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Cluster chemistry. Part 97 [☆]. Some unusual complexes obtained from reactions of $Ru_3(\mu\text{-dppm})(CO)_{10}$ and C_7 or C_8 hydrocarbons

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Abstract

Among the products of reactions between $Ru_3(\mu\text{-dppm})(CO)_{10}$ and impure cycloheptatriene were $Ru_3(\mu_3\text{-}C_7H_8)(\mu\text{-dppm})(CO)_7$ (**3a**) and two isomers of $Ru_3(\mu_3\text{-}C_8H_{10})(\mu\text{-dppm})(CO)_7$ (**2b** and **3b**). On the basis of crystallographic studies, **2b** is judged to be $Ru_3(\mu\text{-H})_2(\mu_3\text{-}C_7H_5Me)(\mu\text{-dppm})(CO)_7$, containing the novel norbornenyne ligand, while complexes **3** contain cyclopentenylacetylide ligands. None of these were obtained when purified cycloheptatriene was used.

Keywords: Ruthenium; Carbonyl; Alkyne ligands; Cycloheptatriene; Crystal structure

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1. Introduction

We have been studying the reactions of $Ru_3(\mu\text{-dppm})(CO)_{10}$ (**1**) with a variety of substrates, finding that they were cleaner than the analogous reactions of $Ru_3(CO)_{12}$ and often giving only one or two products in reasonable yield [2]. We report below the unexpected results that we have obtained with cycloheptatriene.

2. Results and discussion

Cycloheptatriene often contains toluene, from which it is separable by distillation only with difficulty. However, since we have found that toluene does not react with **1**, we deemed that the presence of this impurity, clearly present in our sample (as shown by NMR), would not affect any reaction of the cycloheptatriene.

Reactions between **1** and cycloheptatriene, carried out in refluxing THF or benzene, afforded in addition to well-known thermal alteration products originating solely from **1** [3], small amounts of trinuclear complexes of two types, both with the composition $Ru_3(C_7H_{8-n}Me_n)(dppm)(CO)_7$ ($n = 0\text{–}3$), which were partially purified by crystallisation. Spectroscopic results indicated that several components were present; the mass spectra, for example, contained series of ions differing by 14 amu, whose relative intensities were changed by TLC purification. The IR $\nu(CO)$ spectra of the various fractions were essentially identical. We suggest that complexes of two closely related types, namely the dihydrido-μ_3-alkyne derivatives $Ru_3(\mu\text{-H})_2(\mu_3\text{-}C_7H_{6-n}Me_n)(dppm)(CO)_7$ (**2a**, $n = 0$; **2b**, $n = 1$) and the hydrido-alkynyl clusters $Ru_3(\mu\text{-H})(\mu_3\text{-}C_7H_{7-n}Me_n)(\mu\text{-dppm})(CO)_7$ (**3a**, $n = 0$; **3b**, $n = 1$), as identified by the X-ray structure determinations reported below, were formed. These complexes appear to contain 0–3 methyl groups, or similarly sized alkyl groups. In the case of **3**, the ^1H NMR spectra contained a cluster of high-field resonances between δ 19.3–19.9 ppm, indicating the presence of several hydrido clusters. The product obtained from the reaction in benzene (**3b**) showed a single hydride signal (a doublet at δ 19.85 ppm) which was also found in the mixture obtained from the reaction in THF; the methyl group (found in the X-ray study) resonated at δ 1.29 ppm. The overall yields of all complexes were too small to allow further spectroscopic identification. For this reason, they were

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subjected to room-temperature single-crystal X-ray structural determinations. Their structures, postulated solely on the basis of mass spectral and X-ray studies, are sufficiently interesting to warrant this report despite the fact that we have been unable to identify their precursor(s) unequivocally.

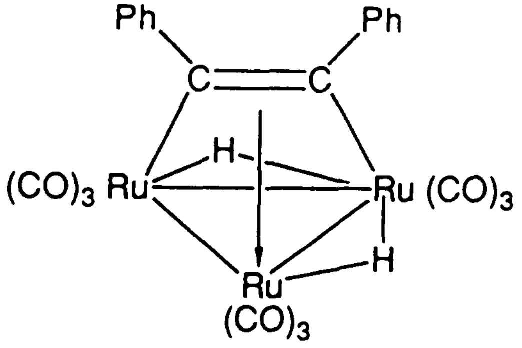
In the light of reports that describe the stabilisation of cyclobutyne on an Os_3 cluster [4], and of tropyne ($C_7H_5^+$) in platinum and zirconium complexes [5], most interest centres on our suggestion that the first product, **2b**, appears to contain the unusual bicyclic alkyne, 2-methylnorbornenyne, attached to the Ru_3 cluster. The other two products, **3a** and **3b**, contain cluster-bound ligands that are reasonably derived from cyclopentenylethynes.

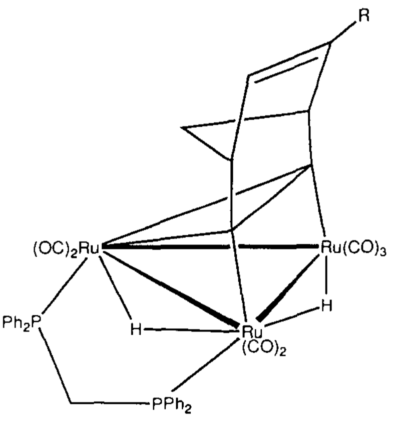
2.1. Molecular structure of $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}C_7H_5Me)(\mu\text{-}dppm)(CO)_7$ (2b)

A plot of a molecule of **2b** is shown in Fig. 1 and some bond parameters are listed in Table 1. An Ru_3 cluster is capped by a bicyclic hydrocarbon in the common $2\sigma, \pi(\|)$ mode characteristic of several alkyne complexes of this cluster, with the Ru(2) – Ru(3) vector parallel to the C(1) – C(2) bond of the putative alkyne. The dppm ligand bridges Ru(1) – Ru(2) and its structural features are generally similar to those found earlier for $Ru_3(\mu_3\text{-}C_2R_2)(CO)_7(PMe_2Ph)_2$ ($R = CO_2Me$ [6], for example).

