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Reactions of 1,8-bis(diphenylphosphino)naphthalene with ruthenium cluster carbonyls: C–H and C–P bond cleavage reactions

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Dedicated to Professor Helmut Werner on the occasion of his 70th birthday, with respect and admiration

Abstract

Reactions between $Ru_3(CO)_{12}$ and 1,8-bis(diphenylphosphino)naphthalene (dppn) have given the four complexes $Ru_3(\mu\text{-H})\{\mu_3\text{-}PPh_2(nap)PPh(C_6H_4)\}(CO)_8$ (**1**), $Ru_4(\mu\text{-H})\{\mu_3\text{-}PPh_2(nap)PPh(C_6H_4)\}(\mu\text{-CO})_3(CO)_7$ (**2**) and $Ru_4(\mu\text{-H})(\mu_3\text{-}C_6H_4)\{\mu\text{-PPh(nap)PPh}_2\}(CO)_{11}$ (**3**) (in refluxing thf), and $Ru_4\{\mu_4\text{-P(nap)PPh}_2\}(\mu_4\text{-}C_6H_4)(\mu\text{-CO})(CO)_9$ (**4**) (in refluxing toluene) which have been characterised by single crystal X-ray studies. They have been formed by aryl C–H and aryl C–P bond cleavage reactions, presumably from an initial (unobserved) chelate dppn complex. The unchanged chelating ligand is found in $Ru_3(\mu\text{-dppm})(CO)_8(dppn)$ (**5**), obtained from $Ru_3(\mu\text{-dppm})(CO)_{10}$ and dppn in refluxing thf.

Keywords: Ruthenium cluster; Phosphine complexes; X-ray structure; Bond cleavage (C–H, C–P)

1. Introduction

The metal complex chemistry of 1,8-bis(diphenylphosphino)naphthalene (dppn), a phosphorus analogue of 1,8-bis(dimethylamino)naphthalene ("proton sponge®"), has attracted attention since the first report of this highly basic phosphine [1]. The two phosphorus atoms are 3.0483 (6) Å apart, i.e. within the sum of the van der Waals radii (3.80 Å), and thus have a rigid chelating interaction with metal centres. Conventional chelate complexes ML_n(dppn) (ML_n = $Mo(CO)_4$ [2], $PdCl_2$, $PtCl_2$ [1,2], $[Pd(\eta\text{-}C_3H_5)]^+$ [3]) have been described, while more recently, accounts of gold(I) and gold(II) complexes $[Au(dppn)_2]Cl$ [4], $\{Au(C{\equiv}CAr)\}_2(\mu\text{-dppn})$ [5] and $[\{AuX(dppn)\}_2]^{2+}$ (X = Br, I), the latter containing an unsupported Au(II)–Au(II) bond [6], have appeared. Platinum(II) complexes of 1,8-$(PRR')_2$naphthalenes (RR′ = Me_2, $Me(C_6F_5)$, Cy_2, Bu^tPh) have also been made [7]. Our interest in the coordination and subsequent bond-cleavage reactions of bidentate phosphines on metal clusters suggested that the close approach of the two phosphorus atoms might induce some unusual reactivity in complexes with polynuclear metal systems and we have instigated a survey of the reactions of dppn with trinuclear Group 8 metal carbonyl clusters. This paper describes some complexes obtained from reactions between dppn and $Ru_3(CO)_{10}(L)_2$ [$L_2 = (CO)_2$, dppm].

2. Results and discussion

The reaction between $Ru_3(CO)_{12}$ and dppn was carried out in refluxing thf and unusually, did not require any initiator for a rapid reaction to ensue. After refluxing the mixture for 5.5 h, all starting cluster carbonyl had been consumed and preparative t.l.c. on silica gel separated three complexes in a total yield of 48%. Trace amounts of other, presently unidentified, complexes

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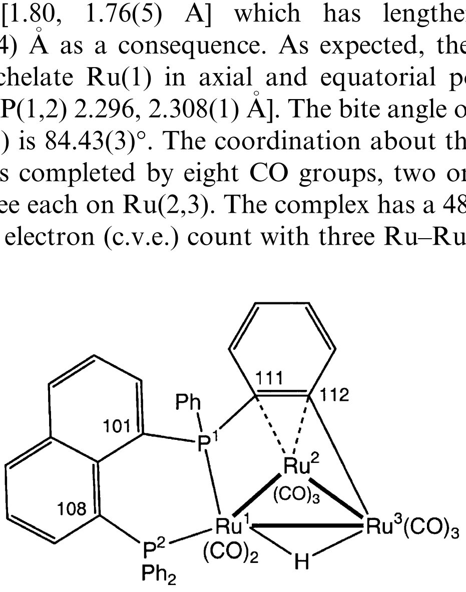
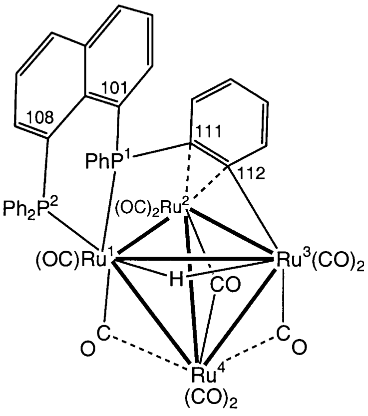
were observed. The pure complexes were identified by single crystal X-ray structural determinations, spectroscopic data being consistent with the solid-state structures being preserved in solution.

