

Reactions of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ with unsaturated hydrocarbons. Pentamethylcyclopentadiene. X-ray structure of $\text{Ru}_4(\mu\text{-H})(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\mu\text{-}\eta^1:\eta^5\text{-CH}_2\text{C}_5\text{Me}_4)(\text{CO})_8$

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 17 January 1996

Abstract

Reactions between $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ and pentamethylcyclopentadiene in refluxing THF afford $\text{Ru}_4(\mu\text{-H})(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\mu\text{-}\eta^1:\eta^5\text{-CH}_2\text{C}_5\text{Me}_4)(\text{CO})_8$ as the major isolable product. The cluster contains a tetrahedral Ru_4 core, one face of which is capped by the $\mu_3\text{-PPhCH}_2\text{PPh}_2$ ligand, with edges bridged by an H atom, two CO groups and a $\mu\text{-}\eta^1:\eta^5\text{-CH}_2\text{C}_5\text{Me}_4$ ligand.

Keywords: Ruthenium; Cluster; Crystal structure; Pentamethylcyclopentadiene

1. Introduction

The chemistry of the bis-tertiary phosphine-substituted cluster $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ (**1**; Scheme 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 binuclear species, but in some reactions concomitant core expansion to Ru_4 or higher nuclearity complexes has also been observed [3].

Continuing our studies of reactions between **1** and unsaturated hydrocarbons, of which we have described those with alkynes [4] and with norbornadiene [5], we have examined some reactions between **1** and cyclopentadienes. Reactions between $\text{Ru}_3(\text{CO})_{12}$ and cyclopentadienes have been used as sources of complexes containing $\text{Ru}(\text{CO})_2(\eta\text{-C}_5\text{R}_5)$ fragments (usually as mono- or binuclear species) [6]. This paper describes the reaction with pentamethylcyclopentadiene (HC_5Me_5 or HCp^*)

from which the two complexes $\text{Ru}_3\{\mu_3\text{-PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}(\text{CO})_9$ (**2**) and $\text{Ru}_4(\mu\text{-H})(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\mu\text{-}\eta^1:\eta^5\text{-CH}_2\text{C}_5\text{Me}_4)(\text{CO})_8$ (**3**) were obtained.

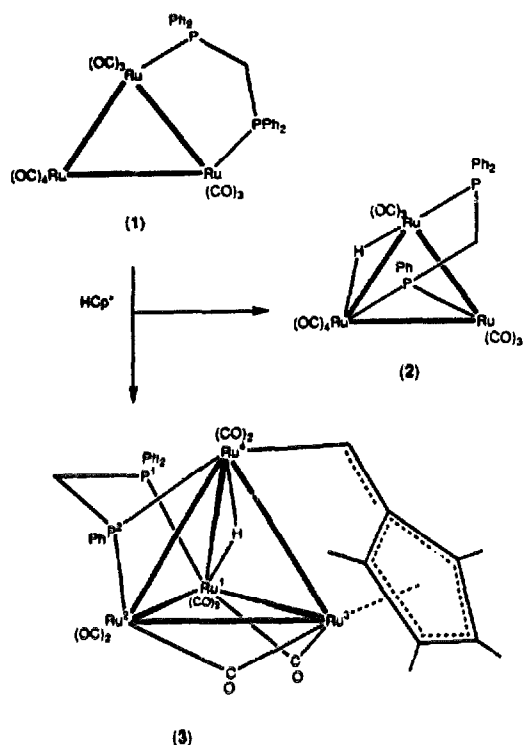
2. Results and discussion

The reaction between **1** and HCp^* was carried out in refluxing THF. Spot thin layer chromatography (TLC) investigation of the reaction showed that a multitude of products was formed and we have not been able to find more selective reaction conditions under which any one or two were the only products. Evidently the first-formed products are sensitive to further reaction(s). However, after a day's heating two major products were present and were separated by preparative TLC.

