

Trapping of a phenyl group by a ruthenium cluster during dephenylation of coordinated $\text{CH}_2(\text{PPh}_2)_2$ (dppm)

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Abstract

Pyrolysis of $\{\text{Ru}_3(\mu\text{-dppm})(\text{CO})_9\}_n(\text{dppa})$ ($n = 1$ or 2) afforded $\text{Ru}_3(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\mu_3\text{-}\eta^1\text{:}\eta^2\text{-P-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{Ph})(\text{CO})_6$, containing an Ru_3 chain bridged by a dephenylated dppm ligand and by C_2PPh_2 and PPh_2 ligands derived from the dppa ligand. The phenyl group from the dppm ligand has been trapped by one of the Ru atoms to give a rare example of a cluster-bound $\sigma\text{-Ph}$ group. The molecular structure of $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-}\eta^1\text{:}\eta^2\text{-CCHP(O)Ph}_2)(\mu\text{-PPh}_2)(\mu\text{-dppm})(\text{CO})_6$, obtained on one occasion from the mono-cluster complex, is also described. © 1997 Elsevier Science S.A.

Keywords: Ruthenium cluster; Dephenylation; Molecular structure

1. Introduction

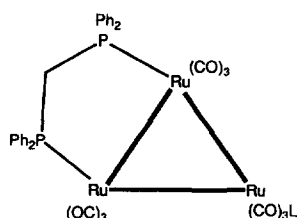
Some of the earliest investigations of cluster complexes containing tertiary phenylphosphine ligands revealed that the coordinated ligands were activated towards further reaction, often involving C–H or P–C(Ph) bond cleavage [1]. In many cases, the observed results were either ortho-metallation of a phenyl group to give $\text{PR}_2(\text{C}_6\text{H}_4)$ or $\text{PR}(\text{C}_6\text{H}_4)$ ligands or the formation of phosphido complexes, with concomitant loss of the phenyl group, probably as benzene by combination with a cluster hydride or the ortho-H atom [2]. Alternatively, combination of C–H and P–C bond cleavage reactions afford cluster-bonded benzyne [2,3], and reactions to give PhCHO have also been described [4]. However, few complexes containing cluster-bound phenyl groups have been described, two examples being the formation of $\text{Ir}_3(\mu_3\text{-PPh})(\mu\text{-dppm})(\text{Ph})(\text{CO})_6$ in the reaction between $\text{IrCl}(\text{CO})_2(\text{NH}_2\text{C}_6\text{H}_4\text{Me-4})$ and $\text{CH}(\text{PPh}_2)_3$ [5] and the pyrolysis of $\text{Pt}(\eta\text{-C}_2\text{H}_4)(\text{PPh}_3)_2$ to various isomers of $\text{Pt}_3(\mu\text{-PPh}_2)_3(\text{Ph})(\text{PPh}_3)_2$, which has recently been the subject of a detailed study [6,7]. In the extensive chemistry of ruthenium and osmium carbonyls, we are aware of four cases. One of the nine

complexes obtained on heating a mixture of $\text{Os}_3(\text{CO})_{12}$ and PPh_3 in refluxing xylene was characterised by an X-ray study as $\text{Os}_3\{\mu_3\text{-PPh}(\text{C}_6\text{H}_4)\}(\mu\text{-PPh}_2)(\mu\text{-Ph})(\text{CO})_8$, in which the phenyl group has been trapped by the Os_3 cluster and bridges an Os–Os bond [8]. Spontaneous P–C bond cleavage is found in the complex $\text{Ru}_3(\text{CO})_{11}\{\text{PPh}_2(\text{C}_5\text{H}_4\text{N-2})\}$. At 25 °C, the released phenyl group is assumed to migrate, firstly to the cluster and then to a coordinated CO group to give the observed product, $\text{Ru}_3\{\mu_3\text{-}\eta^2\text{-PPh}(\text{C}_5\text{H}_4\text{N-2})\}(\mu\text{-}\eta^2\text{-OCPh})(\text{CO})_9$ [9]. More recently, treatment of $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-ampy})(\text{CO})_7(\text{PPh}_3)_2$ with H_2 in refluxing toluene afforded $\text{Ru}_3(\mu_3\text{-ampy})(\mu\text{-PPh}_2)_2(\mu\text{-Ph})(\text{CO})_6$; similar reactions occurred with the analogous PMe_2Ph , $\text{P}(\text{C}_6\text{H}_4\text{Me-4})_3$, PCy_3 and AsPh_3 complexes [10]. Finally, one of the products obtained from the reaction between $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ and cycloocta-1,3,5,7-tetraene is $\text{Ru}_3(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\mu_3\text{-C}_8\text{H}_8)(\text{Ph})(\text{CO})_5$ [11].