Two of the complexes contain the cyclometallated (dppn-H) ligand. Plots of their structures are shown in Fig. 1, with selected bond parameters in Table 1. The faster running of these (R_f 0.56) is $Ru_3(\mu\text{-}H)\{\mu_3\text{-}PPh_2(nap)PPh(C_6H_4)\}(CO)_8$ (**1**; nap = 1,8-$C_{10}H_6$) which formed red crystals (from CH_2Cl_2/hexane). One phenyl group of a molecule of dppn has oxidatively added to the cluster to give a C_6H_4 group which bridges the Ru(2)–Ru(3) bond [2.7078(5) Å] in the η^1:η^2 bonding mode [Ru(3)–C(112) 2.120(4), Ru(2)–C(111, 112) 2.411, 2.323(4) Å]. The H atom is found bridging Ru(1)–Ru(3) [1.80, 1.76(5) Å] which has lengthened to 2.9926(4) Å as a consequence. As expected, the two P atoms chelate Ru(1) in axial and equatorial positions [Ru(1)–P(1,2) 2.296, 2.308(1) Å]. The bite angle of P(1,2) at Ru(1) is 84.43(3)°. The coordination about the metal atoms is completed by eight CO groups, two on Ru(1) and three each on Ru(2,3). The complex has a 48 cluster valence electron (c.v.e.) count with three Ru–Ru bonds.



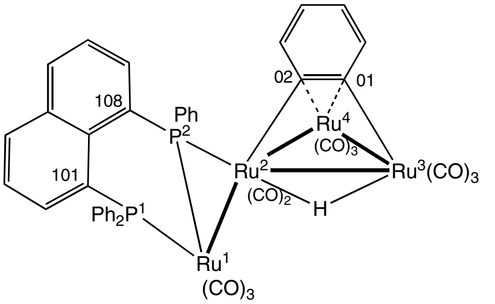
(1)

The second complex, $Ru_4(\mu\text{-}H)\{\mu_3\text{-}PPh_2(nap)PPh(C_6H_4)\}(\mu\text{-}CO)_3(CO)_7$ (**2**; R_f 0.42) forms dark brown–black crystals. The structure (Fig. 1b; bond distances and angles in Table 1) is based on a tetrahedral Ru_4 core, formed by fusion of an $Ru(CO)_2$ unit to **1**, below the Ru_3 plane. The fourth Ru atom caps the other side of the Ru_3 triangle, being attached via three Ru–Ru bonds [Ru(1,2,3)–Ru(4) 2.8836, 2.7128, 2.7493(7) Å] and supported by one fully bridging and two semi-bridging CO ligands. One face of the tetrahedron supports a $PPh_2(nap)PPh(C_6H_4)$ ligand attached as found in **1** above. Thus, the C_6H_4 group bridges the Ru(2)–Ru(3) bond [2.8238(7) Å] in the η^1:η^2 bonding mode [Ru(3)–C(112) 2.120(5), Ru(2)–C(111, 112) 2.314, 2.302(5) Å]. The two P atoms chelate Ru(1) in axial and equatorial positions [Ru(1)–P(1,2) 2.320, 2.341(1) Å] with a bite angle of 83.63(5)°. The H atom bridges the two Ru atoms [Ru(1,3)–H 1.74, 1.85(5) Å] which are chelated to the tertiary bis(phosphine) and σ-bonded by the dehydrophenyl group, respectively. With six Ru–Ru bonds, the c.v.e. count is 60.



(2)

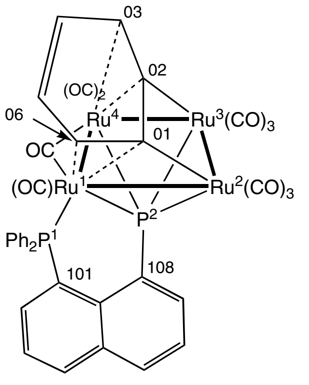
Bright orange crystals of tetranuclear $Ru_4(\mu\text{-}H)(\mu_3\text{-}C_6H_4)\{\mu\text{-}PPh(nap)PPh_2\}(CO)_{11}$ (**3**; R_f 0.50) contain an unusual spiked triangular cluster, in which the Ru(1)–Ru(2) fragment carries the two P atoms and associated groups (see Fig. 2 and Table 2). The Ru(1)–Ru(2) vector is inclined at an angle of 58.50(3)° to the plane of the Ru_3 triangle. The dppn ligand has fragmented into the phosphido–phosphine $PPh(nap)PPh_2$ which bridges the Ru(1)–Ru(2) bond [2.8705(4) Å], a C_6H_4 ring (benzyne) which caps the triangular cluster in the η^1:η^1:η^2 mode [Ru(2)–C(02) 2.108(3), Ru(3)–C(01) 2.088(3), Ru(4)–C(01,02) 2.297, 2.245(3) Å], and an H atom bridging Ru(2)–Ru(3) [3.0014(4); Ru(2,3)–H 1.73, 1.77(4) Å]. Eleven CO groups are distributed three each to Ru(1,3,4) and two on Ru(2). Atom Ru(1) is chelated by the two phosphorus atoms [Ru–P(1,2) 2.3092, 2.3377(8) Å], but having lost a Ph group, atom P(2) is also attached to Ru(2) [2.3287(8) Å]. The chelate bite angle at Ru(1) is 86.27(3)°. The c.v.e. count is 64, as expected for an M_4 cluster with four M–M bonds.