The main feature of interest is the hydrocarbon ligand. The C(1) – C(2) separation is 1.37(1) Å, consistent with a cluster-bound C≡C triple bond, and the C(4) – C(5) distance is also short [1.35(1) Å]. The bicyclic nature of the hydrocarbon ligand suggests that the ligand is best considered as the previously undescribed 2-methylbicyclo[2.2.1]hept-2-en-5-yne (2-methylnorbornenyne) species, stabilised by coordination to the Ru_3 cluster. This is consistent with the ligand being a C_8H_8 isomer.

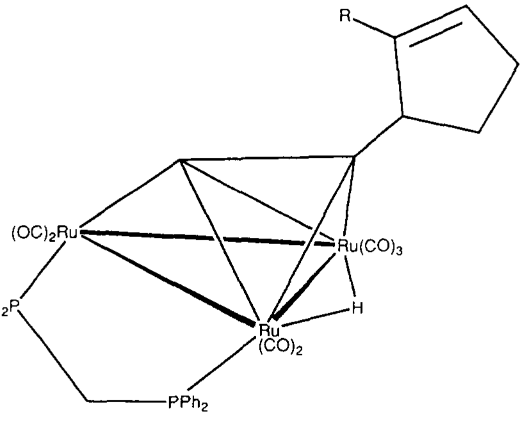
The presence of only seven CO groups, instead of the eight required for an electron-precise cluster, suggested that the complex contained cluster-bound hydride ligands. Close examination of the data enabled successful refinement of two such atoms, bridging the Ru(1) – Ru(2) and Ru(2) – Ru(3) vectors, with Ru – H distances between 1.54(8) and 1.95(7) Å. While the existence of complexes of the general formula $Ru_3(\mu\text{-}H)_2(\mu_3\text{-alkyne})(CO)_9$ has been known since the early days of ruthenium cluster chemistry [7], the first structural characterisation of such a complex occurred during the course of this work [8]. In **2b** the two hydride ligands bridge the longer edges of the Ru_3 cluster [H(1) – Ru(1,2) 1.81(6), 1.54(8); H(2) – Ru(2,3) 1.95(7), 1.58(7) Å], as found with $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}C_2Ph_2)(CO)_9$ (**4**).





2a R = H

2b R = Me



3a R = H

3b R = Me

2.2. Molecular structures of $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2\text{-}c\text{-}C_5H_6R)(\mu\text{-}dppm)(CO)_7$ [R = H (3a) and Me (3b)]

The molecular structures of these two complexes are depicted in Figs. 2 and 3 and significant bond parameters are listed in Table 1. It can be seen that in each complex, a triangular Ru_3 cluster is capped by the usual σ, $2\pi(\perp)$ C_2R unit, while one of the Ru – Ru vectors is bridged by a dppm ligand. The hydride ligand required by the electron count was located and refined in **3b**, bridging Ru(1) – Ru(3) [Ru(1,3)-H 1.54(8), 1.79(6) Å], as found in $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2R)(\mu\text{-}dppm)(CO)_7$ (R = C_6F_5 [2b]), but no H ligand could be refined in the structure of **3a**. The major structural parameters of the cluster and attached ligands do not differ significantly from those found earlier. The nature of the R group is of interest, however. It is clear that both complexes contain C_5 rings attached to the C_2 group and that in **3b** a methyl group is attached to C(7) of this ring. While the problems associated with disorder and libration in the ligand do not permit unequivocal assignment of single- or double-bond character within the C_5 ring, the geometry suggests that C(6) – C(7) [1.48(1) Å] in **3a** may be a double bond. Similarly, in **3b**, the C(6) – C(7) separation of 1.17(2) Å suggests a similar interpretation, but apparent libration is again very high.

The spectroscopic properties of these complexes are consistent with the above solid-state structures. The IR ν(CO) spectra of **3a** and **3b** were virtually identical and had similar profiles to those of related hydrido-alkynyl cluster complexes that we have encountered. Their ^1H NMR spectra contained hydride resonances at δ ca. −19.5 ppm, although the presence of other isomeric products or impurities was indicated in the spectrum of **3a** in which other multiplets were present in the same region. The mass spectra contained M^+ ions which fragmented by loss of CO groups; however, that of **3a** also contained ions at intervals of 14 amu, starting at m/z 1028. These could have arisen from complexes containing up to four extra CH_2 groups. The small amounts of these materials and their derivation from impurities rather than the cycloheptatriene rendered further work impracticable.

