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Carbon–hydrogen and phosphorus–carbon bond cleavage of bis(dimethylphosphino)methane in triruthenium clusters: the molecular structure of $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}Me_2PCHPMe_2)]$

Ljubica Manojlović-Muir *
Department of Chemistry, University of Glasgow, Glasgow G12 8QQ (Great Britain)

Dee Ann Brandes and Richard J. Puddephatt *
Department of Chemistry, University of Western Ontario, London N6A 5B7 (Canada)

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Abstract

Pyrolyses of $[Ru_3(CO)_{10}(\mu\text{-dmpm})]$ and $[Ru_3(CO)_8(\mu\text{-dmpm})_2]$, (dmpm = $Me_2PCH_2PMe_2$) in refluxing toluene gives the novel clusters $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}Me_2PCHPMe_2)]$ (**1**) and $[Ru_3(CO)_7(\mu_3\text{-}\eta^2\text{-}MePCH_2PMe_2)(\mu_3\text{-}\eta^3\text{-}Me_2PCHPMe_2]$ (**2**) which contain the unusual five-electron bridging ligands $Me_2PCHPMe_2$ or $MePCH_2PMe_2$ respectively. The complexes were characterized spectroscopically and the molecular structure of the cluster **1** was determined by X-ray crystallography (monoclinic, $P2_1/n$, $Z = 4$, a 10.442(2), b 15.928(2), c 13.544(2) Å, β 98.89(1)°; $R = 0.022$ for 309 structural parameters and 3482 symmetry independent reflections with $I \geqslant 3\sigma(I)$).

Introduction

There has been much interest in the use of bis(diphenylphosphino)methane (dppm) and bis(dimethylphosphino)methane (dmpm) as bridging ligands which are able to maintain the nuclearity of binuclear and cluster complexes in reactions which otherwise might lead to fragmentation to mononuclear species [1–4]. This use of dppm in iron, ruthenium and osmium cluster chemistry is limited because dppm ligands are easily broken down in these systems [5–14].

On ruthenium clusters, the easiest reaction involves metallation of a phenyl group of a dppm ligand but then further reactions may occur and the reactions have been studied in great detail [6–11]. The products of pyrolysis of $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ and $[Ru_3(CO)_8(\mu\text{-dppm})_2]$ are shown in Scheme 1. It can be seen that, after the initial *ortho*-metallation of a phenyl substituent, further ligand breakdown can occur by P–aryl or P–CH_2 bond cleavage or by a combination of both [7,9,11].

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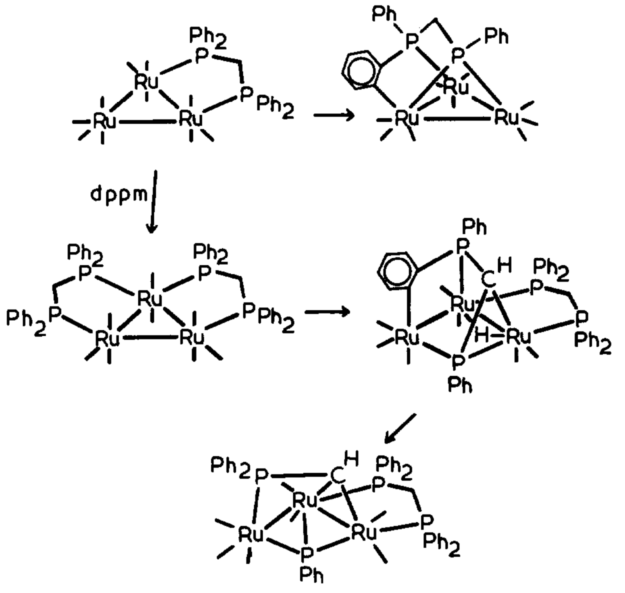


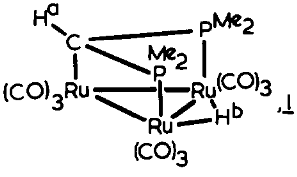
Scheme 1

Metallation reactions often lead to loss of activity of homogeneous catalysts with tertiary phosphine ligands [15], and it is important to understand the factors influencing reactivity in such systems. It was therefore of interest to compare the products of the reactions of Scheme 1 with those obtained by pyrolysis of the recently reported complexes $[Ru_3(CO)_{10}(\mu\text{-dmpm})]$ and $[Ru_3(CO)_8(\mu\text{-dmpm})_2]$ [16]. Since there are no aryl substituents in this case, it was considered probable that the dmpm ligands would be less easily broken down than dppm and that, when reaction did occur, different types of products would be formed. After this work was completed, we learned that A.K. Smith and coworkers have also studied the pyrolysis of these compounds, though under different experimental conditions [17].

Results and discussion

Pyrolysis of $[Ru_3(CO)_{10}(\mu\text{-dmpm})]$

Pyrolysis of $[Ru_3(CO)_{10}(\mu\text{-dmpm})]$ in toluene gave, as the major product, an orange crystalline solid which was characterized by X-ray crystallography as $[Ru_3(CO)_9(\mu\text{-H})(\mu_3\text{-}\eta^3\text{-}Me_2PCHPMe_2)]$ (1). Its crystals are built of discrete molecules separated by normal Van der Waals distances.