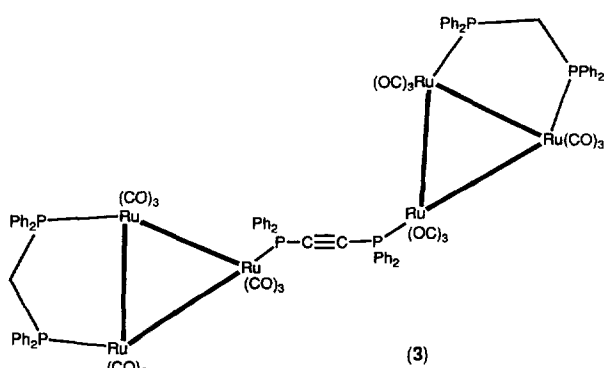
Many reactions of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ (1) have been described in which alteration of the dppm ligand has occurred [12]. These reactions include dephenylation (to give $\mu_3\text{-PPhCH}_2\text{PPh}_2$) [13], metallation (to give $\mu_3\text{-PPh}_2\text{CH}_2\text{PPh}(\text{C}_6\text{H}_4)$) [13], and a combination of both reactions (to give $\mu_3\text{-PPhCH}_n\text{PPh}(\text{C}_6\text{H}_4)$ ($n = 1$ or 2)) [13,14]. Extension of these studies to $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_9(\text{PPh}_3)$ afforded related compounds, as well

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as an acylated benzoylphosphine and the μ -CH₂PPhC₆H₄PPh-2 ligand [15]. Pyrolysis of {Ru₃(CO)₁₁}₂(μ -dppa) gives a high yield of Ru₅(μ_5 -C₂PPh₂)(μ -PPh₂)(CO)₁₃ [16], which has proved to be an excellent precursor for a variety of novel clusters, including the C₂ complex Ru₅(μ_5 -C₂)(μ -SMe)₂(μ -PPh₂)₂(CO)₁₁ [17]. We now report the synthesis of dppa derivatives of **1**, thermolyses of which do not give any higher nuclearity clusters, but afford instead two complexes containing interesting structural features.



(1) L = CO
(2) L = dppa



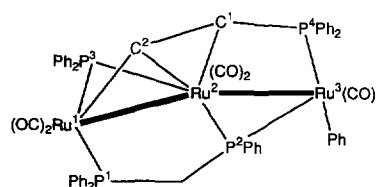
(3)

2. Results

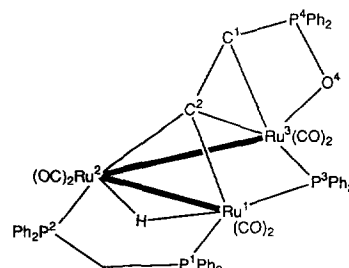
The complexes {Ru₃(μ -dppm)(CO)₉}_n(dppa) ($n = 1$ (**2**) and 2 (**3**)) were prepared by addition of Me₃NO to stoichiometric mixtures of **1** and dppa in tetrahydrofuran at room temperature. Purification by preparative thin-layer chromatography afforded the required complexes in 52% and 81% yields for $n = 1$ and $n = 2$ respectively. In the former reaction, 13% of **3** was also obtained. These compounds were obtained as red (**2**) or orange (**3**), air-stable solids, which were identified by a combination of elemental analysis and spectroscopic methods. The IR ν (CO) spectra are very similar, each containing four bands between 2055 and 1945 cm⁻¹, while the fast atom bombardment mass spectra are distinctly different, containing M⁺ ions at m/z 1335 and 2275 respectively. For **2**, an ion at m/z 1351 was

identified as [M + O]⁺, the ready formation of which is perhaps relevant to its occasional behaviour on pyrolysis (see below).

The products obtained by heating either complex in refluxing toluene for between 1 and 3 h were separated by preparative TLC. The major product in both cases was identified as Ru₃(μ_3 -PPhCH₂PPh₂)(μ_3 - η^1 : η^2 :P-C₂PPh₂)(μ -PPh₂)(Ph)(CO)₆ (**4**) (66% from **2**, 52% from **3**) by a single-crystal X-ray structure determination. On one occasion, the pyrolysis of **2** gave trace amounts of Ru₃(μ -H)(μ_3 - η^1 : η^2 -CCHP(O)Ph₂)(μ -PPh₂)(μ -dppm)(CO)₆ (**5**), only identified crystallographically. The reaction of **3** also gave some **1** (17%) and Ru₃(μ_3 -PPhCH₂PPh(C₆H₄))(CO)₉ (13%), while both reactions also gave considerable amounts of intractable dark-coloured material which was not further examined.