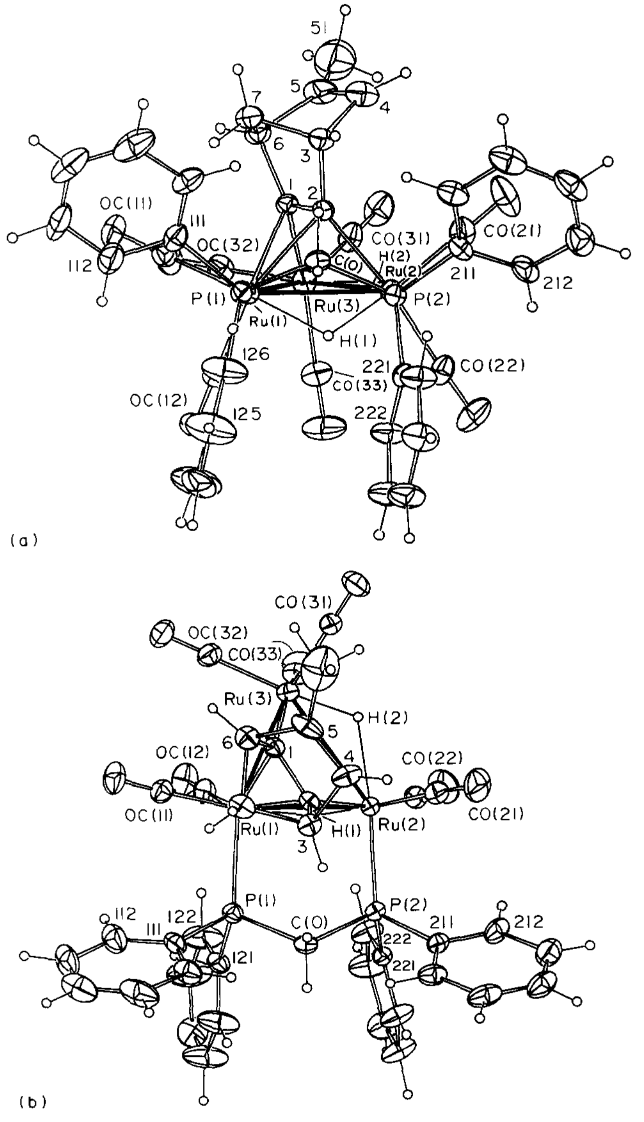


Fig. 1. Plots of a molecule of $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}C_7H_5Me)(\mu\text{-}dppm)(CO)_7$ (**2b**), (a) oblique and (b) normal to the Ru_3 plane, showing the atom-numbering scheme. Non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

Table 1
Selected bond lengths and distances for complexes **2b**, **3a** and **3b**

Atoms	**2b**, *R* = Me	**3a**, *R* = H	**3b**, R = Me
Bond distances (Å)			
Ru(1)–Ru(2)	2.852(1)	2.8041(7)	2.8101(8)
Ru(1)–Ru(3)	2.728(1)	2.7926(8)	2.785(1)
Ru(2)–Ru(3)	3.020(1)	2.7858(7)	2.805(1)
Ru(1)–P(1)	2.332(3)	2.314(2)	2.305(2)
Ru(2)–P(2)	2.319(2)	2.287(2)	2.278(2)
Ru(1)–C(1)	2.26(1)	2.182(7)	2.209(7)
Ru(1)–C(2)	2.24(1)	2.261(7)	2.275(7)
Ru(2)–C(1)	–	1.967(6)	1.984(6)
Ru(2)–C(2)	2.097(7)	–	–
Ru(3)–C(1)	2.050(9)	2.209(7)	2.222(9)
Ru(3)–C(2)	–	2.268(7)	2.27(1)
C(1)–C(2)	1.37(1)	1.286(8)	1.286(9)
C(1)–C(6)	1.54(1)	–	–
C(2)–C(3)	1.56(1)	1.51(1)	1.54(1)
C(6)–C(7)	–	–	1.17(2)
Bond angles (°)			
Ru(2)–Ru(1)–P(1)	93.43(7)	91.94(4)	92.64(5)
Ru(1)–Ru(2)–P(2)	91.92(7)	95.22(5)	94.74(5)
Ru(1)–P(1)–C(0)	111.2(3)	111.5(2)	111.1(3)
Ru(2)–P(2)–C(0)	111.8(2)	112.6(2)	112.2(2)
Ru(2)–C(1)–C(2)	–	154.4(7)	153.3(7)
C(1)–C(2)–C(3)	105.3(7)	141.6(8)	138.2(8)
C(2)–C(1)–C(6)	108.8(7)	–	–

Independent experiments have shown that extensively purified cycloheptatriene does not react with **1** under the conditions that afforded these three complexes. This contrasts with the range of complexes obtained from $Ru_3(CO)_{12}$ under a variety of conditions [9,10]. The source of complexes **2** is equally a mystery at present. Likely precursors (norbornene, norbornadiene) failed to give any reaction when heated with **1**. We have not had occasion to examine the reaction of bicycloheptatriene. We have not been able to identify any impurities in our sample of cycloheptatriene which could have afforded these complexes (which would not have had to be present to a greater extent than 0.5% to give the observed yields of these complexes) although likely precursors for complexes **3** are the corresponding alkynes; we have previously shown that 1-alkynes react cleanly with **1** to give good to excellent yields of the corresponding hydrido-alkynyl complexes [2b].

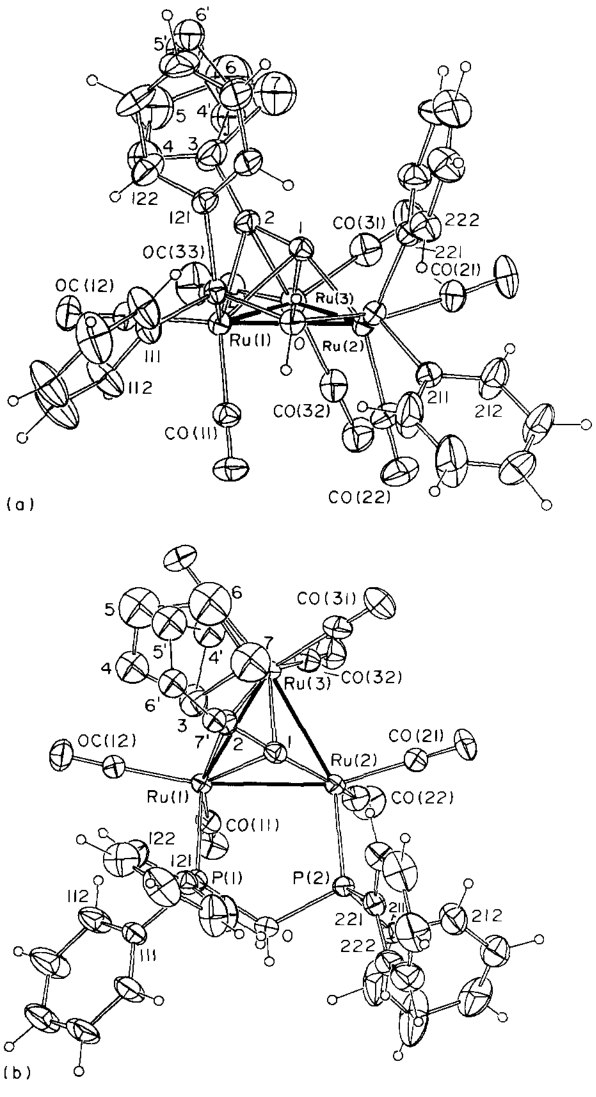


Fig. 2. Plots of a molecule of $Ru_3(\mu\text{-H})(\mu_3\text{-}C_2\text{-c-}C_5H_7)(\mu\text{-dppm})(CO)_7$ (**3a**), (a) oblique and (b) normal to the Ru_3 plane, showing the atom numbering scheme.