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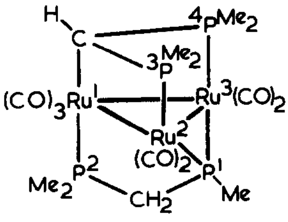

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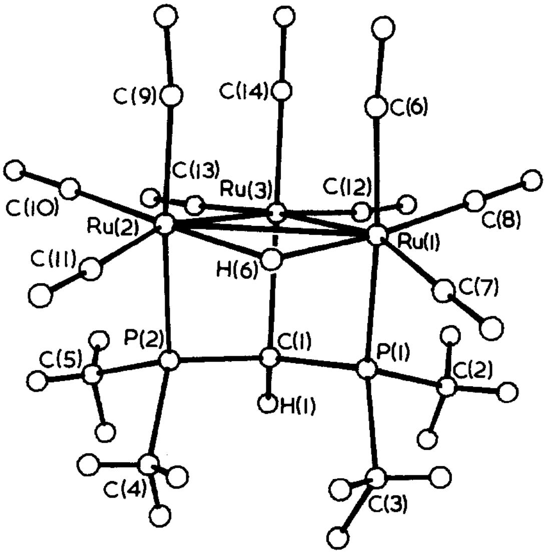

Fig. 1. A view of the molecular structure of $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^3\text{-}Me_2PCHPMe_2)]$ (**1**). The numbering scheme of oxygen and hydrogen atoms is omitted for clarity. In Tables 1–3, the oxygen atoms are labelled by the same numbers as the carbon atoms to which they are bonded; in the methyl group, atom C(n) is attached to H(nA), H(nB) and H(nC), and $n = 2–5$.

The molecular structure of **1**, shown in Fig. 1 and characterized by the bond lengths and angles listed in Table 1, approximates to C_s symmetry, with the mirror plane passing through Ru(3), C(14), O(14), C(1), H(1) and H(6) atoms. It contains a triangular Ru_3 core, with the lengths of all three edges indicative of Ru–Ru single bonds. Each ruthenium atom is coordinated by two equatorial and one axial carbonyl group. The three remaining axial sites, lying on the same side of the Ru_3 triangle, are spanned by the bridging diphosphinomethyl ligand $Me_2PCHPMe_2$, which coordinates the metal centers through one carbon and two phosphorus atoms and thus forms two fused four-membered Ru_2PC dimetallacycles. One edge of the Ru_3 triangle is bridged by the hydrido ligand, whose position was determined by the crystal structure analysis (Ru–H(6) 1.66(5) and 1.75(5) Å). The hydridic hydrogen is slightly displaced from the Ru_3 plane (0.36(5) Å), to lie on the same side of the metal cluster as the diphosphinomethanide ligand. The Ru_3 and P_2C planes are nearly parallel (dihedral angle 3.6°).

The complex **1** can therefore be thought of as comprising a $Ru_3(CO)_9(\mu\text{-}H)$ fragment bridged in a tridentate manner by the five-electron donor ligand $Me_2PCHPMe_2$. Its molecular structure shows that cyclometallation of the methylenic carbon atom of the parent complex $[Ru_3(CO)_{10}(dmpm)]$ occurs with elimination of one carbonyl group and insertion of the Ru_3 cluster into a C–H bond, to form a Ru–C single bond involving one metal centre and a $Ru_2(\mu\text{-}H)$ bridge involving the other two. Mechanistically, CO dissociation is probably followed by C–H oxidative addition at a single ruthenium center, followed by migration of the hydride ligand to the opposite edge of the cluster.

In the Ru_3 fragment, the Ru(1)–Ru(2) bond (3.099(1) Å) is ca. 0.3 Å longer than the Ru(1)–Ru(3) and Ru(2)–Ru(3) bonds (2.812(1), 2.808(1) Å). Similar lengthening

Table 1

Selected parameters of the molecular structure of Ru$_3$(CO)$_9$(μ-H)(μ_3-η^3-Me$_2$PCHPMe$_2$) (1)

Bond lengths (Å)

Ru(1)–Ru(2)	3.099(1) [a]	Ru(1)–Ru(3)	2.812(1)
Ru(1)–P(1)	2.348(2)	Ru(1)–C(6)	1.933(5)
Ru(1)–C(7)	1.916(5)	Ru(1)–C(8)	1.870(5)
Ru(1)–H(6)	1.66(5)	Ru(2)–Ru(3)	2.808(1)
Ru(2)–P(2)	2.350(2)	Ru(2)–C(9)	1.936(5)
Ru(2)–C(10)	1.877(5)	Ru(2)–C(11)	1.937(5)
Ru(2)–H(6)	1.75(5)	Ru(3)–C(1)	2.272(4)
Ru(3)–C(12)	1.896(5)	Ru(3)–C(13)	1.881(5)
Ru(3)–C(14)	1.911(5)	P(1)–C(1)	1.769(4)
P(1)–C(2)	1.830(5)	P(1)–C(3)	1.835(6)
P(2)–C(1)	1.784(4)	P(2)–C(4)	1.816(6)
P(2)–C(5)	1.819(6)		

Bond angles (°)