(4)



(5)

2.1. Ru₃(μ_3 -PPhCH₂PPh₂)(μ_3 - η^1 : η^2 :P-C₂PPh₂)(μ -PPh₂)(Ph)(CO)₆ (**4**)

Fig. 1 is a plot of a molecule of **4** and significant bond parameters are collected in Table 1. The three Ru atoms form a bent chain (Ru(1)–Ru(2)–Ru(3) 131.95(5)°), along which are μ_3 -PPhCH₂PPh₂ and μ_3 -C₂PPh₂ ligands, together with a μ -PPh₂ group. The Ru(1)–Ru(2) separation, which is bridged by the dephenylated dppm ligand, C(2) of the organic ligand and the PPh₂ group, is the shorter, at 2.779(2) Å. The Ru(2)–Ru(3) vector, bridged by P(2) and C(1)–P(1), is considerably longer, at 2.957(2) Å. The various Ru–P separations are found between 2.310(3) and 2.389(3) Å

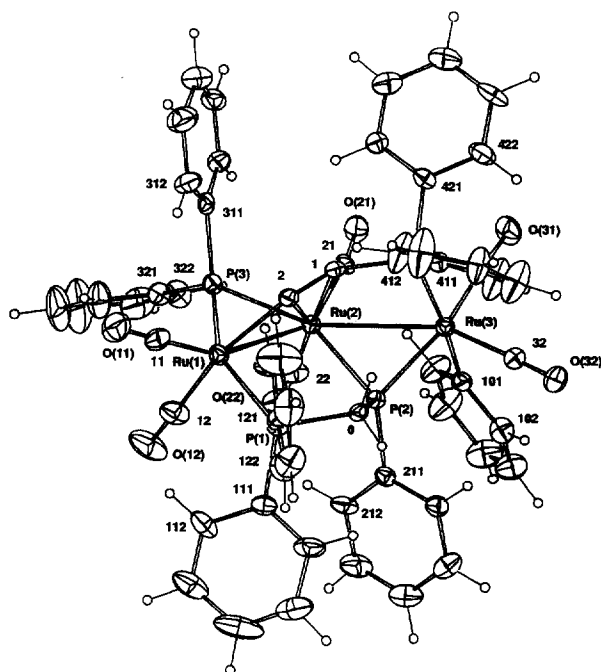


Fig. 1. Plot of a molecule of $\text{Ru}_3(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\mu_3\text{-}\eta^1:\eta^2\text{-P-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{Ph})(\text{CO})_6$ (4), showing the atom numbering scheme, carbon atoms denoted by number only. In this and Fig. 2, non-hydrogen atoms are shown with 20% thermal envelopes; hydrogen atoms have arbitrary radii of 0.1 Å.

and are within the ranges found for many other examples of Ru–P(phosphino) and Ru–P(phosphido) distances. Coordination is completed by two terminal CO ligands on each Ru atom and a σ -phenyl group on Ru(3) (2.11(2) Å). The latter value is similar to that found in $\text{Ru}_3(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\mu_3\text{-C}_8\text{H}_8)(\text{Ph})(\text{CO})_5$ (2.096(3) Å) [11].

The organic ligand is formally obtained by oxidative addition of one P–C bond in the *dppa* across Ru(1)–Ru(2), and becomes attached to all three Ru atoms by means of the Ru(1)–C(2) σ -bond (2.025(9) Å), a π -bond

Table 1

Selected bond parameters for $\text{Ru}_3(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\mu_3\text{-}\eta^1:\eta^2\text{-P-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{Ph})(\text{CO})_6$ (4)