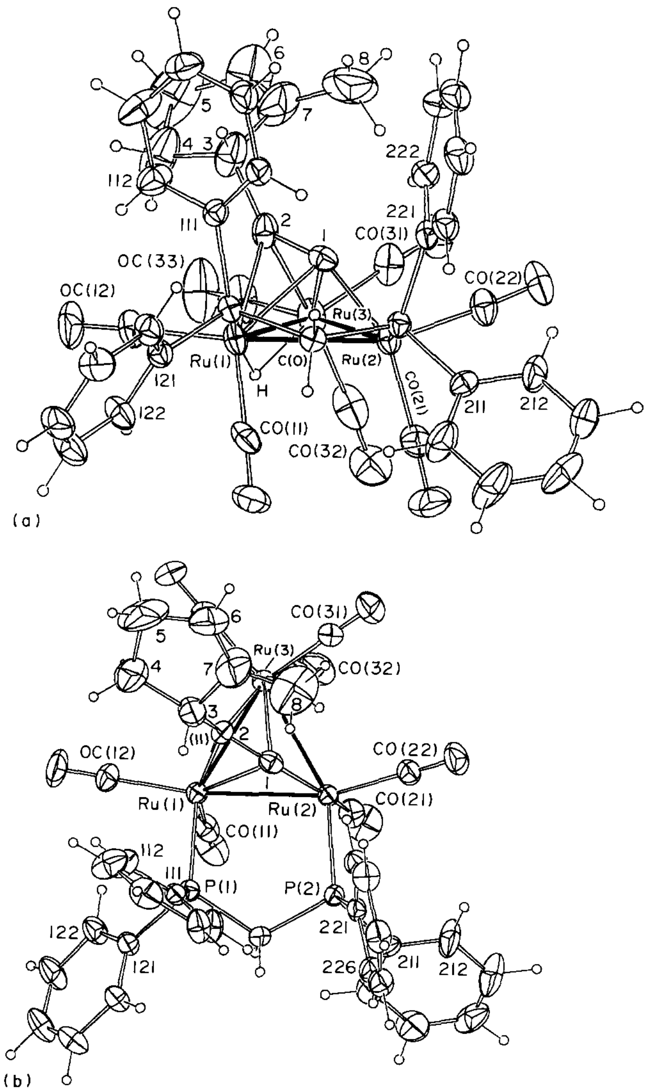


Fig. 3. Plots of a molecule of $Ru_3(\mu\text{-H})(\mu_3\text{-}C_2\text{-c-}C_5H_6Me)(\mu\text{-dppm})(CO)_7$ (**3b**), (a) oblique and (b) normal to the Ru_3 plane, showing the atom-numbering scheme.

3. Experimental details

3.1. General

General reaction conditions were similar to those described in an earlier paper [2a]. $Ru_3(\mu\text{-dppm})(CO)_{10}$ was prepared as described earlier [11]. Cycloheptatriene was obtained from Aldrich.

3.2. Reaction of $Ru_3(\mu\text{-dppm})(CO)_{10}$ with cycloheptatriene in refluxing THF

A THF (40 cm^3) solution of $Ru_3(\mu\text{-dppm})(CO)_{10}$ (218 mg, 0.225 mmol) and C_7H_8 (51.5 mg, 0.56 mmol) was refluxed for 20 h. Following removal of solvent in vacuo, the residue was dissolved in CH_2Cl_2 (2.0 cm^3) and separated into five fractions by preparative TLC (light petroleum/acetone 4 : 1).

Band 1 ($R_f = 0.96$) contained a small amount (3 mg) of an unidentified complex [IR ν(CO) (cyclohexane) (cm^{-1}): 2083 (w), 2064 (vs), 2037 (s), 2025 (s), 2010 (m), 1995 (s), 1975 (w). Mass spectrum (m/z): M^+, 863]. Bands 2 ($R_f = 0.59$), 3 ($R_f = 0.53$) and 4 ($R_f = 0.45$) contained thermal alteration products of **1**, namely $Ru_2(CO)_6\{\mu\text{-PPhCH}_2\text{PPh}(C_6H_4)\}$ (10.6 mg, 6%), $Ru_3(\mu\text{-H})(CO)_9(\mu_3\text{-PPhCH}_2\text{PPh}_2)$ (6.2 mg, 3%) and $Ru_3(CO)_9\{\mu_3\text{-PPhCH}_2\text{PPh}(C_6H_4)\}$ (33.8 mg, 15%), respectively, and were identified by IR and TLC comparison with authentic samples [3]. Band 5 ($R_f = 0.40$) contained a mixture of compounds (5.1 mg) which were crystallised (n-hexane, −25°C) to give **2a** and **2b**, the latter having been characterised by X-ray crystallography. IR (cyclohexane) ν(CO)(cm^{-1}): 2063 (s); 2033 (s); 2003 (s); 1996 (vs); 1975 (w); 1954 (w). The mass spectrum of the mixture contained apparent M^+ ions at m/z 976 (**2a**) and 990 (**2b**) (ratio 976/990 = 3 : 10).