(3)

The only complex which was characterised from a similar reaction carried out under more vigorous conditions (refluxing toluene) was $Ru_4\{\mu_4\text{-}P(nap)PPh_2\}(\mu_4\text{-}C_6H_4)(\mu\text{-}CO)(CO)_9$ (**4**), which formed orange–brown crystals. The molecular structure (Fig. 3, Table 3) comprises a quadrilateral Ru_4 cluster [Ru–Ru 2.8218–2.9420(4) Å], to one side of which is attached a μ_4-C_6H_4

group, while the other side supports the μ_4-P(nap)PPh$_2$ phosphino–phosphinidene ligand. The benzyne ligand is bent across the Ru$_4$ cluster such that the C$_6$-ring and C(01,02)Ru(2,3) groups are approximately coplanar. Bond distances indicate that atoms C(01,06) and C(02,03) are bonded via η^1:η^2 interactions with Ru(2,1) and Ru(3,4), respectively [Ru(2)–C(01) 2.111(2), Ru(3)–C(02) 2.105(3); Ru(1)–C(01,06) 2.270, 2.533(2); Ru(4)–C(02,03) 2.302, 2.577(3) Å]; the η^2 interactions are highly asymmetric, with unusually long separations of C(06,03) from Ru(1,4).



(4)

Atom P(2) is attached to all four Ru atoms, being nearer to Ru(2,3) [Ru–P 2.3582, 2.4075(7) Å] than to Ru(1,4) [Ru–P 2.4221, 2.4259(7) Å], i.e. consistent with the bonding pattern of the C$_6$H$_4$ group. Atom P(1) is attached to Ru(1) [2.2862(6) Å], with a chelate bite angle P(1)–Ru(1)–P(2) of 85.71(2)°. Coordination is completed by ten CO ligands, one of which bridges the Ru(1)–Ru(4) vector. The other nine are distributed three each to Ru(2,3), two on Ru(4) and one on Ru(1). The c.v.e. is 64, as predicted for an M$_4$ cluster with only four M–M bonds.

The reaction between dppn and Ru$_3$(μ-dppm)(CO)$_{10}$ in refluxing thf produced several complexes, but apart from Ru$_3${μ_3-PPhCH$_2$PPh(C$_6$H$_4$)}(CO)$_9$ (a known thermal decomposition product of the starting cluster [8]), the only tractable product was Ru$_3$(μ-dppm)-(CO)$_8$(dppn) (**5**), isolated in small yield. The X-ray structural study showed that a simple substitution of two CO groups on the Ru atom not bonded to the dppm ligand had occurred. As shown in Fig. 4 and Table 4, all P atoms occupy equatorial positions of an Ru$_3$ cluster in which the Ru–Ru separations [2.8703–2.9191(5) Å] appear not to be related to the nature of any of the substituents. In comparison with the structure of the precursor, Ru(1)–Ru(2) [2.8703(6) Å], bridged by the dppm ligand, is of similar length. Chelation of Ru(3) by the dppn ligand [Ru(3)–P(3,4) 2.284, 2.274(1) Å] results in shorter Ru–P distances than found for the edge-bridging dppm [Ru–P 2.308, 2.324(1) Å], as expected from its bite angle of 89.62(4)°.

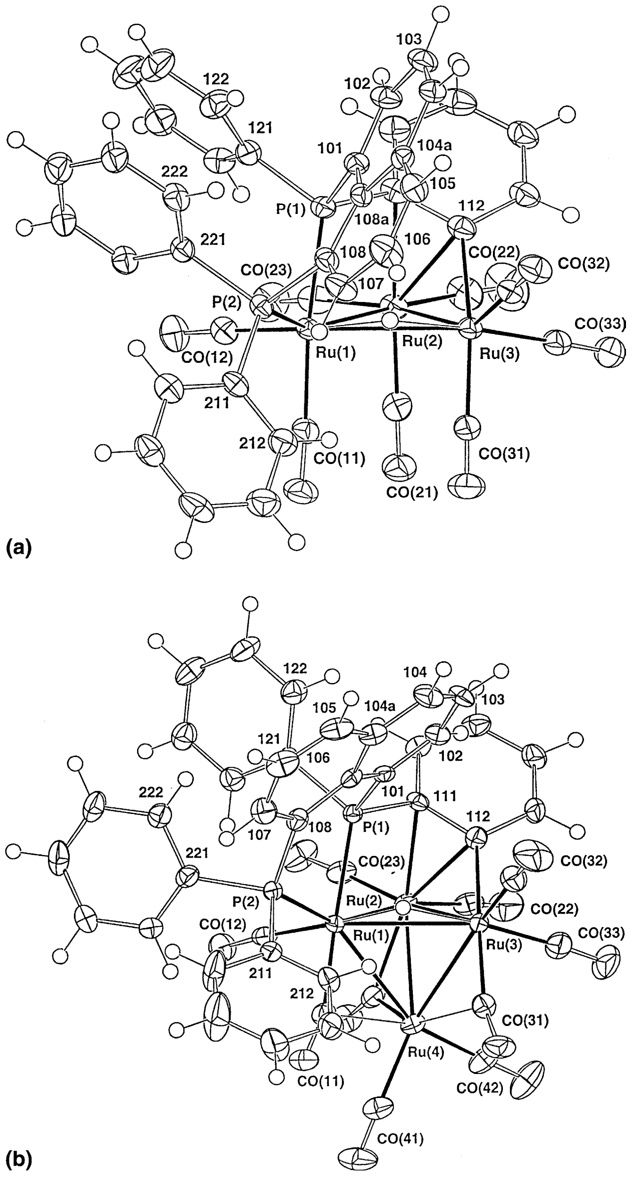
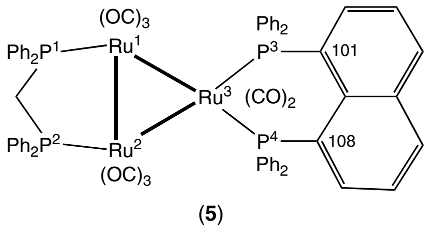


Fig. 1. Molecular projections of (a) Ru$_3$(μ-H){μ_3-PPh$_2$(nap)PPh(C$_6$H$_4$)}(CO)$_8$ (**1**) and (b) Ru$_4$(μ-H){μ_3-PPh$_2$(nap)PPh(C$_6$H$_4$)}(μ-CO)$_3$(CO)$_7$ (**2**), oblique to their Ru$_3$ planes.