Bond lengths (Å)		Bond angles (deg)	
Ru(1)–Ru(2)	2.779(2)	Ru(1)–Ru(2)–Ru(3)	131.95(5)
Ru(2)–Ru(3)	2.957(2)	Ru(1)–P(3)–Ru(2)	73.6(1)
Ru(1)–P(1)	2.389(3)	Ru(2)–P(2)–Ru(3)	77.96(9)
Ru(1)–P(3)	2.310(3)	Ru(1)–C(2)–C(1)	157(2)
Ru(2)–P(2)	2.385(3)	C(2)–C(1)–P(4)	154(1)
Ru(2)–P(3)	2.330(5)	Ru(3)–P(4)–C(1)	102.3(6)
Ru(3)–P(2)	2.314(3)	P(1)–C(0)–P(2)	113.7(6)
Ru(3)–P(4)	2.359(6)	Ru(1)–P(1)–C(0)	108.4(5)
Ru(1)–C(2)	2.025(9)	Ru(2)–P(2)–C(0)	111.6(5)
Ru(2)–C(1)	2.38(2)		
Ru(2)–C(2)	2.32(2)		
Ru(3)–C(101)	2.11(2)		
P(4)–C(1)	1.78(1)		
C(1)–C(2)	1.21(1)		

from C(2)–C(1) to Ru(2) (2.38 Å, 2.32(2) Å respectively) and the Ru(3)–P(1) bond (2.359(6) Å). The C(1)–C(2) separation is short (1.21(2) Å), suggesting only a weak interaction with Ru(2), which is borne out by the long Ru–C distances. Angles at C(2) and C(1) are 157(2) and 154(1)°, again supporting little back-bonding from Ru(2) into the C_2 fragment. If this weak interaction is included, the complex is an electron-precise $50e^-$ system.

The spectroscopic properties are in accord with the solid-state structure, insofar as they are diagnostic. The characteristic multiplet pattern for the two CH_2 protons found in the ^1H NMR spectrum forms the AB part of an ABXY spin system, and the fast-atom bombardment mass spectrum (FAB MS) contains an M^+ ion and several, but not all, of the expected daughter ions formed by loss of CO groups. The IR $\nu(\text{CO})$ spectrum contains four medium to very strong bands between 2030 and 1955 cm^{-1} ; whether a weak band at 1905 cm^{-1} is to be assigned to $\nu(\text{CO})$ or $\nu(\text{CC})$ is not clear.

2.2. $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-}\eta^1,\eta^2\text{-CCHP(O)Ph}_2)(\mu\text{-PPh}_2)(\mu\text{-dppm})(\text{CO})_6$ (5)

Fig. 2 is a plot of a molecule of 5, while important bond parameters are collected in Table 2. The three Ru atoms form a triangular array, of which one edge is too long (Ru(1)–Ru(3) 3.511(1) Å) for there to be any significant bonding interaction, although it is bridged by the PPh_2 ligand (Ru(1,3)–P(3) 2.370, 2.298(2) Å; Ru(1)–P(3)–Ru(3) 97.54(9)°). The long Ru(1)–Ru(2) edge (2.884(1) Å) is bridged by the *dppm* ligand and may also be bridged by the H atom required by the electron count; however, this atom was not located

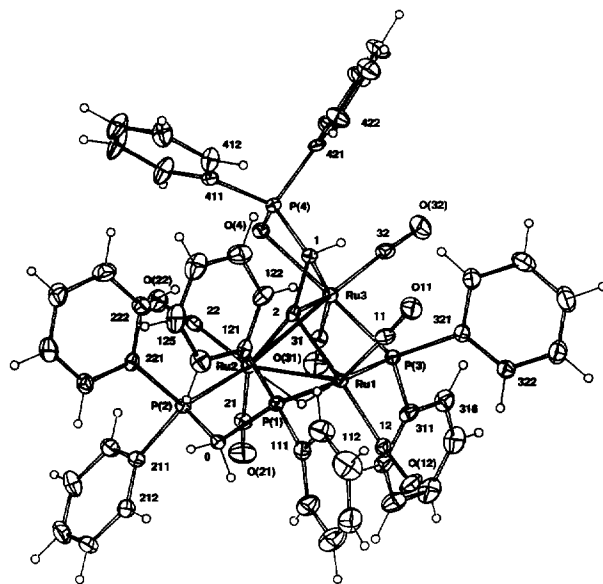


Fig. 2. Plot of a molecule of $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-}\eta^1,\eta^2\text{-CCHP(O)Ph}_2)(\mu\text{-PPh}_2)(\mu\text{-dppm})(\text{CO})_6$ (5), showing the atom numbering scheme.