Band 6 ($R_f = 0.37$; 84 mg, 37%) also contained a mixture of compounds which could not be separated by TLC. Recrystallisation (n-hexane) gave a crystalline product containing complexes of type **3** (46.2 mg, 20%). IR ν(CO) (cyclohexane) (cm^{-1}): 2063 (s); 2009 (s); 1999 (vs); 1982 (m); 1957 (m); 1938 (w). ^{1}H NMR ($CDCl_3$) δ: −19.37 to −19.91 (several signals, including one at δ −19.85 [d, J(HP) = 33.4 Hz, Ru–H]; 0.92–2.58 (m, CH_2–cyclopentene); 3.24 (m, CH_2–dppm); 4.33 (m, CH_2–dppm); 5.62 (m, CH_2–cyclopentene); 5.72 (m, CH–cyclopentene); 6.60–8.05 (m, Ph) ppm. Signals at δ 1.29 and 5.37 ppm also present corresponded to those found in the spectrum of **3b**, obtained as described below). FAB mass spectrum (m/z): 1028–790, 17 ion clusters separated by 14 amu; highest intensity peaks at m/z 1001, 989 and 961 (ratio 962/976/990/1004/1017/1028 = ca. 3 : 2 : 5 : 3 : 1 : 1).

3.3. Reaction of $Ru_3(\mu\text{-dppm})(CO)_{10}$ with cycloheptatriene in refluxing benzene

A benzene (40 cm^3) solution of $Ru_3(\mu\text{-dppm})(CO)_{10}$ (216 mg, 0.223 mmol) and C_7H_8 (515 mg, 5.59 mmol) was gently refluxed for 20 h. Following removal of solvent in vacuo, the residue was dissolved in CH_2Cl_2 (2.0 cm^3) and separated into five fractions by preparative TLC (light petroleum/acetone 4 : 1).

Band 1 ($R_f = 0.96$) contained a small amount (2.2 mg) of material [IR ν(CO) (cyclohexane) (cm^{-1}): 2083 (w); 2064 (vs); 2037 (s); 2025 (s); 2010 (m); 1995 (s); 1975 (w). MS (m/z): 863, M^+] Band 2 ($R_f = 0.45$) contained $Ru_3(CO)_9\{\mu_3\text{-PPhCH}_2\text{PPh}(C_6H_4)\}$ (7.1 mg, 4%), identified by its IR and mass spectrum.

Band 3 ($R_f = 0.37$) gave yellow plates (3.5 mg, 2%) from n-hexane at −25°C, which were characterised as **3b** by a single-crystal X-ray study. IR ν(CO) (cyclohexane) (cm^{-1}): 2063 (s); 2009 (s); 1999 (vs); 1982 (m); 1957 (m); 1938 (w).

^{1}H NMR ($CDCl_3$) δ: −19.84 [d, 1H, J(PH) = 33 Hz, Ru–H]; 0.92 [t, J(HH) = 6.7 Hz, 1H, HC(3)]; 1.29

Table 2
Crystal data and refinement details for complexes **2b**, **3a**, and **3b**

Complex	**2b**	**3a**	**3b**
Formula	$C_{40}H_{32}O_7P_2Ru_3 \cdot \sim 0.25C_6H_{14}$	$C_{39}H_{30}O_7P_2Ru_3 \cdot \sim 0.4CHCl_3$	$C_{40}H_{32}O_7P_2Ru_3 \cdot 0.5C_6H_{14}$
Formula weight	~ 1011.4	~ 1023.6	1032.9
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$C2/c$ (No. 15)	$C2/c$	$P\bar{1}$ (No. 2)
a Å	22.916(5)	20.633(2)	18.380(3)
b Å	27.124(6)	16.382(2)	11.522(2)
c Å	15.257(6)	27.206(4)	11.240(2)
α (°)			69.14(1)
β (°)	118.04(2)	112.51(1)	81.78(1)
γ (°)			88.07(1)
U (Å^3)	8370(4)	8495(2)	2201.2(7)
Z	8	8	2
D_c (g cm^{-3})	1.60	1.60	1.56
F(000)	~ 4012	~ 4041.6	1030
μ (cm^{-1})	11.9	12.4	11.3
Crystal size (mm)	0.37 × 0.07 × 0.18	0.20 × 0.32 × 0.38	0.27 × 0.35 × 0.06
A^* (min, max)	1.08, 1.18	1.29, 1.46	1.07, 1.49
$2\theta_{max}$	50	60	55
N	7003	12357	10074
N_o	3824	6973	5597
R	0.044	0.049	0.047
R_w	0.043	0.058	0.048

(s, 3H, Me–C_8H_9); 2.01–2.58 (m, 4H, CH_2–C_8H_9); 3.24 (m, 1H, CH_2–dppm); 4.33 (m, 1H, CH_2–dppm); 5.38 (s, 1H, CH–C_8H_9); 6.61 (m, 1H, Ph); 6.95 (m, 1H, Ph); 7.18 (m, 1H, Ph); 7.46–7.57 (m, 15H, Ph); 8.05 (m, 1H, Ph) ppm. FAB mass spectrum (m/z): M^+, 991; $[M - nCO]^+ (n = 1–7)$, 963–795.

3.4. Crystallography

Unique room-temperature diffractometer data sets (T ca. 295 K; $2\theta/\theta$ scan mode; monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å) yielded N independent reflections, N_0 with $I > 3\sigma(I)$ being considered 'observed' and used in the large block/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 constrained at estimated values. Conventional residuals R, R_w on $|F|$ at convergence are quoted; statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ were used. Neutral atom complex scattering factors were employed; computation used the XTAL 3.0 program system implemented by Hall and Stewart [12]. Pertinent results are given in the figures and in Tables 2–5. Tables of hydrogen and thermal parameters and complete lists of bond angles and distances have been deposited at the Cambridge Crystallographic Data Centre.