The first of these was the known complex $\text{Ru}_3\{\mu_3\text{-PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}(\text{CO})_9$ (**2**) which has been structurally characterised on a previous occasion [2] and is a product of thermal alteration of the dppm ligand. In this case, metallation of one of the *P*-phenyl groups is followed by elimination of a second phenyl group as benzene by combination with the H atom displaced to the cluster by the metallation reaction.

The second product was identified as the tetranuclear derivative $\text{Ru}_4(\mu\text{-H})(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\mu\text{-}\eta^1:\eta^5\text{-CH}_2\text{C}_5\text{Me}_4)(\text{CO})_8$ (**3**) from its FAB mass spectrum.

* Corresponding author.



Scheme 1.

which showed a parent ion at m/z 1072 with an isotopic pattern consistent with that required for an Ru_4 species. Further consideration of the stoichiometry suggested that dephenylation of the dppm ligand had occurred. The fragmentation pattern suggested the presence of eight CO ligands. The molecular structure of **3** has been determined from a single-crystal X-ray study.

Fig. 1 is a plot of a molecule of **3**; selected structural parameters are collected in Table 1. As can be seen, the complex is indeed an Ru_4 cluster, containing a tetrahedral core, one face of which [Ru(1,2,4)] is capped by the μ_3 -PPhCH₂PPh₂ ligand. The Ru(3,4) edge is bridged by a $\text{CH}_2\text{C}_5\text{Me}_4$ group, and coordination is completed by a hydride ligand and two bridging and six terminal CO groups.

The range of Ru–Ru bond distances [2.705–2.990(1) Å] is characteristic of other ruthenium clusters. The shortest bonds [Ru(1,2)–Ru(3) 2.761(1), 2.705(1) Å] are asymmetrically bridged by CO(31) and CO(32) [Ru(3)–C(31,32) 1.942(7), 1.956(8), Ru(1)–C(31) 2.247(7), Ru(2)–C(32) 2.259(8) Å] ligands, while the longest [Ru(1)–Ru(4) 2.990(1) Å] is bridged by a hydrogen atom [located and refined in the structural determination, with Ru(4,1)–H 1.81(6), 1.85(5) Å]. The μ_3 -PPhCH₂PPh₂ ligand, formed by loss of Ph from the original dppm ligand in **1**, caps the Ru(1,2,4) face, with P(1) being attached to Ru(1) [2.316(2) Å] by a normal $2e^-$ donor bond, while the phosphido atom P(2) bridges the Ru(2)–Ru(4) vector [Ru(2,4)–P(2) 2.243, 2.351(2) Å]. In $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\text{CO})_9$, these dis-

tances are 2.384(1) and 2.306, 2.332(1) Å respectively, while the Ru–Ru edge bridged by the hydrogen is 3.012(1) Å [2]. A closely related complex is $\text{Ru}_4(\mu\text{-H})_3(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\text{CO})_{10}$, obtained by pyrolysis of $\text{Ru}_4(\mu\text{-H})_4(\mu\text{-dppm})(\text{CO})_{10}$ [7]. In this complex, the corresponding distances are 2.349(2) and 2.303(2), 2.305(3) Å respectively, while the Ru–Ru edge bridged by H are 2.977–2.990(1) Å. Interestingly, while one edge of an Ru_3 face is bridged by the phosphido-P atom, the other two are bridged by CO groups as found in **3**, with lengths of 2.756(1) and 2.764(1) Å.

The Ru(3)–Ru(4) edge is bridged by a $\text{CH}_2\text{C}_5\text{Me}_4$ ligand, formed by formal deprotonation of a C_5Me_5 group. Attachment of the ring CH_2 group to Ru(4) is characterised by a very long Ru–C interaction [Ru(4)–C(1011) 2.287(7) Å] and a small Ru(4)–C(1011)–C(101) angle [95.9(4)°]. There is also an η^5 interaction of the C_5 ring with Ru(3) [Ru(3)–C(ring) 2.206–2.276(7), av. 2.25 Å]. These data suggest that the organic ligand is bonded mainly as the tetramethylfulvene ligand, rather than as a σ/π metallated cyclopentadienylmethyl group.