(5)

The naphthyl group is commonly regarded as a relatively rigid platform for substituents. The free dppn ligand shows considerable distortion as a result of interphenyl group contacts [1]. In the present series of

Table 1
Selected interatomic distances (Å) (**1**, **2**)

Atoms	Distance	Atoms	Distance
Ru(1)–Ru(2)	2.8158(5), 2.8129(6)	Ru(1)–P(1)	2.296(1), 2.320(1)
Ru(1)–Ru(3)	2.9926(4), 2.9361(6)	Ru(1)–P(2)	2.308(1), 2.341(1)
Ru(2)–Ru(3)	2.7078(5), 2.8238(7)	Ru(2)–C(112)	2.323(4), 2.302(5)
Ru(2)–C(111)	2.411(4), 2.314(5)	Ru(3)–C(112)	2.120(4), 2.120(5)
Ru(1)–H	1.80(5), 1.74(5)	Ru(3)–H	1.76(5), 1.85(5)
P(1)–C(101)	1.832(4), 1.823(5)	P(2)–C(108)	1.815(4), 1.822(5)
P(1)–C(111)	1.802(4), 1.789(5)	P(2)–C(211)	1.822(4), 1.819(5)
P(1)–C(121)	1.812(4), 1.826(5)	P(2)–C(221)	1.819(4), 1.814(5)
C(111)–C(112)	1.436(6), 1.423(7)	Ru(2)–C(21)	1.868(4), 2.095(6)
Ru(1)–C(11)	1.907(4), 1.927(5)	Ru(2)–C(22)	1.892(5), 1.877(6)
Ru(1)–C(12)	1.876(4), 1.879(5)	Ru(2)–C(23)	1.889(5), 1.861(6)
Ru(3)–C(31)	1.932(4), 1.948(5)	Ru(3)–C(33)	1.887(4), 1.878(6)
Ru(3)–C(32)	1.897(4), 1.925(6)		

In **2**, Ru(4)–Ru(1,2,3),C(41,42) are: 2.8836(8), 2.7128(6), 2.7493(7), 1.870(6), 1.834(6) Å. Ru(4)...C(11,21,31) are 2.569(5), 1.949(6), 2.666(5) with associated Ru(n1)–C(n1)–O(n1) 161.7(5), 135.9(5), 164.0(5)°. Ru(4)–C(21)–O(21) is 139.9(5)°.

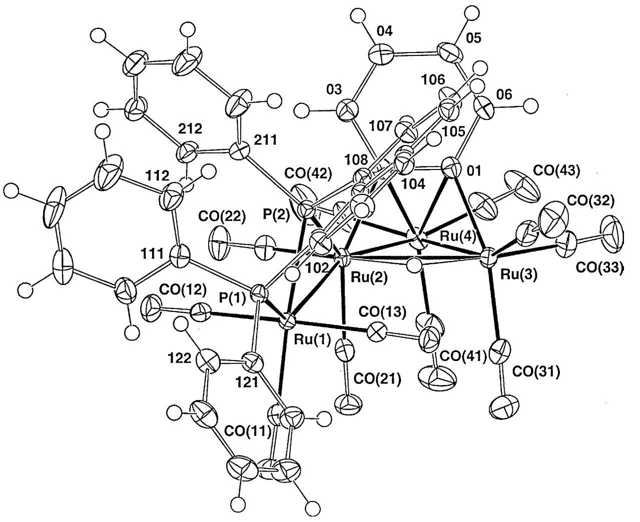


Fig. 2. Molecular projection of $Ru_4(\mu\text{-}H)(\mu_3\text{-}C_6H_4)\{\mu\text{-}PPh(nap)PPh_2\}(CO)_{11}$ (**3**), normal to the Ru_3 plane.

Table 2
Selected interatomic distances (Å) (**3**)

Atoms	Distance	Atoms	Distance
Ru(1)–Ru(2)	2.8705(4)	Ru(1)–P(1)	2.3092(8)
Ru(2)–Ru(3)	3.0014(4)	Ru(1)–P(2)	2.3377(8)
Ru(2)–Ru(4)	2.7498(4)	Ru(2)–P(2)	2.3287(8)
Ru(3)–Ru(4)	2.7133(4)	Ru(2)–C(02)	2.108(3)
Ru(4)–C(01)	2.297(3)	Ru(3)–C(01)	2.088(3)
Ru(4)–C(02)	2.245(3)	Ru(2)–H	1.73(4)
P(1)–C(101)	1.846(3)	Ru(3)–H	1.77(4)
P(1)–C(111)	1.818(4)	P(2)–C(108)	1.812(3)
P(1)–C(121)	1.837(3)	P(2)–C(211)	1.828(3)
C(01)–C(02)	1.414(5)	Ru(1)–C(11)	1.942(3)
Ru(1)–C(12)	1.953(3)	Ru(1)–C(13)	1.943(3)
Ru(2)–C(21)	1.942(4)	Ru(3)–C(31)	1.948(4)
Ru(2)–C(22)	1.882(3)	Ru(3)–C(32)	1.914(4)
Ru(4)–C(41)	1.884(4)	Ru(3)–C(33)	1.902(4)
Ru(4)–C(42)	1.928(4)	Ru(4)–C(43)	1.890(4)

The C_6 plane has a dihedral angle of 66.28(9)° to the Ru_3 plane. Ru(1) lies 0.878(2) Å out of the latter.