3.4.1. Abnormal features and variations in procedure

Compound **2b**: Difference map artefacts in tunnels along c were modelled as hexane of solvation with site occupancy refining to 0.25; solvent carbon atom thermal parameters were modelled using the isotropic form. Despite difficulties associated with the solvent, the complex itself was well resolved and well behaved, so much so that two further artefacts refined satisfactorily in (x, y, z, U_{iso}) as cluster-bound hydrides. The ligand model is consistent with its description as a methyl-substituted cluster-bound norbornenyne; C(1)–C(2) and C(4)–C(5) are short [1.37(1) and 1.37(1) Å, respectively] as is C(5)–C(51) [1.37(2) Å] also. The latter is the only equivocal geometric feature of the ligand. Libration at the methyl group is high; refinement of its site occupancy yielded a value not greatly differing from unity, at which it was constrained.

Table 3
Non-hydrogen atom coordinates and equivalent isotropic thermal parameters for **2b**

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.88274(4)	0.62167(3)	0.90245(5)	0.0441(3)
Ru(2)	0.75324(4)	0.58405(3)	0.84256(5)	0.0468(3)
Ru(3)	0.87680(4)	0.54921(3)	1.02199(5)	0.0510(4)
C(11)	0.9596(4)	0.6541(4)	0.9915(7)	0.062(5)
O(11)	1.0077(3)	0.6721(3)	1.0481(5)	0.095(4)
C(12)	0.9334(4)	0.5794(4)	0.8680(7)	0.063(5)
O(12)	0.9650(3)	0.5523(3)	0.8500(5)	0.085(4)
C(21)	0.6843(5)	0.5867(4)	0.8755(7)	0.074(5)
O(21)	0.6424(4)	0.5894(4)	0.8955(6)	0.129(6)
C(22)	0.7227(5)	0.5246(4)	0.7649(7)	0.071(5)
O(22)	0.7051(4)	0.4878(3)	0.7258(6)	0.119(5)
C(31)	0.8554(4)	0.5223(3)	1.1168(7)	0.064(5)
O(31)	0.8419(4)	0.5073(3)	1.1746(5)	0.096(4)
C(32)	0.9661(5)	0.5581(4)	1.1126(7)	0.066(5)
O(32)	1.0205(3)	0.5653(3)	1.1699(5)	0.092(4)
C(33)	0.8878(5)	0.4890(4)	0.9611(7)	0.070(6)
O(33)	0.8918(5)	0.4556(3)	0.9198(6)	0.120(6)
P(1)	0.8451(1)	0.68306(9)	0.7812(2)	0.049(1)
C(111)	0.8835(5)	0.7444(3)	0.8190(6)	0.063(5)
C(112)	0.9477(5)	0.7488(4)	0.8359(8)	0.090(7)
C(113)	0.9803(6)	0.7935(5)	0.8632(8)	0.113(8)
C(114)	0.9500(7)	0.8342(5)	0.8728(8)	0.126(9)
C(115)	0.8863(8)	0.8301(4)	0.8543(9)	0.13(1)
C(116)	0.8517(5)	0.7860(4)	0.8265(7)	0.079(6)
C(121)	0.8505(4)	0.6759(3)	0.6657(6)	0.054(5)
C(122)	0.8840(7)	0.6367(4)	0.6543(8)	0.109(8)
C(123)	0.8912(8)	0.6320(5)	0.5704(9)	0.14(1)
C(124)	0.8647(6)	0.6631(5)	0.4973(7)	0.102(7)
C(125)	0.8345(8)	0.7017(5)	0.5083(9)	0.14(1)
C(126)	0.8272(7)	0.7087(4)	0.5931(9)	0.118(9)
C(0)	0.7574(4)	0.6954(3)	0.7362(6)	0.049(4)
P(2)	0.7065(1)	0.63982(9)	0.7125(2)	0.047(1)
C(211)	0.6253(4)	0.6632(3)	0.6839(6)	0.053(5)
C(212)	0.5749(5)	0.6285(4)	0.6525(7)	0.073(5)
C(213)	0.5112(5)	0.6409(4)	0.6275(8)	0.094(7)
C(214)	0.4981(5)	0.6890(5)	0.6380(8)	0.099(7)
C(215)	0.5467(6)	0.7244(4)	0.6733(8)	0.095(7)
C(216)	0.6109(5)	0.7108(4)	0.6951(7)	0.072(6)
C(221)	0.6935(4)	0.6215(3)	0.5894(6)	0.049(4)
C(222)	0.7257(5)	0.5823(4)	0.5753(7)	0.078(6)
C(223)	0.7203(6)	0.5702(4)	0.4848(8)	0.103(8)
C(224)	0.6804(6)	0.5978(5)	0.4052(7)	0.100(7)
C(225)	0.6478(5)	0.6379(5)	0.4170(7)	0.098(6)
C(226)	0.6550(5)	0.6496(4)	0.5093(7)	0.085(6)
C(1)	0.8580(4)	0.6226(3)	1.0292(6)	0.046(4)
C(2)	0.8042(4)	0.6398(3)	0.9457(6)	0.045(4)
C(3)	0.7853(4)	0.6892(3)	0.9777(6)	0.056(5)
C(4)	0.7616(5)	0.6739(4)	1.0535(7)	0.074(6)
C(5)	0.8186(6)	0.6590(4)	1.1315(7)	0.082(7)
C(51)	0.8245(8)	0.6393(6)	1.218(1)	0.18(1)
C(6)	0.8779(5)	0.6611(3)	1.1122(6)	0.059(5)
C(7)	0.8549(5)	0.7091(3)	1.0493(7)	0.065(5)
C(01) [a]	0.501(3)	0.492(1)	0.629(3)	0.14(2)
C(02) [a]	0.503(2)	0.4655(7)	0.715(2)	0.11(2)
C(03) [a]	0.483(1)	0.499(1)	0.772(3)	0.21(4)
C(04) [a]	0.5226(7)	0.487(1)	0.885(2)	0.17(3)
C(05) [a]	0.472(1)	0.477(1)	0.926(2)	0.20(3)
C(06) [a]	0.492(2)	0.506(2)	1.020(4)	0.11(2)

[a] Site occupancy factor = 0.25.