Ru(2)–Ru(1)–Ru(3)	56.5(1)	Ru(2)–Ru(1)–P(1)	89.2(1)
Ru(2)–Ru(1)–C(6)	86.5(2)	Ru(2)–Ru(1)–C(7)	118.7(2)
Ru(2)–Ru(1)–C(8)	141.2(2)	Ru(2)–Ru(1)–H(6)	25.5(17)
Ru(3)–Ru(1)–P(1)	69.9(1)	Ru(3)–Ru(1)–C(6)	100.9(2)
Ru(3)–Ru(1)–C(7)	163.0(2)	Ru(3)–Ru(1)–C(8)	87.1(2)
Ru(3)–Ru(1)–H(6)	79.0(17)	P(1)–Ru(1)–C(6)	170.8(2)
P(1)–Ru(1)–C(7)	94.5(2)	P(1)–Ru(1)–C(8)	90.1(2)
P(1)–Ru(1)–H(6)	86.3(17)	C(6)–Ru(1)–C(7)	94.8(3)
C(6)–Ru(1)–C(8)	88.2(2)	C(6)–Ru(1)–H(6)	93.3(17)
C(7)–Ru(1)–C(8)	100.1(3)	C(7)–Ru(1)–H(6)	93.7(17)
C(8)–Ru(1)–H(6)	166.0(17)	Ru(1)–Ru(2)–Ru(3)	56.6(1)
Ru(1)–Ru(2)–P(2)	88.6(1)	Ru(1)–Ru(2)–C(9)	87.8(2)
Ru(1)–Ru(2)–C(10)	145.4(2)	Ru(1)–Ru(2)–C(11)	115.9(2)
Ru(1)–Ru(2)–H(6)	24.1(16)	Ru(3)–Ru(2)–P(2)	70.7(1)
Ru(3)–Ru(2)–C(9)	100.4(2)	Ru(3)–Ru(2)–C(10)	90.3(2)
Ru(3)–Ru(2)–C(11)	164.0(2)	Ru(3)–Ru(2)–H(6)	77.9(16)
P(2)–Ru(2)–C(9)	170.9(2)	P(2)–Ru(2)–C(10)	89.2(2)
P(2)–Ru(2)–C(11)	96.0(2)	P(2)–Ru(2)–H(6)	85.3(16)
C(9)–Ru(2)–C(10)	89.0(2)	C(9)–Ru(2)–C(11)	93.1(2)
C(9)–Ru(2)–H(6)	94.7(16)	C(10)–Ru(2)–C(11)	98.7(2)
C(10)–Ru(2)–H(6)	168.0(16)	C(11)–Ru(2)–H(6)	92.5(16)
Ru(1)–Ru(3)–Ru(2)	66.9(1)	Ru(1)–Ru(3)–C(1)	79.7(1)
Ru(1)–Ru(3)–C(12)	101.2(2)	Ru(1)–Ru(3)–C(13)	165.6(2)
Ru(1)–Ru(3)–C(14)	87.1(2)	Ru(2)–Ru(3)–C(1)	79.9(1)
Ru(2)–Ru(3)–C(12)	168.0(2)	Ru(2)–Ru(3)–C(13)	98.8(2)
Ru(2)–Ru(3)–C(14)	87.1(2)	C(1)–Ru(3)–C(12)	96.7(2)
C(1)–Ru(3)–C(13)	96.0(2)	C(1)–Ru(3)–C(14)	164.3(2)
C(12)–Ru(3)–C(13)	93.0(2)	C(12)–Ru(3)–C(14)	94.1(2)
C(13)–Ru(3)–C(14)	94.7(2)	Ru(1)–P(1)–C(1)	104.9(2)
Ru(1)–P(1)–C(2)	118.5(3)	Ru(1)–P(1)–C(3)	116.5(2)
C(1)–P(1)–C(2)	104.7(3)	C(1)–P(1)–C(3)	113.0(3)
C(2)–P(1)–C(3)	98.9(3)	Ru(2)–P(2)–C(1)	104.6(2)
Ru(2)–P(2)–C(4)	115.2(2)	Ru(2)–P(2)–C(5)	118.6(2)
C(1)–P(2)–C(4)	114.4(3)	C(1)–P(2)–C(5)	104.5(3)
C(4)–P(2)–C(5)	99.5(3)	Ru(3)–C(1)–P(1)	94.3(2)
Ru(3)–C(1)–P(2)	95.0(2)	P(1)–C(1)–P(2)	115.6(2)
Ru(1)–H(6)–Ru(2)	130.5(30)		

Table 1 (continued)

Torsion angles (°)

Ru(1)-P(1)-C(1)-P(2)	−66.9(2)	Ru(3)-Ru(1)-P(1)-C(1)	−26.0(2)
Ru(2)-P(2)-C(1)-P(1)	68.4(2)	P(2)-Ru(2)-Ru(3)-C(1)	−18.5(1)
P(1)-Ru(1)-Ru(3)-C(1)	19.6(1)	Ru(2)-Ru(3)-C(1)-P(2)	23.3(2)
Ru(1)-Ru(3)-C(1)-P(1)	−24.7(2)	Ru(2)-P(2)-C(1)-Ru(3)	−28.7(1)
Ru(1)-P(1)-C(1)-Ru(3)	30.7(1)	Ru(3)-Ru(2)-P(2)-C(1)	24.2(2)

[a] Here, and in the Tables 2 and 3, the values shown in parentheses are estimated standard deviations.

of hydrido-bridged Ru–Ru distances has been observed in other Ru_3 clusters, such as, for example, $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}PhPCH_2PPh_2)]$ [9] and $[Ru_3(CO)_{10}(\mu\text{-}H)\{\mu\text{-}N_2C_3H(CF_3)_2\text{-}3,5\}]$ [18].

