ligand. For the first time, we have isolated a complex (**3**) in which the phenyl group has not been eliminated completely, but trapped on the cluster as a σ-bonded phenyl group. Consequently, the P–Ph bond can be said to have oxidatively added to Ru(2), which is also involved in bonding to at least three of the ring carbons.

In contrast, the formation of **4** involves loss of (Ph + H) from the ligand, again in a process mediated by the cluster. A separate experiment showed that on heating in refluxing toluene, **2** was converted to **4** (albeit in only 30% isolated yield), together with an isomer of **2**, containing a static cot ligand (NMR) which we have been unable to characterise further.

4. Experimental

4.1. Instrumentation

IR: Perkin-Elmer 1700X FT IR. NMR: Bruker CXP300 or ACP300 (^{1}H NMR at 300.13 MHz). FAB MS: VG ZAB 2HF (using 3-nitrobenzyl alcohol as matrix, exciting gas Ar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 7 kV).

4.2. General reaction conditions

Reactions were carried out under an atmosphere of nitrogen, but no special precautions were taken to exclude oxygen during work-up.

4.3. Starting materials

$Ru_3(\mu\text{-dppm})(CO)_{10}$ was prepared by the literature method [21]; cyclooctatetraene (Aldrich) was used as-supplied.

4.4. Reaction of $Ru_3(\mu\text{-dppm})(CO)_{10}$ with cycloocta-1,3,5,7-tetraene

(a) A mixture of $Ru_3(\mu\text{-dppm})(CO)_{10}$ (255 mg, 0.264 mmol) and cot (520 mg, 5.0 mmol) was heated in refluxing thf (30 ml) for 45 h. After removal of solvent (rotary evaporator), preparative TLC (acetone–hexane 1:2) separated several coloured bands. An orange-red band (R_f 0.74) gave red crystals, shown to be $Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(\mu_3\text{-}C_8H_8)(Ph)(CO)_5$ (3) by an X-ray structure determination. IR (CH_2Cl_2): $\nu(CO)$ 2073vs, 2034vs, 2028vs, 2006vs, 1987s, 1962m, 1937 (sh) cm^{-1}. FAB MS (m/z): 933, M$^+$. Band 5 (orange-yellow, R_f 0.72) afforded orange crystals (from CH_2Cl_2–MeOH) of $Ru_3(\mu\text{-}H)\{\mu_3\text{-}PPh_2CHPPh(C_6H_4)\}(\mu\text{-}C_8H_9)(\mu\text{-}CO)(CO)_4$ (5) (43 mg, 17%), m.p. > 170°C (dec.). Found: C, 48.56; H, 3.25; $C_{38}H_{30}O_5P_2Ru_3$ requires C, 48.98; H, 3.25%. IR (cyclohexane): $\nu(CO)$ 2030vs, 1980s, 1972s, 1964vs, 1941w, 1894w cm^{-1}. ^{1}H NMR: $\delta(CDCl_3)$ −15.91 (dd, J(HP) = 19, 4 Hz, 1H, RuH), 2.58–3.82 (m, 9H, C_8H_9), 4.60 (t, J(HP) = 6.6 Hz, 1H, PCHP), 5.97–7.71 (m, 19H, Ph + C_6H_4). FAB MS (m/z, relative intensity): 933, 100, M$^+$; 905, 17, [M − CO]$^+$; 877, 19, [M − 2CO]$^+$; 849, 28, [M − 3CO]$^+$; 821, 36, [M − 4CO]$^+$; 793, 48, [M − 5CO]$^+$. Band 6 (orange, R_f 0.58) gave red crystals (from CH_2Cl_2–MeOH) of $Ru_3\{\mu_3\text{-}PPhCH_2PPh(C_6H_4)\}(\mu\text{-}C_8H_8)(\mu\text{-}CO)(CO)_4$ (4) (8 mg, 4%), m.p. > 180°C (dec.). Found: C, 44.68; H, 3.15; $C_{32}H_{24}O_5P_2Ru_3$ requires C, 45.02; H, 2.83%. IR (cyclohexane): $\nu(CO)$ 2026m, 1978vs, 1969m, 1947m, 1861w cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 2.97–3.18 (m, ABXY pattern, 2H, CH_2), 4.38 (s, 8H, C_8H_8), 5.79–7.85 (m, 14H, Ph + C_6H_4). FAB MS (m/z, relative intensity): 855, 58, M$^+$; 827, 59, [M − CO]$^+$; 799, 86, [M − 2CO]$^+$; 771, 100, [M − 3CO]$^+$; 743, 51, [M − 4CO]$^+$; 715, 76, [M − 5CO]$^+$. Band 8 (red, R_f 0.54) gave red-brown crystals (from CH_2Cl_2–MeOH) of $Ru_3(\mu\text{-dppm})(\mu\text{-}C_8H_8)(CO)_6$ (2) (74 mg, 29%), m.p. > 180°C (dec.). Found: C, 48.32; H, 3.28; $C_{39}H_{30}O_6P_2Ru_3$ requires C, 48.80; H, 3.15%. IR (cyclohexane): $\nu(CO)$ 2033s, 1977vs, 1964s, 1944s, 1922w, 1906w cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 4.12 (s, 8H, C_8H_8), 4.51 (t, J(HP) = 10 Hz, 2H, CH_2), 7.21–7.59 (m, 20H, Ph). FAB MS (m/z, relative intensity): 961, 54, M$^+$; 933, 62, [M − CO]$^+$; 905, 92, [M − 2CO]$^+$; 877, 65, [M − 3CO]$^+$; 849, 77, [M − 4CO]$^+$; 821, 65, [M − 5CO]$^+$; 793, 100, [M − 6CO]$^+$. Other bands contained only trace amounts of unidentified materials.