Compound **3a**: Difference map artefacts in the region of a putative cluster-bound C_2 substituent were modelled as a disordered pair of five-membered ring components, populations refined as x, $1 - x$, with $x = 0.695(6)$, the problems of appropriate description being compounded by apparent high librational amplitudes. Associated hydrogen atoms were omitted because of the uncertain nature of their description. Artefacts in voids about the 2-axis were best modelled as disordered chlo-

Table 4
Non-hydrogen atom coordinates and equivalent isotropic displacement parameters for **3a**

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.31321(3)	0.21937(3)	0.43118(2)	0.0501(2)
Ru(2)	0.26782(3)	0.32363(3)	0.34269(2)	0.0518(2)
Ru(3)	0.34974(3)	0.38445(3)	0.44296(2)	0.0625(2)
C(11)	0.2169(3)	0.2090(4)	0.4185(3)	0.065(3)
O(11)	0.1598(2)	0.2007(3)	0.4106(2)	0.092(3)
C(12)	0.3545(4)	0.1666(4)	0.4973(2)	0.064(3)
O(12)	0.3790(3)	0.1362(3)	0.5380(2)	0.095(3)
C(21)	0.2731(4)	0.4077(4)	0.2977(3)	0.074(3)
O(21)	0.2787(3)	0.4576(3)	0.2702(2)	0.114(3)
C(22)	0.1753(4)	0.3502(4)	0.3336(3)	0.074(3)
O(22)	0.1211(3)	0.3693(4)	0.3296(2)	0.112(3)
C(31)	0.3876(4)	0.4690(4)	0.4133(3)	0.089(4)
O(31)	0.4068(4)	0.5198(4)	0.3940(3)	0.142(4)
C(32)	0.2675(4)	0.4461(4)	0.4335(3)	0.078(4)
O(32)	0.2195(3)	0.4848(3)	0.4285(2)	0.105(3)
C(33)	0.4044(4)	0.4077(4)	0.5149(3)	0.085(4)
O(33)	0.4358(3)	0.4244(4)	0.5587(2)	0.129(3)
P(1)	0.30623(9)	0.10630(9)	0.37840(6)	0.0536(7)
C(111)	0.2757(4)	0.0096(4)	0.3958(3)	0.070(3)
C(112)	0.2507(5)	0.0056(5)	0.4359(3)	0.111(5)
C(113)	0.2262(7)	−0.0686(6)	0.4462(4)	0.169(9)
C(114)	0.2266(7)	−0.1380(5)	0.4188(4)	0.144(7)
C(115)	0.2482(7)	−0.1313(5)	0.3787(4)	0.147(7)
C(116)	0.2741(5)	−0.0584(4)	0.3666(3)	0.112(6)
C(121)	0.3875(3)	0.0725(4)	0.3723(3)	0.064(3)
C(122)	0.4420(4)	0.0522(5)	0.4182(3)	0.102(4)
C(123)	0.5035(4)	0.0213(6)	0.4148(4)	0.126(5)
C(124)	0.5110(5)	0.0145(6)	0.3688(4)	0.131(6)
C(125)	0.4570(5)	0.0331(6)	0.3226(4)	0.127(6)
C(126)	0.3961(4)	0.0614(5)	0.3248(3)	0.097(4)
C(0)	0.2395(3)	0.1199(3)	0.3110(2)	0.056(3)
P(2)	0.23634(9)	0.2211(1)	0.28094(6)	0.0519(6)
C(211)	0.1484(3)	0.2278(4)	0.2307(2)	0.061(3)
C(212)	0.1298(5)	0.2907(5)	0.1989(4)	0.135(5)
C(213)	0.0643(5)	0.3013(6)	0.1595(4)	0.131(5)
C(214)	0.0163(5)	0.2486(8)	0.1541(4)	0.148(6)
C(215)	0.0350(6)	0.176(1)	0.1826(6)	0.28(1)
C(216)	0.1009(5)	0.1702(8)	0.2207(5)	0.196(7)
C(221)	0.2885(3)	0.2071(4)	0.2405(3)	0.062(3)
C(222)	0.2671(4)	0.1551(4)	0.1977(3)	0.084(4)
C(223)	0.3092(5)	0.1395(5)	0.1701(4)	0.113(5)
C(224)	0.3715(6)	0.1772(6)	0.1829(4)	0.139(7)
C(225)	0.3957(5)	0.2317(6)	0.2249(4)	0.130(6)
C(226)	0.3530(4)	0.2478(5)	0.2550(3)	0.092(4)
C(1)	0.3639(3)	0.2920(3)	0.3888(2)	0.056(3)
C(2)	0.4139(3)	0.2774(4)	0.4338(3)	0.065(3)
C(3)	0.4908(4)	0.2562(5)	0.4579(3)	0.103(4)
C(4) [a,b]	0.5206(7)	0.2429(8)	0.5164(5)	0.115(5)
C(5) [a,b]	0.5830(9)	0.296(1)	0.5364(6)	0.183(8)
C(6) [a,b]	0.586(1)	0.349(1)	0.4878(7)	0.208(9)
C(7) [a,b]	0.5378(9)	0.326(1)	0.4317(6)	0.174(7)
C(4′) [a,b]	0.542(1)	0.331(1)	0.479(1)	0.11(1)
C(5′) [a,b]	0.616(1)	0.290(2)	0.501(1)	0.13(1)
C(6′) [a,b]	0.607(1)	0.228(1)	0.4657(8)	0.088(8)
C(7′) [a,b]	0.529(1)	0.238(1)	0.4259(6)	0.063(6)
Cl(1) [b]	0.5614(8)	0.4621(9)	0.2492(9)	0.39(2)
Cl(2) [b]	0.4265(8)	0.4795(7)	0.1979(6)	0.29(1)
Cl(3) [b]	0.502(2)	0.429(2)	0.316(1)	0.65(2)
C(0) [a,b]	1/2	0.476(3)	1/4	0.44(3)

[a] Isotropic thermal parameters.