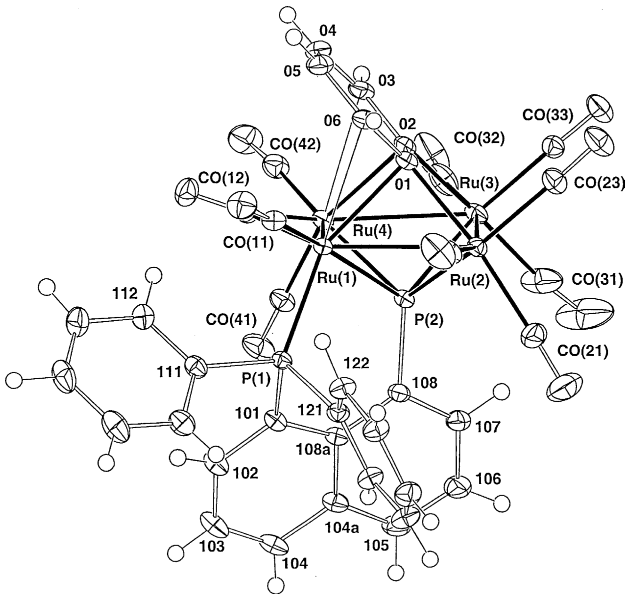


Fig. 3. Molecular projection of $Ru_4\{\mu_4\text{-}P(nap)PPh_2\}(\mu_4\text{-}C_6H_4)(\mu\text{-}CO)(CO)_9$ (**4**), oblique to the Ru_4 plane.

complexes, the geometries of the dppn and dppn-derived ligands, while showing consistent chelating behaviour towards one ruthenium atom, are also involved in other interactions. The extent to which the resulting distortions (see Table 5) can be attributed to coordination is debatable. Thus, the 'bite' distance of the ligand varies by more than 0.1 Å, supporting 'bite' angles which vary by up to 6°. The associated P–C(nap) distances vary by up to 0.05 Å, which in turn impact on ring angles (particularly exocyclic). Defining atom deviations of the C_{10} ring planes approach up to 0.1 Å in most of the structures. Considerable deviations are also found for the P atoms and the chelated Ru, which may occur either side of the ring plane.

Table 3
Selected interatomic distances (Å) (**4**)

Atoms	Distance	Atoms	Distance
Ru(1)–Ru(2)	2.9010(4)	Ru(1)–P(1)	2.2862(6)
Ru(1)–Ru(4)	2.8218(4)	Ru(1)–P(2)	2.4221(8)
Ru(2)–Ru(3)	2.9420(4)	Ru(2)–P(2)	2.3582(7)
Ru(3)–Ru(4)	2.8912(4)	Ru(3)–P(2)	2.4075(6)
C(01)–C(02)	1.445(4)	Ru(4)–P(2)	2.4259(7)
C(01)–Ru(1)	2.270(2)	C(02)–Ru(3)	2.105(3)
C(01)–Ru(2)	2.111(2)	C(02)–Ru(4)	2.302(3)
Ru(1)–C(06)	2.533(2)	Ru(3)–C(31)	1.936(5)
Ru(4)–C(03)	2.577(3)	Ru(3)–C(32)	1.903(3)
Ru(1)–C(11)	1.873(3)	Ru(3)–C(33)	1.916(2)
Ru(1)–C(12)	2.017(3)	Ru(4)–C(41)	1.873(3)
Ru(2)–C(21)	1.961(3)	Ru(4)–C(42)	1.897(3)
Ru(2)–C(22)	1.897(3)	P(1)–C(101)	1.817(3)
Ru(2)–C(23)	1.927(3)	P(1)–C(111)	1.824(3)
Ru(4)–C(12)	2.090(3)	P(1)–C(121)	1.834(3)
P(2)–C(108)	1.826(3)		

The Ru$_4$/C$_6$ interplanar dihedral angle is 74.07(3)°; P(2) lies 1.265(1) Å out of the Ru$_4$ plane.

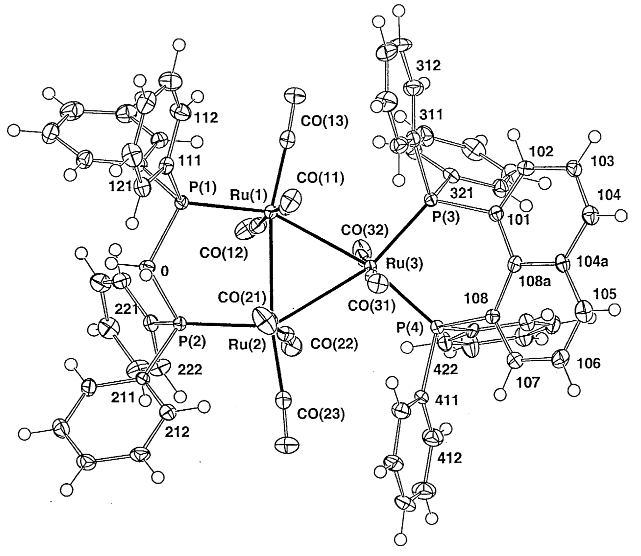


Fig. 4. Molecular projection of Ru$_3$(μ-dppm)(CO)$_8$(dppn) (**5**), normal to the Ru$_3$ plane.

Table 4
Selected interatomic distances (Å) (**5**)

Atoms	Distance	Atoms	Distance
Ru(1)–P(1)	2.308(1)	P(1)–C(0)	1.860(4)
Ru(2)–P(2)	2.324(1)	P(2)–C(0)	1.859(4)
Ru(3)–P(3)	2.284(1)	P(3)–C(101)	1.860(4)
Ru(3)–P(4)	2.274(1)	P(4)–C(108)	1.854(4)
Ru(1)–Ru(2)	2.8703(6)	Ru(2)–Ru(3)	2.9191(5)
Ru(1)–Ru(3)	2.8841(5)		

Ru(*n*)–P(*n*)–C(0)($n = 1,2$) are 112.7(1), 115.0(1); Ru(3)–P(3)–C(101), Ru(3)–P(4)–C(108) are 117.7(1), 114.4(1)°.