The $Me_2PCHPMe_2$ ligand (P ··· P 3.006(2) Å) shows staggered conformations about both P–C(CH) bonds and the four-membered Ru_2PC rings are non-planar, as is evident from the torsion angles listed in Table 1. All Ru(CO) moieties are essentially linear (Ru–C–O 173.0(4)–178.8(5)°).

Steric requirements of the ligands, and especially metallation of the deprotonated methylenic carbon atom of the diphosphinomethyl ligand, lead to substantial angular distortions of the molecular geometry and to some short intramolecular non-bonding distances. Thus the closure of the fused four-membered Ru_2PC rings results in severe distortions of the ring angles (Ru(3)–Ru–P 69.9(1), 70.7(1); Ru–Ru(3)–C(1) 79.7(1), 79.9(1); Ru(3)–C(1)–P 94.3(2), 95.0(2)°), and in short transannular Ru(3) ··· P distances (2.981(1), 3.008(1) Å). These distances could be indicative of some weak electronic interations. Normal electron counting suggests that Ru(3) is electron deficient whereas Ru(1) and Ru(2) are electron rich in complex **1**.

The spectroscopic data were fully consistent with the structure **1** (see Experimental). The ^1H NMR spectrum contained resonances in a 6/6/1/1 ratio due to the two types of *Me*P groups, and the CHP_2 and $Ru_2(\mu\text{-}H)$ protons. Long range coupling $^4J(HH)$ between the $C\mathit{H}P_2$ and $Ru_2(\mu\text{-}\mathit{H})$ protons was observed (Fig. 2), and was confirmed by homonuclear decoupling experiments. The $Ru_2(\mu\text{-}H)$ hydrogen atom is distorted out of the Ru_3 plane towards the CH group, as discussed above, but the H(6)–C(1) distance is clearly too long for any direct interaction and the coupling presumably operates through the bonds $^4J(HRuRuCH)$. The chemical shift of the $C\mathit{H}P_2$ proton was δ 1.32 ppm, close to the value in $Fe_2(\mu\text{-}H)(CO)_6(\mu\text{-}CO)(\mu_2\text{-}\eta^3\text{-}Ph_2PCHPPh_2)]$, which has δ 1.3 ppm. The $\mathit{C}HP_2$ carbon atom appeared in the ^{13}C NMR spectrum at δ 223.4 ppm, close to values for alkylidyne carbons in $[Ru_3(CO)_9(\mu\text{-}H)_3(\mu^3\text{-}CR)]$, δ 219.3, R = Me; 232.6, R = Et, but far removed from the $\mathit{C}HP_2$ resonance in $[Fe_2(\mu\text{-}H)(CO)_6(\mu\text{-}CO)(\mu_2\text{-}\eta^3\text{-}Ph_2PCHPPh_2)]$ with δ −11.7 ppm [19,20]. The assignment of the CHP_2 resonance was confirmed by recording the DEPT ^{13}C spectrum. The ^{31}P NMR spectrum of **1** contained only a singlet resonance as expected.

Pyrolysis of $[Ru_3(CO)_8(\mu\text{-}dmpm)_2]$

Pyrolysis in toluene solution gave as the major product, $[Ru_3(CO)_7(\mu_3\text{-}\eta^2\text{-}MeP^1CH_2P^2Me_2)(\mu_3\text{-}\eta^3\text{-}Me_2P^3CHP^4Me_2)]$ (**2**) which was characterized by spectroscopic methods. The empirical formula of **2** was given by the mass spectrum and

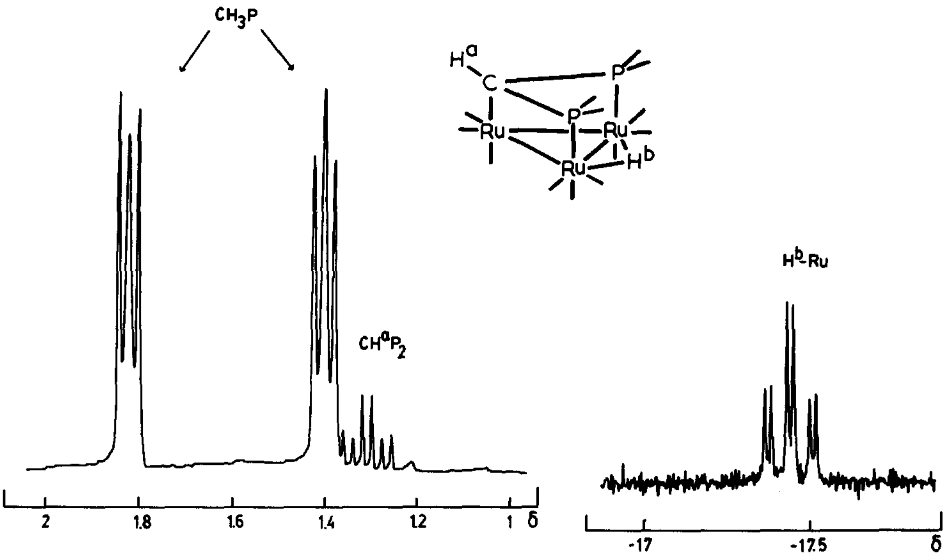

Fig. 2. The ^1H NMR spectrum (200 MHz) of complex 1.