[b] Site occupancy factors: C(4)–C(7), 0.695(6); C(4′)–C(7′), 1−0.695(6); Cl(1)–Cl(3), 0.4; C(0′), 0.8.

Table 5
Non-hydrogen atom coordinates and isotropic displacement parameters for **3b**

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.18838(3)	0.74270(6)	0.80375(6)	0.0609(3)
Ru(2)	0.33681(3)	0.80172(5)	0.70166(5)	0.0534(2)
Ru(3)	0.28810(3)	0.75883(7)	0.96212(6)	0.0763(3)
C(11)	0.1741(4)	0.9047(8)	0.6947(9)	0.081(4)
O(11)	0.1646(3)	1.0048(6)	0.6307(7)	0.115(4)
C(12)	0.0932(4)	0.6910(8)	0.9005(8)	0.089(4)
O(12)	0.0370(3)	0.6643(7)	0.9571(7)	0.133(4)
C(21)	0.3412(4)	0.9764(8)	0.6122(9)	0.083(4)
O(21)	0.3421(4)	1.0813(6)	0.5613(7)	0.124(4)
C(22)	0.4390(4)	0.7852(8)	0.6973(8)	0.081(4)
O(22)	0.5002(3)	0.7686(6)	0.6961(6)	0.115(4)
C(31)	0.3820(5)	0.7095(9)	1.0152(8)	0.095(5)
O(31)	0.4378(3)	0.6855(7)	1.0457(7)	0.128(4)
C(32)	0.3108(5)	0.926(1)	0.914(1)	0.112(6)
O(32)	0.3210(4)	1.0327(7)	0.8849(8)	0.134(5)
C(33)	0.2364(5)	0.718(1)	1.1330(9)	0.111(6)
O(33)	0.2063(4)	0.6980(9)	1.2318(7)	0.176(6)
P(1)	0.16950(9)	0.6676(2)	0.6458(2)	0.0518(7)
C(111)	0.1723(3)	0.5000(6)	0.6870(6)	0.056(3)
C(112)	0.1250(5)	0.4298(8)	0.7935(8)	0.092(4)
C(113)	0.1236(7)	0.3040(9)	0.8311(9)	0.119(6)
C(114)	0.1680(6)	0.2457(8)	0.767(1)	0.100(5)
C(115)	0.2145(4)	0.3111(8)	0.660(1)	0.092(5)
C(116)	0.2154(4)	0.4398(7)	0.6201(8)	0.080(4)
C(121)	0.0831(3)	0.7050(6)	0.5770(7)	0.060(3)
C(122)	0.0360(4)	0.7931(8)	0.6008(8)	0.084(4)
C(123)	−0.0266(4)	0.8226(9)	0.543(1)	0.109(6)
C(124)	−0.0440(4)	0.7654(9)	0.467(1)	0.103(5)
C(125)	0.0016(5)	0.6784(8)	0.4399(9)	0.096(5)
C(126)	0.0655(4)	0.6485(7)	0.4956(8)	0.076(4)
C(0)	0.2351(3)	0.7382(6)	0.4993(6)	0.052(3)
P(2)	0.33018(9)	0.7556(2)	0.5225(2)	0.0513(7)
C(211)	0.3713(4)	0.8677(6)	0.3681(6)	0.060(3)
C(212)	0.4442(5)	0.8788(9)	0.341(1)	0.120(5)
C(213)	0.4776(6)	0.965(1)	0.226(1)	0.145(7)
C(214)	0.4372(8)	1.038(1)	0.142(1)	0.125(7)
C(215)	0.3651(7)	1.031(1)	0.167(1)	0.146(7)
C(216)	0.3314(5)	0.9468(9)	0.2810(9)	0.113(5)
C(221)	0.3709(3)	0.6117(6)	0.5173(7)	0.056(3)
C(222)	0.3896(4)	0.5207(7)	0.6268(7)	0.065(3)
C(223)	0.4126(4)	0.4061(7)	0.6216(9)	0.084(4)
C(224)	0.4177(4)	0.3843(8)	0.509(1)	0.090(5)
C(225)	0.4012(4)	0.475(1)	0.3993(9)	0.089(5)
C(226)	0.3783(4)	0.5886(7)	0.4028(7)	0.070(4)
C(1)	0.2937(4)	0.6466(6)	0.8362(7)	0.062(3)
C(2)	0.2491(4)	0.5856(8)	0.9370(7)	0.073(4)
C(3)	0.2334(6)	0.450(1)	1.0260(9)	0.123(6)
C(4)	0.1711(7)	0.434(1)	1.134(1)	0.180(9)
C(5)	0.207(1)	0.352(2)	1.254(1)	0.27(1)
C(6)	0.283(1)	0.346(2)	1.204(2)	0.20(1)
C(7)	0.2975(9)	0.394(1)	1.093(2)	0.174(9)
C(8)	0.365(1)	0.385(1)	1.015(2)	0.23(1)
C(01)	−0.107(1)	1.008(2)	0.800(2)	0.29(2)
C(02)	−0.066(2)	1.034(2)	0.911(3)	0.33(3)
C(03)	−0.002(2)	0.981(3)	0.943(5)	0.54(5)

roform of solvation, site occupancy of the Cl atoms (established by refinement) being set at 0.4. Decomposition of the crystal by ca. 16% during data collection was compensated by scaling. The unit cell contents have a quasi-F centred orthorhombic aspect.

Compound **3b**: Difference map artefacts in lattice voids were again modelled as hexane, albeit with a site occupancy constrained at unity after refinement and with constrained geometries, with high apparent librational amplitudes (possibly a foil for disorder?). A further artefact refined satisfactorily in (x, y, z, U_{iso}) as a cluster-bound hydride. The C_2 substituent was modelled as MeC_5H_6, with a double bond at C(6)–C(7), again to be taken cum grano salis in view of the magnitude of associated librational amplitudes.

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