It is likely that the first-formed complex in the reaction of dppn with Ru$_3$(CO)$_{12}$ is a simple chelate complex, Ru$_3$(CO)$_{10}$(dppn), as found in the formation of **5**. Activation of the dppn by coordination to the Ru$_3$ cluster, along with the presence of readily accessible coordination sites (by loss of CO), then results in (a) aryl C–H bond cleavage to give (aryl + H), as in **1** and **2**, followed by (b) aryl C–P bond cleavage (to give C$_6$H$_4$ + phosphide), as in **3**. A third reaction involves loss of benzene by combination of (H + Ph) to give phosphinidene, as in **4**. It is not possible to say whether aryl C–P bond cleavage to give Ph occurs before the aryl C–H cleavage. Cluster-bonded Ph groups are rare, either elimination as benzene or further degradation to benzyne on the cluster occurring (see Table 6).

There do not appear to be any other structurally characterised examples of Ru$_3$ carbonyl clusters in which one edge is bridged by a bidentate phosphine and the third metal atom is chelated by the same or a different phosphine. The nearest analogues in the Cambridge Data Base are examples where a monodentate phosphine is attached to the third metal atom, such as Ru$_3$(μ-dppm)(CO)$_9$(PR$_3$) [PR$_3$ = P(OMe)$_3$ [9], PPh$_2$-(C$_6$H$_4$N=CHPh-2) [10], PPh$_2${C$_6$H$_4$NHC(O)Ph-2} [11], PPh$_2$(C$_6$H$_4$CHO-2) [11] and Ru$_3${μ-(PPh$_2$)$_2$-C=CH$_2$}(CO)$_9${PPh$_2$CH$_2$CH[(PPh$_2$)$_2$Fe(CO)$_3$]} [12]].

3. Conclusions

This preliminary study of the reactions of the sterically demanding dppn ligand with trinuclear ruthenium carbonyl clusters has shown that the close separation of the two phosphorus atoms in the bis(tertiary phosphine) results in exclusive chelation to one metal centre, as expected. The marked tendency for C–H and P–C bond cleavage reactions found with phosphine-substituted ruthenium and osmium cluster carbonyls, usually upon heating [13], is also evident here. Under relatively mild conditions (refluxing thf), complexes containing *ortho*-metallated phenyl or benzyne ligands are formed by C–H and C–P bond cleavage, respectively.

Coordination of the P–C$_6$H$_4$ ligand is found in the η^1:η^2 mode, while in the two benzyne-containing clusters, examples of μ_3-η^1:η^1:η^2-(as a four-electron donor in **3**) and μ_4-η^1:η^1;η^2:η^2-bonding modes (as a six-electron donor in **4**) have been characterised. These have precedents in several thermal decomposition (alteration) products from phosphine-containing Ru$_3$ and Os$_3$ clusters [14] and, more recently, in studies of C$_6$H$_4$ on Ir {1 0 0} surfaces. In the latter, the plane of the di-σ-bonded benzyne ring is tilted at 47.2° to the surface normal [15]. In **3** and **4**, corresponding angles are 66.28(9) and 49.35(7)°, respectively, and are consistent with the bonding modes mentioned above. Alternatively, theoretical studies of the surface-adsorbed species have concluded that the tilt arises from back-bonding of the C$_6$ π-system to the metal d orbitals [16].

In the present work, we have not been able to isolate any complexes in which the C$_{10}$ group interacts with the

Table 5
Naphthyl chelate descriptors

Atoms	**1**	**2**	**3**	**4**	**5**[a]	**L**[b]
Distances (Å)						
P...P	3.094(1)	3.107(2)	3.177(1)	3.2040(9)	3.118(1)	3.0483(6)
P–C(101)	1.832(4)	1.823(5)	1.846(3)	1.817(3)	1.860(4)	1.851(2)
P–C(108)	1.815(4)	1.822(5)	1.812(3)	1.826(3)	1.854(4)	1.840(2)
Angles (degrees)						
P–Ru–P	84.43(3)	83.63(5)	86.27(3)	85.71(2)	89.62(4)	
Ru–P–C(101)	117.0(1)	113.4(2)	113.8(1)	119.96(7)	117.7(1)	
Ru–P–C(108)	111.2(1)	120.3(2)	111.5(1)	120.86(9)	114.4(1)	
P–C(101)–C(102)	114.2(3)	117.7(4)	115.2(2)	117.6(2)	113.6(3)	117.6(2)
P–C(108)–C(107)	118.1(3)	115.0(4)	114.6(2)	115.3(2)	117.2(3)	118.0(1)
P–C(101)–C(108a)	125.9(3)	122.2(4)	126.1(2)	121.2(2)	126.8(3)	124.1(1)
P–C(108)–C(108a)	122.1(3)	125.2(4)	124.8(2)	125.1(2)	123.7(3)	122.2(2)
Torsion angles (degrees)						
P(2)–Ru–P(1)–C(101)	41.31(1)	53.2(2)	−47.3(1)	−37.6(1)	−32.6(2)	
Ru–P(1)–C(101)–C(108a)	−12.4(4)	−55.2(4)	27.3(3)	56.2(2)	7.8(4)	
P(1)–C(101)–C(108a)–C(108)	−14.3(5)	10.1(7)	3.3(5)	−20.6(3)	13.1(6)	−8.0(2)
C(101)–C(108a)–C(108)–P(2)	−8.3(5)	17.8(8)	6.2(5)	−20.7(4)	6.2(6)	−12.8(2)
C(108a)–C(108)–P(2)–Ru	53.5(3)	2.9(5)	−43.8(3)	24.9(3)	−43.4(4)	
C(108)–P(2)–Ru–P(1)	−57.4(1)	−33.3(2)	54.2(1)	5.3(1)	46.5(2)	
C_{10} plane parameters (deviations, δ, in Å)						
χ^2(plane)	1131	1331	1871	1214	10679	
δP(1)	0.438(4)	0.437(5)	0.706(3)	0.377(4)	0.333(2)	
δP(2)	−0.331(4)	−0.508(6)	−0.586(3)	−0.301(4)	−0.474(2)	
δRu	1.242(5)	−1.070(8)	−0.324(4)	0.970(6)		
C_{10}/Ru_3 dihedral (°)	58.60(7)		70.07(5) [Ru_4]	34.56(8)		