The more common mode of bonding of fulvene ligands bridging two metal atoms is the $\mu\text{-}\eta^1:\eta^5$ mode. Quite recently, the complex $\text{Ru}_6\text{C}(\mu\text{-}\eta^1:\eta^5\text{-CH}_2\text{C}_5\text{H}_4)(\mu\text{-CO})_2(\text{CO})_{12}$ has been isolated as a minor product from the reaction of $\text{Ru}_6\text{C}(\text{CO})_{17}$ with cyclopentadiene in the presence of Me_3NO [8]. The fulvene ligand bridges an Ru–Ru edge [of length 2.805(1) Å] in the same manner as that found in **3** [2.855(1) Å], with Ru–C(σ) and Ru–C(π) distances of 2.204(10) and 2.170–2.254(10) Å respectively. Interestingly, the η^5 -bonded Ru atom also has two bridging CO ligands attached to it. Within the fulvene ring, C–C distances are 1.388–1.447(14) Å, while the C(ring)–C(CH_2) separation is 1.435(14) Å. In **3**, comparable values are 1.43–1.45(1) Å within the ring, and 1.43(1) Å for the C(101)–C(1011) separation. These data indicate a significant degree of electron delocalisation over the six carbon atoms of the fulvene skeleton.

Comparable structural parameters for the M–C σ bonds in some Os clusters, which are 2.15(1) Å in $\text{Os}_4(\mu\text{-}\eta^1:\eta^5\text{-CH}_2\text{C}_5\text{Me}_4)(\text{CO})_{11}$ and 2.17(2) Å in $\text{Os}_4(\mu\text{-H})_3(\mu_3\text{-}2\eta^1:\eta^5\text{-(CH}_2)_2\text{C}_5\text{Me}_3)(\text{CO})_9$ [9], are considerably shorter than those found in **3**. This shortening is paralleled in the $[\text{OsCp}^*(\text{CH}_2\text{C}_5\text{Me}_3)]^+$ cation, where the Os– CH_2 separation [2.244(5) Å] is also shorter than two of the Os–ring C distances. The CH_2 -ring C bond is 1.426(7) Å [10].

The spectroscopic properties of **3** are consistent with its solid-state structure, the IR spectrum showing two weak bridging $\nu(\text{CO})$ absorptions at 1864 and 1831 cm^{-1} . In the ^1H NMR spectrum, the Ru–H resonance is found at δ – 16.09 coupled to two different ^{31}P nuclei. Other proton signals were assigned to the four unchanged Me groups (between δ 0.88 and 2.01), the ring

Table 1
Selected bond lengths (Å) and angles (deg) for $\text{Ru}_4(\mu\text{-HX})(\mu\text{-dppm})(\mu\text{-}\eta^5\text{-CH}_2\text{C}_5\text{Me}_4)(\text{CO})_8$ (3)

Bond lengths	
Ru(1)–Ru(2)	2.813(1)
Ru(1)–Ru(3)	2.761(1)
Ru(1)–Ru(4)	2.990(1)
Ru(2)–Ru(3)	2.705(1)
Ru(2)–Ru(4)	2.793(1)
Ru(3)–Ru(4)	2.855(2)
Ru(1)–P(1)	2.316(2)
Ru(2)–P(2)	2.243(2)
Ru(4)–P(2)	2.351(2)
Ru(3)–C(01–05)	2.276, 2.222, 2.263, 2.266, 2.206(7)
Ru(3)–C(Cp [*]) (av.)	2.25
Ru(4)–C(1011)	2.287(7)
Bond angles	
Ru(3)–C(31)–O(31)	147.7(6)
Ru(3)–C(32)–O(32)	147.3(6)
Ru(4)–C(1011)–C(101)	95.9(4)
P(1)–C(0)–P(2)	108.0(4)

CH_2 group (an AB quartet centred at δ 2.58) and the CH_2P group (at δ 2.42 and 3.65).