Table 2

Selected bond parameters for $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-}\eta^1, \eta^2\text{-CCHP(O)Ph}_2)(\mu\text{-PPh}_2)(\mu\text{-dppm})(\text{CO})_6$ (**5**)

Bond lengths (Å)		Bond angles (deg)	
Ru(1)–Ru(2)	2.884(1)	Ru(1)–Ru(2)–Ru(3)	75.89(2)
Ru(1)–Ru(3)	3.511(1)	Ru(1)–P(3)–Ru(3)	97.54(9)
Ru(2)–Ru(3)	2.825(1)	Ru(1)–P(1)–C(0)	110.9(3)
Ru(1)–P(1)	2.372(2)	Ru(2)–P(2)–C(0)	110.8(2)
Ru(1)–P(3)	2.370(2)	Ru(3)–O(4)–P(4)	91.6(2)
Ru(2)–P(2)	2.322(2)	Ru(1)–C(2)–C(1)	126.3(5)
Ru(3)–P(3)	2.298(2)	Ru(2)–C(2)–C(1)	140.5(5)
Ru(3)–O(4)	2.309(6)	C(2)–C(1)–P(4)	122.0(5)
Ru(1)–C(2)	2.137(8)	C(1)–P(4)–O(4)	107.3(3)
Ru(2)–C(2)	1.976(7)		
Ru(3)–C(1)	2.317(7)		
Ru(3)–C(2)	2.297(7)		
P(4)–O(4)	1.526(5)		
P(1)–C(0)	1.836(8)		
P(2)–C(0)	1.824(8)		
P(4)–C(1)	1.784(8)		
C(1)–C(2)	1.44(1)		

during the refinement. Values for Ru–Ru bonds bridged by dppm alone have been reported at 2.843(1) Å in **1** [18] and 2.839(1) Å in $\text{Ru}_3(\mu\text{-dppm})(\mu\text{-C}_8\text{H}_8)(\text{CO})_6$ [11].

The major point of interest is the organic ligand, which is a μ_3 -vinylidene carrying as one of the substituents on C(1) a P(O)Ph₂ group, of which the O atom is bonded to Ru(3) (2.309(6) Å), with P(4)–O(4) 1.526(5) Å. These values can be compared with those found in $\text{Ru}_2(\mu\text{-PPh}_2\text{O})(\mu\text{-C}_2\text{Bu}^t)(\text{CO})_6$ [19], where the Ru–O bond is 2.135(2) Å and the P–O bond 1.544(2) Å, and are consistent with considerable multiple bond character in the P–O bond and with donation to Ru(3) by a lone pair from O(4). There must also be a hydrogen atom attached to C(1), although this was not located directly.

The vinylidene is attached in the familiar $\mu_3\text{-}\eta^1\text{:}\eta^2$ mode, with Ru(1,2)–C(2) 2.137(8), 1.976(7) Å and Ru(3)–C(1,2) 2.317, 2.297(7) Å. There are three other crystallographically characterised μ_3 -vinylidene complexes of ruthenium, namely $\text{Ru}_3\{\text{C}=\text{CPr}^i(\text{PPh}_2)\}(\text{CO})_9$ (**6**) [20], $\text{Ru}_3(\mu\text{-H})_2(\mu_3\text{-CCMePh})(\text{CO})_9$ (**7**) [21] and $\text{Ru}_3(\mu_3\text{-CCHPh})(\mu_4\text{-PPh})(\mu\text{-PPh}_2)(\text{CO})_9\text{Cp}^*$ (**8**) [22]. Comparisons with the situation in **5** are not straightforward, because of the differing chelating natures of the vinylidenes in **5** and **6**, the presence of cluster-bound H atoms in **7** and the larger cluster in **8**, of which the vinylidene spans only one face. The μ_3 -vinylidene ligand in **6**, for example, in which the PPh₂ group chelates one of the σ -bonded Ru atoms, contrasts with the C(1)–C(2) unit in **5** which is attached more strongly (presumably because of the formation of a larger ring), while there is considerably greater asymmetry of σ -bonding of C(2) to the other two Ru atoms (1.976(7) and 2.137(8) Å) than found in **6** (2.126, 2.182(5) Å). In

the other two complexes, the Ru–Ru separations range from 2.735–2.840(1) Å (in **7**) and 2.739–2.939(3) Å (in **8**), while the Ru–C(σ) bonds are 2.03, 2.06(1) Å in **7** and 1.93, 2.19(2) Å in **8**. In the four complexes **5**–**8**, the C–C separations are 1.43(1) Å, 1.408(7) Å, 1.379(8) Å and 1.44(3) Å respectively.

Spectroscopic properties include a six-band $\nu(\text{CO})$ spectrum and the observation of M^+ and $[\text{M} \pi\text{-CO}]^+$ ($n = 1\text{--}6$) ions in the FAB MS. The small amount of material obtained precluded our getting a ¹H NMR spectrum and thereby confirming the presence of the cluster-bound H atom.