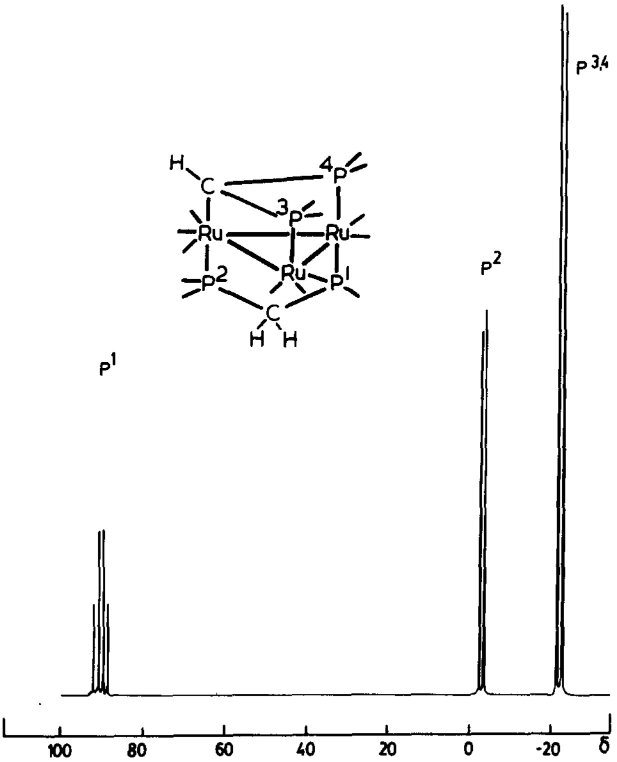

Fig. 3. The $^{31}P\{^1H\}$ NMR spectrum (121 MHz) of complex 2.

analytical data, and the stereochemistry of the diphosphine-derived ligands was defined by the ^1H and ^{31}P NMR data. In the ^{31}P $\{^1H\}$ NMR spectrum (Fig. 3), three resonances were observed in a 1/1/2 ratio owing to P^1, P^2 and P^3, P^4 respectively. The chemical shift of P^1 is indicative of a bridging phosphido ligand [21], and the equivalence of the atoms P^3 and P^4, which are coupled to P^1, shows that there is a mirror plane bisecting the Ru^2–Ru^3 bond. The $C\mathit{H}P_2$ resonance of the $Me_2PCHPMe_2$ ligand occurred at δ 1.24 ppm, close to the value for the analogous proton in complex **1**. The $C\mathit{H}_2P_2$ resonance of the Me_2PCH_2PMe ligand occurred at δ 2.85 ppm, as a symmetrical resonance with the expected ^{31}P couplings, showing that there is a plane of symmetry containing the P^1CP^2 skeleton (otherwise the CH_2P_2 protons would be non-equivalent). The only problem is in defining the positions of the carbonyl ligands so as to maintain the 2-fold symmetry required by the NMR data. Two carbonyls are placed on each ruthenium and the seventh carbonyl could then either bridge the Ru^2–Ru^3 bond or be terminal on Ru^1. Since the IR spectrum shows that no μ-CO groups are present, the latter arrangement is indicated. This leaves Ru^1 electron rich and Ru^2, Ru^3 electron poor, and the assignment of the position of this carbonyl ligand is therefore considered tentative.

Discussion

The pyrolyses of Ru_3(μ-dmpm) and Ru_3(μ-dppm) complexes occur with different selectivity as had been predicted. In each case, the most facile reaction involves oxidative addition of a C–H group to the Ru_3 cluster, but with dppm a CH bond of a phenyl substituent is involved and with dmpm a CH bond of a CH_2P_2 group is involved. This leads to the unusual 5-electron triply bridging $Me_2PCHPMe_2$ ligand in complexes **1** and **2**.

By conducting the pyrolysis of $[Ru_3(CO)_8(\mu\text{-dmpm})_2]$ in the solvent benzene, the complex $[Ru_3(CO)_8(\mu\text{-H})(\mu_3\text{-}\eta^3\text{-}Me_2PCHPMe_2)(\mu\text{-dmpm})]$ (**3**) has been obtained [17]. The product **2**, isolated from pyrolysis of $[Ru_3(CO)_8(\mu\text{-dmpm})_2]$ in the higher boiling solvent toluene, is then probably formed, after initial formation of **3**, by further loss of CO, oxidative addition of a P–Me bond to the Ru_3 cluster and then reductive elimination of methane. The sequence clearly indicates that the H–CHP_2 addition occurs before the P–Me addition. In no case has cleavage of a P–CH_2P bond been observed in the dmpm complexes, though it is known for analogous dppm complexes [7,9,11]. Complex **2** contains two strongly bound capping ligands and may be expected to be particularly inert towards fragmentation of the Ru_3 cluster.