Across the six compounds, mean values are: Distances C(101)–C(102), C(107)–C(108) 1.380(8), 1.378(4); C(102)–C(103), C(106)–C(107) 1.402(5), 1.404(10); C(103)–C(104), C(105)–C(106) 1.353(13), 1.353(12); C(104a)–C(104, 105) 1.410(10), 1.415(7); C(104a)–C(108a) 1.436(6); C(108a)–C(101, 108) 1.439(11), 1.440(11) Å. Angles C(108a)–C(101)–C(102), C(108a)–C(108)–C(107) 119.2(6), 119.4(6); C(101)–C(102)–C(103), C(106)–C(107)–C(108) 122.8(7), 122.5(7); C(102)–C(103)–C(104), C(105)–C(106)–C(107) 119.0(5), 119.4(4); C(104a)–C(104)–C(103), C(104a)–C(105)–C(106) 121.2(8), 121.0(5); C(108a)–C(104a)–C(104, 105) 120.6(6), 120.5(6); C(104a)–C(108a)–C(101, 108) 116.8(2), 116.9(5); C(101)–C(108a)–C(108) 126.4(6); C(104)–C(104a)–C(105) 118.9(12)°.

[a] For P(1,2) read P(3,4).

[b] Ref. [1].

clusters, no doubt because of the more easily cleaved P–Ph bonds in dppn. Studies of similar reactions with 1,8-bis(dimethylphosphino)naphthalene are directed to the incorporation of the naphthyl group on the cluster and will be reported elsewhere.

4. Experimental

4.1. General experimental conditions

All reactions were carried out under dry, high purity nitrogen using standard Schlenk techniques. Common solvents were dried, distilled under argon and degassed before use.

4.2. Instrumentation

Infrared spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Spectra in CH_2Cl_2 were obtained using a solution cell of 0.5 mm path-length with NaCl windows. NMR spectra were recorded on Bruker AM300WB or ACP300 (^1H at 300.13 MHz, ^{31}P NMR at 121.50 MHz) or 600 Unity Nova (^1H at 599.92 MHz) instruments. Samples were dissolved in $CDCl_3$ and contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethysilane. Mass spectra were recorded on a VG Platform 2 instrument. Solutions were infused directly into the instrument. Chemical aids to ionisation were used as required [17]. Elemental analyses were performed at the Centre for Micro-analytical Services (CMAS), Belmont, Vic.

4.3. Reagents

$Ru_3(CO)_{12}$ [18], $Ru_3(\mu\text{-dppm})(CO)_{10}$ [19] and dppn [1,20] were prepared by the cited methods.

4.4. Reaction of $Ru_3(CO)_{12}$ with dppn in thf

A mixture of $Ru_3(CO)_{12}$ (40 mg, 0.063 mmol) and dppn (31 mg, 0.062 mmol) in thf (12 ml) was heated at

Table 6
Crystal data and refinement details

	Compound				
	1	**2**	**3**	**4**	**5**
Formula	$C_{42}H_{26}O_8P_2Ru_3 \cdot CH_2Cl_2$	$C_{44}H_{26}O_{10}P_2Ru_4$	$C_{45}H_{26}O_{11}P_2Ru_4 \cdot CH_2Cl_2$	$C_{38}H_{20}O_{10}P_2Ru_4$	$C_{67}H_{48}O_8P_4Ru_3 \cdot CH_2Cl_2$
MW	1108.75	1180.91	1293.85	1102.80	1493.15
Crystal system	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	*Pccn*	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	10.3090(9)	11.495(2)	17.547(1)	19.034(2)	12.679(2)
b (Å)	13.954(1)	35.788(5)	13.457(8)	9.533(1)	25.824(3)
c (Å)	15.020(1)	19.517(3)	19.198(1)	21.455(2)	18.863(2)
α (°)	86.355(2)				
β (°)	85.653(2)		91.984(2)	113.273(3)	95.237(3)
γ (°)	85.104(2)				
V (Å^3)	2143	8029	4531	3576	6150
Z	2	8	4	4	4
D_c (g cm^{-3})	1.71_7	1.95_4	1.89_7	2.04_8	1.61_2
μ (mm^{-1})	1.29	1.62	1.56	1.81	0.98
Crystal size (mm)	0.24 × 0.22 × 0.09	0.25 × 0.22 × 0.11	0.30 × 0.24 × 0.16	0.44 × 0.28 × 0.26	0.38 × 0.14 × 0.12
‘T’$_{min/max}$	0.85	0.80	0.81	0.81	0.90
$2\theta_{max}$ (°)	70	55	65	75	58
N_{tot}	39,584	80,360	73,008	47,439	74,744
N (R_{int})	18,766 (0.033)	9234 (0.075)	16,507 (0.047)	18,805 (0.037)	16,165 (0.067)
N_o	9216	7090	12,637	14,254	12,085
R	0.039	0.043	0.042	0.040	0.047
R_w	0.052	0.054	0.045	0.048	0.064