(b) A similar reaction between $Ru_3(\mu\text{-dppm})(CO)_{10}$ (0.264 mmol) and cot (0.77 mmol) for 52 h gave $Ru_3\{\mu_3\text{-}PPhCH_2PPh(C_6H_4)\}(CO)_9$ (16%), 5 (3%) and 2 (21%).

4.5. Pyrolysis of $Ru_3(\mu\text{-dppm})(\mu\text{-}C_8H_8)(CO)_6$ (2)

A solution of $Ru_3(\mu\text{-dppm})(\mu\text{-}C_8H_8)(CO)_6$ (30 mg, 0.031 mmol) was heated in refluxing toluene (15 ml) for 2.5 h, after which time solvent was removed under vacuum. Preparative TLC (acetone–hexane 3:7) gave two major products. Band 1 (yellow, R_f 0.78) gave yellow crystals having the composition $Ru_3(CO)_6(dppm)(C_8H_8)$ (8 mg, 23%), of undetermined structure. IR (CH_2Cl_2): $\nu(CO)$ 2070vw, 2006w, 1978vs, 1938(sh), 1931m cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 3.41 (s, 4H, C_8H_8), 3.98 (m, 2H, C_8H_8), 4.10–4.20 (m, 2H, C_8H_8), 5.26 (t, J(HP) = 10 Hz, 2H, CH_2), 7.17–7.87 (m, 20H, Ph). FAB MS (m/z, relative intensity): 961, 35, M$^+$; 933, 100, [M − CO]$^+$; 905, 88, [M − 2CO]$^+$; 877, 35, [M − 3CO]$^+$; 849, 61, [M − 4CO]$^+$; 821, 67, [M − 5CO]$^+$; 793, 70, [M − 6CO]$^+$. Band 2 (orange, R_f 0.69) gave red crystals (from CH_2Cl_2–MeOH) of 4 (8 mg, 30%), identified by TLC and IR. Several other products were present in trace amounts only.

5. Crystallography

Unique data sets were measured at ca. 295 K within the specified $2\theta_{max}$ limits using an Enraf–Nonius CAD4 diffractometer (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 3.0 program system [22] implemented by Hall and Stewart; neutral atom complex scattering factors were employed. Pertinent results are given in the figures and Tables 1–9. Material deposited at the Cambridge Crystallographic Data Centre comprises thermal and hydrogen parameters, and full molecular non-hydrogen geometries.

5.1. Abnormal features / variations in procedure

(2). (x, y, z, U_{iso}) were refined for H(1–8); residuals for the alternative chirality were 0.028, 0.030.

(3), (4). (x, y, z, U_{iso}) were refined for all H atoms.

(5). Data from the small specimen were weak and limited and would support meaningful anisotropic thermal parameter refinement for Ru, P only.

Acknowledgements

We thank the Australian Research Council for support of this work and Johnson Matthey Technology plc for a generous gift of $RuCl_3 \cdot nH_2O$.