3. Discussion

We have described the preparation of derivatives of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ in which one of the CO groups on the unique ruthenium atom has been replaced by the P-donor group in dppa. Since this ligand cannot chelate, addition of up to two of the Ru_3 clusters is possible, giving complexes **2** and **3**. Thermolysis of these compounds has given the same complex in both cases, characterised as **4** by X-ray crystallography and containing a bent Ru_3 chain. On one occasion, a rare example of a phosphinoxy-vinylidene ligand was found spanning an open Ru_3 cluster in **5**.

Formation of these complexes can be understood in terms of the well-known cleavage of P–C(sp) bonds in alkynylphosphines coordinated to metal clusters. Dephenylation of the dppm ligand is a common reaction, as noted above, although the present instance joins that found with a cycloocta-1,3,5,7-tetraene– Ru_3 cluster [11] as only the second instance when the phenyl group has been trapped by the cluster. A related example is found in $\text{Ru}_3(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\mu_3\text{-PhC}_2\text{Bu}^t)(\text{CO})_6$ [23], in which the Ph group has been transferred to a coordinated alkynyl group. The formation of **5** probably results from addition of traces of water to the C_2PPh_2 ligand formed by P–C(sp) bond cleavage, this reaction occurring either during the synthesis or during work-up. Both H–O bonds are broken, with the oxygen attaching to a PPh₂ group, one hydrogen to the vinylidene C $_{\beta}$ atom and the other to the metal cluster.

Both clusters are electron precise (50-e), although the apparently weak interaction of the C $\equiv$ C triple bond with Ru(2) in **4** (short C(1)–C(2) bond, long Ru(2)–C(1,2) separations, together with the geometry about the two carbon atoms) suggests that steric constraints control the final molecular structure in this complex. In **5**, the presence of an H atom bridging one of the Ru–Ru bonds in the cluster is inferred and is consistent with this electron count.

In conclusion, these results have shown that heating either **2** or **3** does not lead to higher nuclearity clusters, but instead fragmentation of the tertiary phosphine lig-

ands occurs. This can be rationalised by the tendency of $\text{Ru}_3\text{-dppm}$ clusters to preserve the Ru_3 core.

4. Experimental

4.1. Instrumentation

IR: Perkin–Elmer 1700X FT IR. NMR: Bruker CXP300 or ACP300 (^1H NMR at 300.13 MHz, ^{13}C NMR at 75.47 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

The complex $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ was prepared as described earlier [24]; dppa was a commercial product, used as-received.

4.4. Preparation of $\text{Ru}_3(\mu\text{-dppm})(\eta^1\text{-dppa})(\text{CO})_9$ (2)

To a stirred solution of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ (224 mg, 0.231 mmol) and dppa (97 mg, 0.25 mmol) in thf (20 ml) was added Me_3NO (24 mg, 0.32 mmol). After stirring at room temperature for 10 min the solvent was removed in vacuo. Preparative TLC (acetone–light petroleum 3:7) showed three major bands. Band 1 (red-orange, R_f 0.48) was crystallised from $\text{CH}_2\text{Cl}_2\text{-MeOH}$ to give red crystals of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_9(\eta^1\text{-dppa})$ (2) (159 mg, 52%) m.p. > 180 °C (dec.). Found: C, 53.13; H, 3.21; $\text{C}_{60}\text{H}_{42}\text{O}_9\text{P}_4\text{Ru}_3 \cdot 0.5\text{CH}_2\text{Cl}_2$ requires C, 52.79; H, 3.15%. Infrared (cyclohexane): $\nu(\text{CO})$ 2054w, 1995s, 1979vs, 1945w cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ 4.15 [t, $J(\text{PH}) = 10.2$ Hz, 2 H, CH_2], 5.30 (s, 1 H, CH_2Cl_2), 7.26–7.72 (m, 40 H, Ph). FAB MS (m/z): 1351, $[\text{M} + \text{O}]^+$, 17; 1335, M^+ , 20; 1223, $[\text{M} - 4\text{CO}]^+$, 33; 1195, $[\text{M} - 5\text{CO}]^+$, 100. Band 2 (orange, R_f 0.34) was precipitated by the addition of MeOH to a CH_2Cl_2 extract. The orange compound was collected and identified as $\{\text{Ru}_3(\mu\text{-dppm})(\text{CO})_9\}_2(\mu\text{-dppa})$ (3) (34 mg, 13%) by spot TLC and its IR $\nu(\text{CO})$ spectrum. Band 3 (orange, R_f 0.26) was not identified (7 mg, 2%). Infrared (cyclohexane): $\nu(\text{CO})$ 2055w, 2000s, 1984vs, 1953w cm^{-1} . FAB MS (m/z): 1350, $[\text{M}]^+$.