Formation of the hydrocarbon ligand could occur by

oxidative addition of the hydrocarbon HCp^* to the cluster to give an intermediate containing an $\eta^5\text{-Cp}^*$ ligand attached to one ruthenium atom. The acidic H atom of the diene becomes attached to the cluster. Subsequently, a C–H bond of one of the ring Me groups is broken by addition to the cluster to give an Ru–C σ bond and a second cluster-bound hydrogen atom. Dephenylation of the dppm ligand may result by combination of one of these H atoms with the Ph group with elimination of benzene. We cannot determine at which point cluster expansion occurs. The cluster valence electron count is 60 [$1(\text{H}) + 8 \times 2(\text{CO}) + 5(\text{dppm-Ph}) + 6(\text{CH}_2\text{C}_5\text{Me}_4) + 32(4 \times \text{Ru})$], as expected for a tetrahedral Ru_4 cluster. Individually, atoms Ru(1) and Ru(2) have 19 and 17e[−] counts respectively, the electron density being redistributed in some part by the semi-bridging CO groups.

Considering the nature of the $\text{CH}_2\text{C}_5\text{Me}_4$ ligand, the distribution of ring C–C bond lengths and the geometry about the methylene carbon atom C(1011) suggest that this moiety is best described as a tetramethylfulvene. Although direct comparisons are of limited use, it is interesting to find that the interactions of the methylene