References

[1] A.J. Deeming, in E.W. Abel, F.G.A. Stone and G. Wilkinson (eds.), *Comprehensive Organometallic Chemistry*, Vol. 7, Elsevier, Oxford, 2nd edn., 1995, Chapter 12, p. 683.

[2] N. Lugan, J.-J. Bonnet and J.A. Ibers, *J. Am. Chem. Soc.*, *107* (1985) 4484.

[3] (a) M.I. Bruce, J.R. Hinchliffe, R.J. Surynt, B.W. Skelton and A.H. White, *J. Organomet. Chem.*, *469* (1994) 89; (b) M.I. Bruce, N.N. Zaitseva, B.W. Skelton and A.H. White, *J. Organomet. Chem.*, in press.

[4] (a) M.I. Bruce, P.A. Humphrey, H. Miyamae, B.W. Skelton and A.H. White, *J. Organomet. Chem.*, *429* (1992) 187; (b) M.I. Bruce, P.A. Humphrey, E. Horn, E.R.T. Tiekink, B.W. Skelton and A.H. White, *J. Organomet. Chem.*, *429* (1992) 207.

[5] M.I. Bruce, J.R. Hinchliffe, B.W. Skelton and A.H. White, *J. Organomet. Chem.*, *495* (1995) 141.

[6] M.I. Bruce, P.A. Humphrey, B.W. Skelton and A.H. White, *J. Organomet. Chem.*, in press.

[7] M.I. Bruce, M. Cooke, M. Green and F.G.A. Stone, *Chem. Commun.*, (1967) 523; M.I. Bruce, M. Cooke and M. Green, *J. Organomet. Chem.*, *13* (1968) 227.

[8] F.A. Cotton, A. Davison and A. Musco, *J. Am. Chem.Soc.*, *89* (1967) 6796.

[9] F.A. Cotton and R. Eiss, *J. Am. Chem. Soc.*, *91* (1969) 6593.

[10] F.A. Cotton and W.T. Edwards, *J. Am. Chem. Soc.*, *90* (1968) 5412.

[11] M.J. Bennett, F.A. Cotton and P. Legzdins, *J. Am. Chem. Soc.*, *90* (1968) 6335.

[12] W.K. Bratton, F.A. Cotton, A. Davidson, A. Musco and J.W. Faller, *Proc. Nat. Acad. Sci. US*, *58* (1967) 1324; F.A. Cotton, A. Davison, T.J. Marks and A. Musco, *J. Am. Chem. Soc.*, *91* (1969) 6598.

[13] J.D. Edwards, J.A.K. Howard, S.A.R. Knox, V. Riera, F.G.A. Stone and P. Woodward, *J. Chem. Soc. Dalton Trans.*, (1976) 75; J.D. Edwards, J.A.K. Howard, S.A.R. Knox, V. Riera and F.G.A. Stone, *J. Chem. Soc. Dalton Trans.*, (1980) 552.

[14] S.A.R. Knox and F.G.A. Stone, *Acc. Chem. Res.*, *7* (1974) 321.

[15] A.W. Coleman, D.F. Jones, P.H. Dixneuf, C. Brisson, J.-J. Bonnet and G. Lavigne, *Inorg. Chem.*, *23* (1984) 952.

[16] T.A. Cresswell, J.A.K. Howard, F.G. Kennedy, S.A.R. Knox and H. Wadepohl, *J. Chem. Soc. Dalton Trans.*, (1981) 2220.

[17] D. Braga and B.F.G. Johnson, *Chem. Rev.*, *94* (1994) 1585.

[18] R. Bau, B.C.-K. Chou, S.A.R. Knox, V. Riera and F.G.A. Stone, *J. Organomet. Chem.*, *82* (1974) C43.

[19] J.A. Clucas, D.F. Foster, M.M. Harding and A.K. Smith, *J. Chem. Soc. Dalton Trans.*, (1987) 277.

[20] R. Goddard and P. Woodward, *J. Chem. Soc. Dalton Trans.*, (1980) 559.

[21] M.I. Bruce, B.K. Nicholson and M.L. Williams, *Inorg. Synth.*, *26* (1989) 276; *28* (1990) 224.

[22] S.R. Hall and J.M. Stewart (eds.), XTAL *Users' Manual, Version 3.0*, 1990, Universities of Western Australia and Maryland.