4.5. Preparation of $\{\text{Ru}_3(\mu\text{-dppm})(\text{CO})_9\}_2(\mu\text{-dppa})$ (3)

To a stirred solution of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ (156 mg, 0.161 mmol) and dppa (32 mg, 0.081 mmol) in thf (10 ml) was added Me_3NO (14 mg, 0.19 mmol). After

stirring at room temperature for 30 min, the reaction mixture was evaporated to dryness. This residue was dissolved in acetone (40 ml) and filtered through a Celite plug. Evaporation (rotary evaporator) to ca. 10 ml yielded $\{\text{Ru}_3(\mu\text{-dppm})(\text{CO})_9\}_2(\mu\text{-dppa})$ (3) as an orange powder (148 mg, 81%), m.p. > 180 °C (dec.). Found: C, 49.08; H, 2.83; $\text{C}_{94}\text{H}_{64}\text{O}_{18}\text{P}_6\text{Ru}_6$ requires C, 49.65; H, 2.84%. Infrared (CH_2Cl_2): $\nu(\text{CO})$ 2055w, 1996vs, 1980vs, 1947w cm^{-1} . ^1H NMR: δ 4.14 [t, $J(\text{PH}) = 10$ Hz, 4 H, $2 \times \text{CH}_2$], 7.34 (m, 60 H, Ph). FAB MS (m/z): 2275, M^+ .

4.6. Pyrolysis of $\text{Ru}_3(\mu\text{-dppm})(\eta^1\text{-dppa})(\text{CO})_9$

A solution of $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_9(\eta^1\text{-dppa})$ (99 mg, 0.074 mmol) in thf (20 ml) was heated at reflux point for 2.5 h. After evaporation to dryness (rotary evaporator), preparative TLC (acetone–light petroleum 3:7) separated one major product in a yellow band (R_f 0.59). Crystallisation ($\text{CH}_2\text{Cl}_2\text{-MeOH}$) gave bright yellow crystals of $\text{Ru}_3(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\mu_3\text{-}\eta^1\text{:}\eta^2\text{:P-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{Ph})(\text{CO})_6$ (4) (61 mg, 66%), m.p. > 180 °C (dec.). Found: C, 54.60; H, 3.43; $\text{C}_{57}\text{H}_{42}\text{O}_6\text{P}_4\text{Ru}_3$ requires: C, 54.77; H, 3.39%. Infrared (CH_2Cl_2): $\nu(\text{CO})$ 2030m, 2016vs, 1989m, 1957s, 1905w cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ 2.60–2.69 (m, ABXY, 1H, CH_2), 3.23–3.32 (m, ABXY, 1H, CH_2), 6.20–7.55 (m, 35 H, Ph), 7.87–7.97 (m, 5 H, Ru–Ph). FAB MS (m/z): 1251, M^+ , 8; 1223, $[\text{M} - \text{CO}]^+$, 82; 1195, $[\text{M} - 2\text{CO}]^+$, 100; 1174, $[\text{M} - \text{Ph}]^+$, 29.

On one occasion a trace band (yellow-orange, R_f 0.31) was crystallised from $\text{CH}_2\text{Cl}_2\text{-MeOH}$ to give orange crystals of $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-}\eta^1\text{:}\eta^2\text{-CCHP(O)Ph}_2)(\mu\text{-PPh}_2)(\mu\text{-dppm})(\text{CO})_6$ (5) identified by X-ray crystallography. Found: C, 52.23; H, 3.48; $\text{C}_{57}\text{H}_{44}\text{O}_7\text{P}_4\text{Ru}_3 \cdot 0.5\text{CH}_2\text{Cl}_2$ requires C, 52.69; H, 3.44%. Infrared (CH_2Cl_2): $\nu(\text{CO})$ 2019m, 2004vs, 1976m, 1959m, 1950m, 1942(sh) cm^{-1} . FAB MS (m/z): 1268, M^+ , 5; 1240, $[\text{M} - \text{CO}]^+$, 18; 1212, $[\text{M} - 2\text{CO}]^+$, 42; 1184, $[\text{M} - 3\text{CO}]^+$, 28; 1156, $[\text{M} - 4\text{CO}]^+$, 56; 1128, $[\text{M} - 5\text{CO}]^+$, 72; 1100, $[\text{M} - 6\text{CO}]^+$, 70; 1078, $[\text{M} - 4\text{CO} - \text{Ph}]^+$, 16; 1050, $[\text{M} - 5\text{CO} - \text{Ph}]^+$, 46; 1022, $[\text{M} - 6\text{CO} - \text{Ph}]^+$, 100.