The $Me_2PCHPMe_2$ and $MePCH_2PMe_2$ ligands are both 5-electron donors and act as powerful locking ligands for the Ru_3 triangle. Interestingly, preliminary experiments have shown that pyrolyses of $[Ru_3(CO)_{10}(\mu\text{-dmpm})]$ and $[Ru_3(CO)_8(\mu\text{-dmpm})_2]$ under hydrogen give as major products, $[Ru_3(CO)_9(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-}MePCH_2PMe_2)]$ and $[Ru_3(CO)_6H(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-}MePCH_2PMe_2)(dmpm)]$, indicating that the $Me_2PCHPMe_2$ and $MePCH_2PMe_2$ ligands have similar bridging abilities [22]. Both 5-electron ligands should be of great utility in the development of the chemistry of trinuclear cluster complexes which are stabilized with respect to fragmentation. We know of no prior reports of the Me_2PCH_2PMe ligand but there are earlier reports of the $Me_2PCHPMe_2$ ligand [1].

Experimental

The ^1H NMR spectra were recorded using Varian XL100 or XL200 spectrometers. The $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded using a Varian XL300 spectrometer. Spectra were referenced to Me_4Si (^1H and ^{13}C) or $(MeO)_3PO$ (^{31}P). IR spectra were recorded as solutions, using a Bruker/IBM FTIR32 spectrometer and mass spectra using a Varian MAT311A spectrometer.

$[Ru_3(CO)_{10}(\mu\text{-dmpm})]$ and $[Ru_3(CO)_8(\mu\text{-dmpm})_2]$ were prepared as reported elsewhere [16]. Pyrolyses were carried out under an atmosphere of dry nitrogen.

Pyrolysis of $[Ru_3(CO)_{10}(\mu\text{-dmpm})]$

A solution of $[Ru_3(CO)_{10}(\mu\text{-dmpm})]$ (0.398 g) in toluene (50 ml) was heated under reflux for 3 h. The solvent was removed from the resulting solution under vacuum, and the products were separated by chromatography on silica gel.

Elution with hexane/toluene (1/1) gave an orange compound identified as $[Ru_3(CO)_9(\mu\text{-H})(\mu_3\text{-}\eta^3\text{-}Me_2PCHPMe_2)]$. Yield 0.286 g; m.p. 140 °C (dec.). Anal. Found: C, 23.90; H, 1.97. $C_{14}H_{19}O_9P_2Ru_3$ calc: C, 24.23; H, 2.03%. MS: envelope centered at *m/e* 694 (calc 694, for $^{102}Ru_3$ isotopomer). IR (C_6H_{12}), $\nu(CO)$: 2079, 2047, 2022, 2010, 1995, 1985, 1968, 1948 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.80 [pseudo t, 6H, $^2J(PH) + {}^4J(PH) = 8$, *Me*P]; 1.41 [pseudo t, 6H, $^2J(PH) + {}^4J(PH) = 8$, *Me*P; 1.32 [dt, 1H, $^4J(HH) = 4$, $^2J(PH) = 8$, C*H*P_2]; −17.44 [dt, ^1H, $^4J(HH) = 4$, $^2J(PH) = 13.5$, Ru_2*H*]; ^{31}P NMR (CD_2Cl_2): $\delta = -15.99$ [s, ^{31}P]; $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 31.11$ [pseudo t, $^1J(PC) + {}^3J(PC) = 10$, *Me*P]; 223.41 [t, $^1J(PC) = 19$, *C*HP_2].

Elution with toluene gave a green complex (7 mg), which could not be fully characterized.

Pyrolysis of $[Ru_3(CO)_8(\mu\text{-dmpm})_2]$

A solution of $[Ru_3(CO)_8(\mu\text{-dmpm})_2]$ (180 mg) in toluene (50 ml) was heated under reflux for 5 h. The solvent was evaporated under vacuum and the products were separated by chromatography on silica gel.

Elution with hexane/toluene (1/1) gave an orange solid, identified as $[Ru_3(CO)_7(\mu_3\text{-}\eta^2\text{-}MePCH_2PMe_2)(\mu_3\text{-}\eta^3\text{-}Me_2PCHPMe_2)]$. Yield 88 mg; m.p. 174 °C (dec.). Anal. Found: C, 25.71; H, 3.20. $C_{16}H_{24}O_7P_4Ru_3$ calc: C, 25.35; H, 3.19%. MS: envelope centered at *m/e* 757 (calc for $^{102}Ru_3$ isotopomer, 758). IR (C_6H_{12}); $\nu(CO)$: 2060, 2012, 1981, 1946 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 2.85$ [ddt, 2H, $^2J(PH) = 9, 12$, $^4J(PH) = 5$, C*H*$_2P_2$]; 1.76 [overlapping multiplets, 15H, *Me*P]; 1.47 [pseudo t, 6H, $^2J(PH) + {}^4J(PH) = 8$, *Me*P]; 1.24 [m, 1H, *CH*P_2]; RuH resonances absent. ^{31}P NMR ($CDCl_3$): $\delta = 91.10$ [dt, 1P, $^2J(P^1P^2) = 134$, $^2J(P^1P^{3,4}) = 144$, P^1]; −1.70 [d, 1P, $^2J(P^1P^2) = 134$, P^2]; −20.73 [d, 2P, $^2J(P^1P^{3,4}) = 144$, $P^{3,4}$].