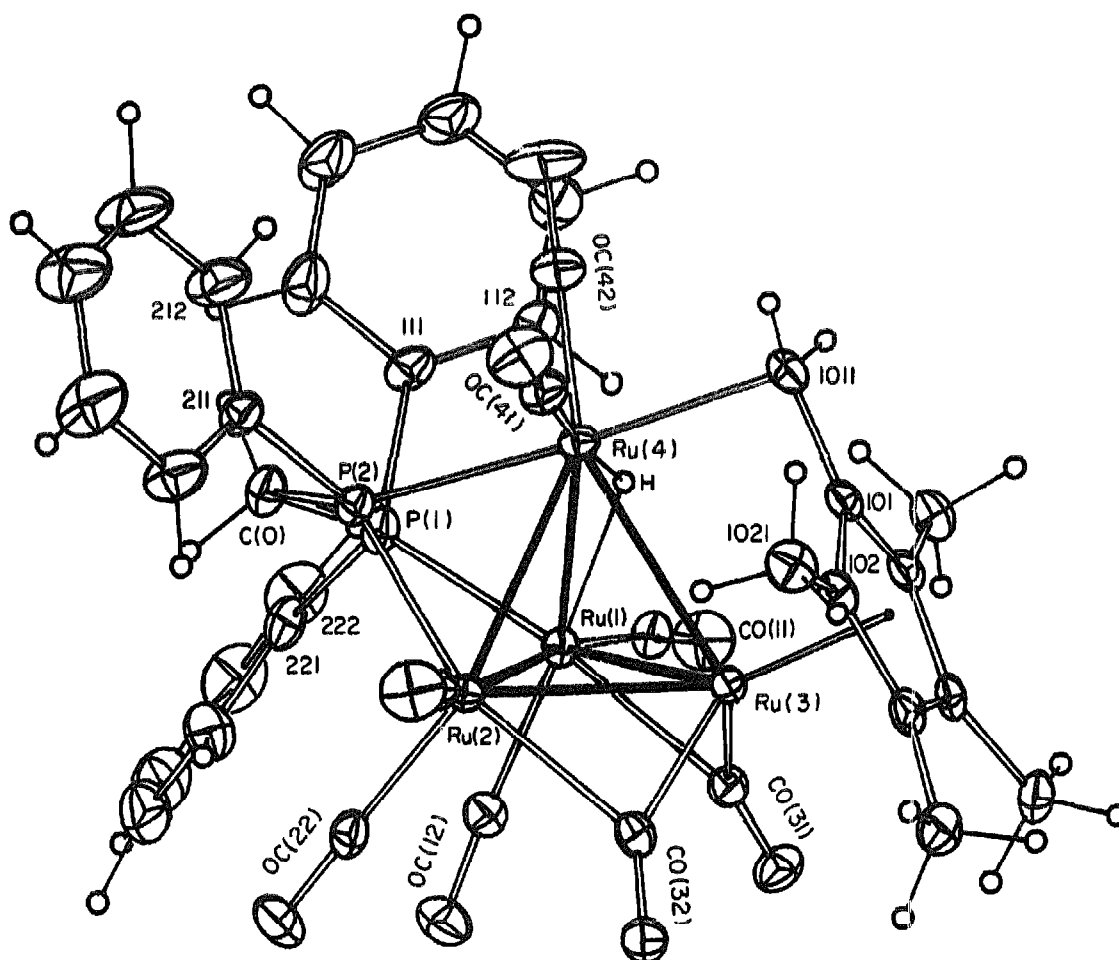


Fig. 1. Plot of a molecule of $\text{Ru}_4(\mu\text{-HX})(\mu\text{-dppm})(\mu\text{-}\eta^5\text{-CH}_2\text{C}_5\text{Me}_4)(\text{CO})_8$ (3) showing the atom numbering scheme. Non-hydrogen atoms are shown with 20% thermal envelopes; hydrogen atoms have arbitrary radii of 0.1 Å.

group with the metal centres in **3** and the osmium complexes parallel the change from weak to strong bonding found in the metallocenylcarbonium cation mentioned above [10].

In the reactions described above, we have not succeeded in identifying any cluster containing an unaltered $\eta^5\text{-Cp}^*$ ligand. In the chemistry of osmium cluster carbonyls, Pomeroy and coworkers [9] have described the pyrolysis of $\text{Os}_4(\mu\text{-H})(\text{CO})_{12}\text{Cp}^*$ above 90°C to give the three clusters $\text{Os}_4(\mu\text{-H})_2(\mu\text{-}\eta^1, \eta^5\text{-CH}_2\text{C}_5\text{Me}_4)(\text{CO})_{10}$, $\text{Os}_4(\mu\text{-}\eta^1, \eta^5\text{-CH}_2\text{C}_5\text{Me}_4)(\text{CO})_{11}$, and $\text{Os}_4(\mu\text{-H})_3(\mu_3\text{-}2\eta^1, \eta^5\text{-(CH}_2)_2\text{C}_5\text{Me}_3)(\text{CO})_9$, showing the successive C–H cleavage reactions of one and two methyl groups of the Cp^* ligand. Undoubtedly, similar reactions are involved in the formation of **3**.

3. Conclusions

Double oxidative addition of HCp^* involving the ring C–H and one methyl C–H bonds occurs in its reaction with **1**. Both reactions occur on the cluster with elimination of C_6H_6 , probably formed by combination of cluster-bound H and a Ph group from the dppm ligand to form the product $\text{Ru}_4(\mu\text{-H})(\mu_3\text{-PPhCH}_2\text{-PPh}_2)(\mu\text{-}\eta^1: \eta^5\text{-CH}_2\text{C}_5\text{Me}_4)(\text{CO})_8$ (**3**). During the reaction, a fourth ruthenium carbonyl residue, probably originating from cluster degradation reactions to as yet uncharacterised products, is added to the original Ru_3 cluster.

4. Experimental

4.1. Instrumentation

IR: Perkin-Elmer 1700X FT IR. NMR: Bruker CXP300 or ACP300 (^1H 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

$\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ [11] and HCp^* [12] were obtained by the cited procedures.

4.4. Reaction of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ with HC_5Me_5

A mixture of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ (197 mg, 0.204 mmol) and HC_5Me_5 (150 mg, 1.06 mmol) in THF (32