4.7. Pyrolysis of $\{\text{Ru}_3(\mu\text{-dppm})(\text{CO})_9\}_2(\mu\text{-dppa})$

A solution of $\{\text{Ru}_3(\mu\text{-dppm})(\text{CO})_9\}_2(\mu\text{-dppa})$ (156 mg, 0.069 mmol) in toluene (15 ml) was heated at reflux point for 1.25 h. After evaporation to dryness (rotary evaporator), preparative TLC (acetone–light petroleum 3:7) showed three major bands. Bands 1 (red-orange, R_f 0.62) and 2 (orange, R_f 0.48) were identified as $\text{Ru}_3\{\mu_3\text{-PPhCH}_2\text{PPh}(\text{C}_6\text{H}_4)\}(\text{CO})_9$ (15 mg, 13%) and $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ (1) (20 mg, 17%) respectively, by comparison of their IR $\nu(\text{CO})$ spectra with those of authentic samples. Band 3 (yellow, R_f 0.43) gave yellow feathery crystals (from $\text{CH}_2\text{Cl}_2\text{-MeOH}$) of $\text{Ru}_3(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\mu_3\text{-}\eta^1\text{:}\eta^2\text{:P-}$

$C_2PPh_2)(\mu-PPh_2)(Ph)(CO)_6$ (**4**) (45 mg, 52%) identified by spot TLC and solution IR.

4.8. Crystallography

Unique data sets were measured at ca. 295 K using an Enraf–Nonius CAD4 diffractometer (2θ – θ scan mode; monochromatic Mo K α radiation, λ 0.71073 Å); 9920 independent reflections were obtained for **4** (14 183 for **5**), 4844 (7577) 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 constrained at estimated values. Conventional residuals R, R' on $|F|$ are 0.057 (0.055), 0.055 (0.054) respectively, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computation used the XTAL 3.2 program system [25] implemented by Hall; neutral atom complex scattering factors were employed. Pertinent results are given in the figures and tables; material deposited comprises positional and thermal parameters for all atoms, full molecular non-hydrogen geometries and structure factor amplitudes.

4.8.1. Crystal data

(**4**) $Ru_3(\mu_3-PPhCH_2PPh_2)(\mu_3-\eta^1:\eta^2:P-C_2PPh_2)(\mu-PPh_2)(Ph)(CO)_6 \equiv C_{57}H_{42}O_6P_4Ru_3$, M.W. = 1250.1. Monoclinic, space group $C2/c$, $a = 41.65(1)$, $b = 12.738(5)$, $c = 29.733(8)$ Å, $\beta = 134.29(2)^\circ$, $V = 11290$ Å³, $Z = 8$, $\rho_c = 1.47$ g cm^{−3}; $F(000) = 4992$. $\mu(Mo K\alpha)$ 8.5 cm^{−1}; specimen: $0.07 \times 0.55 \times 0.16$ mm³; $A^*(min,max) = 1.11, 1.19, 2\theta_{max} = 50^\circ$.

(**5**) $Ru_3(\mu-H)(\mu_3-\eta^1:\eta^2-CCHP(O)Ph_2)(\mu-PPh_2)(\mu-dppm)(CO)_6 \cdot 2CHCl_3 \equiv C_{59}H_{46}Cl_6O_7P_4Ru_3$, M.W. = 1506.8. Monoclinic, space group $P2_1/c$, $a = 10.983(4)$, $b = 24.560(9)$, $c = 24.031(5)$ Å, $\beta = 107.01(2)^\circ$, $V = 6199$ Å³, $Z = 4$, $\rho_c = 1.61$ g cm^{−3}; $F(000) = 3000$. $\mu(Mo K\alpha)$ 11.3 cm^{−1}; specimen: $0.42 \times 0.19 \times 0.08$ mm³; $A^*(min,max) = 1.10, 1.27, 2\theta_{max} = 55^\circ$.

4.8.2. Further comments

In **5**, the hydrogen atom attached to C(1) and that bridging Ru(1) and Ru(2) were located and refined in (x, y, z, U_{iso}) . Solvent populations were constrained at unity after trial refinement.

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