Elution with CH_2Cl_2 gave a second orange solid (18 mg), which has not yet been fully characterized. No other products were eluted.

Crystal structure analysis of $[Ru_3(CO)_9(\mu\text{-H})(\mu_3\text{-}\eta^3\text{-}Me_2PCHPMe_2)]$ *(1)*

Prismatic orange-yellow crystals of **1** were obtained from an ethanol solution.

Crystal data. $C_{14}H_{14}O_9P_2Ru_3$, $M = 691.4$, monoclinic, space group $P2_1/n$ (alternative setting of $P2_1/c$, No. 14), *a* 10.442(2), *b* 15.928(2), *c* 13.544(2) Å, β 98.89(1)°, *V* 2226 $Å^3$, $Z = 4$, D_c 2.063 g cm^{-3}, $F(000) = 1328$, $\mu(Mo\text{-}K_\alpha)$ 21.5 cm^{-1}, λ 0.71069 Å, *T* 22.5 °C.

Measurements. A crystal of approximate dimensions 0.32 × 0.12 × 0.08 mm was mounted on an Enraf–Nonius CAD4 diffractometer and exposed to graphite-monochromated Mo-K_α radiation.

The unit cell constants were determined by a least-squares treatment of 23 reflections in the 2θ-range 27–35°. The space group symmetry was established from systematic absences of reflections.

Table 2

Fractional atomic coordinates for $Ru_3(CO)_9(\mu\text{-H})(\mu_3\text{-}\eta^3\text{-Me}_2PCHPMe_2)$ (1)

Atom	x	y	z
Ru(1)	0.00877(3)	−0.32616(2)	0.33511(2)
Ru(2)	0.17052(2)	−0.19624(2)	0.23677(2)
Ru(3)	−0.06190(3)	−0.26596(2)	0.13905(2)
P(1)	−0.15764(9)	−0.22636(8)	0.33005(7)
P(2)	0.00153(9)	−0.09911(7)	0.23876(7)
O(6)	0.2126(3)	−0.4589(2)	0.3074(3)
O(7)	0.0457(4)	0.3436(3)	0.5627(3)
O(8)	−0.1885(4)	−0.4636(3)	0.2823(4)
O(9)	0.3685(3)	−0.3329(2)	0.2064(3)
O(10)	0.2220(3)	−0.1199(2)	0.0428(2)
O(11)	0.3758(4)	−0.0979(3)	0.3764(3)
O(12)	−0.3122(3)	−0.3601(3)	0.0694(3)
O(13)	−0.0841(3)	−0.1746(2)	−0.0586(2)
O(14)	0.0989(3)	−0.4074(2)	0.0697(3)
C(1)	−0.1418(3)	−0.1617(3)	0.2264(3)
C(2)	−0.3258(4)	−0.2628(4)	0.3069(4)
C(3)	−0.1630(6)	−0.1666(4)	0.4452(4)
C(4)	0.0212(6)	−0.0279(3)	0.3447(4)
C(5)	−0.0299(5)	−0.0232(3)	0.1375(4)
C(6)	0.1409(4)	−0.4070(3)	0.3161(3)
C(7)	0.0362(4)	−0.3357(3)	0.4779(3)
C(8)	−0.1146(4)	−0.4107(3)	0.3020(4)
C(9)	0.2904(4)	−0.2860(3)	0.2201(3)
C(10)	0.2030(4)	−0.1496(3)	0.1158(3)
C(11)	0.2985(4)	−0.1344(3)	0.3272(3)
C(12)	−0.2213(4)	−0.3226(3)	0.0997(3)
C(13)	−0.0749(4)	−0.2067(3)	0.0178(3)
C(14)	0.0405(4)	−0.3548(3)	0.0973(3)
H(1)	−0.233(4)	−0.121(3)	0.202(3)
H(2A)	−0.376(5)	−0.210(4)	0.306(4)
H(2B)	−0.345(4)	−0.303(3)	0.361(4)
H(2C)	−0.348(5)	−0.299(3)	0.240(4)
H(3A)	−0.179(5)	−0.212(4)	0.494(5)
H(3B)	−0.086(6)	−0.143(4)	0.477(4)
H(3C)	−0.222(5)	−0.097(4)	0.424(5)
H(4A)	0.089(5)	0.007(4)	0.339(4)
H(4B)	−0.048(5)	0.003(4)	0.353(4)
H(4C)	0.044(5)	−0.048(4)	0.406(4)
H(5A)	0.039(4)	0.014(3)	0.143(3)
H(5B)	−0.107(6)	0.014(4)	0.153(4)
H(5C)	−0.057(5)	−0.044(4)	0.081(4)
H(6)	0.109(4)	−0.245(3)	0.335(4)