ml) was refluxed until spot TLC showed that no $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ remained (approximately 23 h). Preparative TLC (acetone/light petroleum, 7/13) showed two major bands and a plethora of minor bands. Band 5 (orange, R_f 0.75) was identified as $\text{Ru}_3\{\mu_3\text{-PPhCH}_2\text{PPh}(C_6H_4)\}(\text{CO})_9$ (**2**) (33 mg, 19%) by comparison of its IR $\nu(\text{CO})$ spectrum with that of an authentic sample. Band 7 (purple, R_f 0.61) was crystallised ($\text{CH}_2\text{Cl}_2/\text{MeOH}$) to give black crystals of $\text{Ru}_4(\mu\text{-H})(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\mu\text{-CH}_2\text{C}_5\text{Me}_4)(\text{CO})_8$ (**3**) (34 mg, 21%), m.p. 178–180°C. Anal. Found: C, 41.11; H, 2.97. $\text{C}_{37}\text{H}_{32}\text{O}_8\text{P}_2\text{Ru}_4$ Calc.: C, 41.50; H, 3.01%. IR (CH_2Cl_2): $\nu(\text{CO})$ 2021w, 1994s, 1973vs, 1942w, 1915vw, 1864w, 1831vw cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ –16.09 [dd, $J(\text{PH}) = 12$ Hz, $J(\text{PH}) = 6$ Hz, 1H, Ru–H], 0.88 (s, 3H, Me), 0.94 (s, 3H, Me), 1.99 (s, 3H, Me), 2.01 (s, 3H, Me), 2.42 [d, $J(\text{HH}) = 5$ Hz, 1H, $\text{Cp}^*\text{-CH}_2$], 2.73 [d, $J(\text{HH}) = 5$ Hz, 1H, $\text{Cp}^*\text{-CH}_2$], 3.65 [dt, $J(\text{HH}) = 16$ Hz, $J(\text{PH}) = 11$ Hz, 1H, CH_2], 4.35 (m, ABXY pattern, 1H, CH_2), 7.26–7.77 (m, 15H, Ph). FAB mass spectrum (m/z): 1072, M^+ , 91; 1044, $[M - \text{CO}]^+$, 63; 1016, $[M - 2\text{CO}]^+$, 15; 988, $[M - 3\text{CO}]^+$, 100; 960, $[M - 4\text{CO}]^+$, 79; 932, $[M - 5\text{CO}]^+$, 67; 904, $[M - 6\text{CO}]^+$, 58; 876, $[M - 7\text{CO}]^+$, 77; 848, $[M - 8\text{CO}]^+$, 62.

4.5. Structure determination

A unique data set was measured at ca. 295 K to $2\theta_{\text{max}} = 50^\circ$ using a Syntex P2₁ diffractometer ($2\theta/\theta$ scan mode; monochromatic Mo K α radiation, λ 0.7107₃ Å); 7019 independent reflections were obtained, 4913 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})₁₁ were included, constrained at estimated values. Conventional residuals R , R' on $|F|$ are 0.036, 0.039, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{\text{diff}}) + 0.0004\sigma^4(I_{\text{diff}})$ being used. Computation used the XTAL 3.0 program system [13] implemented by Hall; neutral atom complex scattering factors were employed. Pertinent results are given in the figure and tables; material deposited comprises thermal and hydrogen parameters, full molecular non-hydrogen geometries and structure factor amplitudes.

4.6. Crystal data

$\text{Ru}_4(\mu\text{-H})(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\mu\text{-CH}_2\text{C}_5\text{Me}_4)(\text{CO})_8$ $\equiv \text{C}_{37}\text{H}_{32}\text{O}_8\text{P}_2\text{Ru}_4$, $M = 1070.9$. Monoclinic, space group $P2_1/c$ (C_{2h}^5 , No. 14), $a = 9.436(5)$, $b = 17.490(9)$, $c = 26.191(9)$ Å, $\beta = 106.72(3)^\circ$, $V = 4139$ Å³, $Z = 4$, $D_c = 1.72$ g cm^{-3} . Crystal dimensions 0.38 \times 0.36 \times 0.11 mm³, $\mu(\text{Mo K}\alpha) = 14.0$ cm^{-1} , A^* (min, max) = 1.21, 1.82, $F(000) = 2096$.

4.7. Abnormal features / variations in procedure

The second highest difference map feature, located in a plausible location, was refined in (x , y , z , U_{iso}) as the cluster-bound H atom; the final maximal residue was $0.9 \text{ e } \text{Å}^{-3}$.

Acknowledgements

We thank the Australian Research Council for support of this work and Johnson Matthey Technology plc for a generous gift of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$. PAH held an Australian Postgraduate Research Award.

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