Table 3

Vibrational atomic parameters (Å^2) for $Ru_2(CO)_9(\mu\text{-H})(\mu_3\text{-}\eta^3\text{-}Me_2PCHPMe_2)$ (1)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23} [a]
Ru(1)	0.0328(2)	0.0331(2)	0.0331(2)	−0.0033(1)	0.0043(1)	0.0094(1)
Ru(2)	0.0262(1)	0.0251(2)	0.0299(1)	−0.0007(1)	0.0048(1)	0.0008(1)
Ru(3)	0.0294(1)	0.0331(2)	0.0265(1)	−0.0034(1)	0.0026(1)	0.0011(1)
P(1)	0.0330(4)	0.0477(7)	0.0353(5)	−0.0003(5)	0.0127(4)	0.0065(5)
P(2)	0.0350(4)	0.0285(5)	0.0347(5)	0.0040(4)	0.0092(4)	0.0031(4)
O(6)	0.068(2)	0.044(2)	0.117(3)	0.018(2)	0.016(2)	0.008(2)
O(7)	0.102(3)	0.139(5)	0.039(2)	−0.015(3)	0.000(2)	0.025(2)
O(8)	0.072(2)	0.065(3)	0.135(4)	−0.036(2)	0.005(2)	0.010(3)
O(9)	0.055(2)	0.057(2)	0.069(2)	0.022(2)	0.013(2)	−0.004(2)
O(10)	0.074(2)	0.070(3)	0.043(2)	0.000(2)	0.026(2)	0.012(2)
O(11)	0.083(2)	0.064(3)	0.084(3)	−0.027(2)	−0.034(2)	−0.005(2)
O(12)	0.060(2)	0.098(3)	0.069(2)	−0.041(2)	−0.003(2)	−0.004(2)
O(13)	0.087(2)	0.071(3)	0.035(2)	−0.015(2)	−0.002(2)	0.015(2)
O(14)	0.072(2)	0.056(2)	0.070(2)	0.011(2)	0.014(2)	−0.017(2)
C(1)	0.031(2)	0.040(2)	0.037(2)	0.003(2)	0.010(1)	0.006(2)
C(2)	0.040(2)	0.072(4)	0.067(3)	−0.005(3)	0.020(2)	0.015(3)
C(3)	0.076(3)	0.074(4)	0.047(3)	−0.001(3)	0.031(3)	−0.003(3)
C(4)	0.063(3)	0.037(3)	0.054(3)	0.001(2)	0.014(2)	−0.009(2)
C(5)	0.052(3)	0.036(3)	0.051(3)	0.006(2)	0.009(2)	0.017(2)
C(6)	0.045(2)	0.038(3)	0.058(3)	−0.004(2)	0.003(2)	0.011(2)
C(7)	0.056(2)	0.062(3)	0.048(3)	−0.006(2)	0.002(2)	0.016(2)
C(8)	0.048(2)	0.052(3)	0.072(3)	−0.010(2)	0.007(2)	0.013(3)
C(9)	0.038(2)	0.036(2)	0.040(2)	−0.001(2)	0.005(2)	0.002(2)
C(10)	0.037(2)	0.042(3)	0.043(2)	0.000(2)	0.011(2)	−0.001(2)
C(11)	0.046(2)	0.038(2)	0.048(2)	−0.003(2)	0.003(2)	0.009(2)
C(12)	0.046(2)	0.052(3)	0.040(2)	−0.009(2)	0.004(2)	0.001(2)
C(13)	0.040(2)	0.047(3)	0.037(2)	−0.005(2)	0.002(2)	−0.003(2)
C(14)	0.047(2)	0.047(3)	0.038(2)	−0.004(2)	0.004(2)	−0.002(2)

[a] These parameters were used in the expression $\exp(-2\pi^2\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}h_ih_ja_i^{\star}a_j^{\star})$.

Intensities of 7071 reflections with $2 < \theta < 27°$ were measured by continuous $\theta/2\theta$ scans of $(0.62 + 0.35 \tan\theta)°$ in θ. Scan speeds were adjusted to give $\sigma(I)/I < 0.02$, subject to a time limit of 120 s. Two strong reflections remeasured every 2 h displayed only random fluctuations of intensities, not exceeding 3% of the mean values. The integrated intensities of all reflections, derived in the usual manner [23], were corrected for background, Lorentz, polarization and absorption effects; the absorption factors (on F) of 0.90–1.40 were calculated by an empirical method [24]. Averaging 3948 symmetry related reflections, to get 1908 independent ones, gave R (internal) of 0.022. Rejection of 1353 reflections with $I < 3\sigma(I)$ yielded 3482 unique structure amplitudes, and only these were used in the crystal structure analysis.

Structure solution and refinement. The positions of the ruthenium atoms were determined from a Patterson function and those of the remaining atoms, including all hydrogens, from difference electron density maps. The structure was refined by full-matrix least-squares, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(|F_o|)$. The hydrogen atoms were allowed isotropic, and all other atoms anisotropic thermal vibrations. The refinement of 309 parameters converged at $R = 0.22$ and $R_w = 0.028$ ($R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, $R_w = |\Sigma w(|F_o| - |F_c|)^2/$

$w|F_o|^2]^{1/2}$, with the largest parameter-shift/error ratio of 0.02 and the error in an observation of unit weight of 1.6. In the final difference electron density map the function values range from -0.38 to $+0.53$ eÅ^{-3}. The final atomic parameters are shown in Tables 2 and 3.

All calculations were performed on a GOULD SEL 32/27 supermini computer, using the locally developed 'GX' program package [25]. The neutral atom scattering factors and anomalous dispersion corrections were taken from ref. 26. A list of observed and calculated structure amplitudes is available from the authors.

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