reflux point for 5.5 h. After evaporation to dryness (rotary evaporator), preparative t.l.c. (acetone/hexane, 3/7) separated three major products. Band 1 (orange, R_f 0.56) afforded $Ru_3(\mu\text{-}H)\{\mu_3\text{-}Ph_2P(nap)PPhC_6H_4\}(CO)_8$ (**1**) (16.4 mg, 26%) as red crystals from CH_2Cl_2/hexane. *Anal.* Calc. $C_{42}H_{26}O_8P_2Ru_3$: C, 49.27; H, 2.56. Found: C, 49.30; H, 2.60%. *M*, 1025. IR (CH_2Cl_2): ν(CO) 2063s, 2023vs, 2003s, 1992(sh), 1966m, 1948(sh) cm^{-1}. ^{1}H NMR: δ-17.11 [d of d, 1H, *J*(PH) 20.4, 12.9 Hz, Ru–H], 6.36–8.03 (m, 25H, Ph + nap + C_6H_4). ES-MS (positive ion, MeOH, *m/z*): 1025, [M]$^+$; (+ve ion, MeOH + NaOMe, *m/z*): 1048, [M + Na]$^+$; (negative ion, MeOH + NaOMe): 1056, [M + OMe]$^-$. Band 2 (orange–yellow, R_f 0.50) afforded $Ru_4(\mu\text{-}H)(\mu_3\text{-}C_6H_4)\{\mu\text{-}Ph_2P(nap)PPh\}(CO)_{11} \cdot CH_2Cl_2$ (**3**) as bright orange crystals (9.1 mg, 12%) from CH_2Cl_2/MeOH. *Anal.* Calc. $C_{45}H_{26}O_{11}P_2Ru_4 \cdot CH_2Cl_2$: C, 42.70; H, 2.18. Found: C, 42.67; H, 2.20%. *M*, 1210. IR (CH_2Cl_2): ν(CO) 2082w, 2057m, 2029vs, 2014m, 1993w, 1983m, 1977(sh), 1929w cm^{-1}. ^{1}H NMR: δ-21.26 [d of d, 1H, *J*(PH) 12.3, 1.8 Hz, RuH), 5.30 (s, 2H, CH_2Cl_2), 6.26–8.07 (m, 25H, Ph + nap + C_6H_4). ES-MS (positive ion, MeOH + NaOMe, *m/z*): 1233, [M + Na]$^+$; 1210, M$^+$; 1177, [M + Na−2CO]$^+$; 1154, [M−2CO]$^+$. Band 3 (brown, R_f 0.42) contained $Ru_4(\mu\text{-}H)\{\mu_3\text{-}Ph_2P(nap)PPh(C_6H_4)\}(\mu\text{-}CO)_3(CO)_7$ (**2**) (7.0 mg, 10%) as dark brown–black crystals from CH_2Cl_2/MeOH. *Anal.* Calc. $C_{44}H_{26}O_{10}P_2Ru_4$: C, 44.75; H, 2.20. Found: C, 44.62; H 2.15%. *M*, 1182. IR (CH_2Cl_2): ν(CO) 2062m, 2025vs, 2001vs, 1989(sh), 1959w, 1939w, 1769w (br) cm^{-1}. ^{1}H NMR: δ-17.57 [d of d, 1H, *J*(PH) 22.8, 8.7 Hz, Ru–H], 6.16–8.05 (m, 25H, Ph + nap + C_6H_4). ES-MS (positive ion, MeOH, *m/z*): 1182, M$^+$; (+ve ion, MeOH + NaOMe, *m/z*): 1205, [M + Na]$^+$; (negative ion, MeOH, *m/z*): 1212, [M + OMe]$^-$. Other bands contained trace amounts of unidentified products.

4.5. Reaction of $Ru_3(CO)_{12}$ with dppn in toluene

Preparative t.l.c. (acetone/hexane, 1/2) of a similar reaction between $Ru_3(CO)_{12}$ (50 mg, 0.078 mmol) and dppn (39 mg, 0.079 mmol) in refluxing toluene (18 ml) gave an orange band at R_f 0.72 which was crystallized from CH_2Cl_2/hexane to give orange–brown crystals of $Ru_4\{\mu_4\text{-}P(nap)PPh_2\}(\mu_4\text{-}C_6H_4)(\mu\text{-}CO)(CO)_9$ (**4**) (4.2 mg, 5%). The small amount of this complex precluded an elemental analysis and it was characterised by the X-ray study. IR ν(CO) (CH_2Cl_2) 2073s, 2036vs, 2014vs, 1981m, 1877w(br), 1771w(br) cm^{-1}. ES-MS (positive ion, MeOH + NaOMe, *m/z*): 1127, [M + Na]$^+$ ($C_{38}H_{20}O_{10}P_2Ru_4$ Calc.: *M*, 1104).

4.6. Reaction of $Ru_3(\mu\text{-}dppm)(CO)_{10}$ with dppn

A mixture of $Ru_3(\mu\text{-}dppm)(CO)_{10}$ (80 mg, 0.083 mmol) and dppn (41 mg, 0.083 mmol) in thf (16 ml) was heated at reflux for 6.5 h. After evaporation to dryness preparative t.l.c. (acetone/hexane, 1/2) showed a number of bands. Band 1 (red, R_f 0.32) was crystallised from CH_2Cl_2/hexane to give $Ru_3(\mu\text{-}dppm)(CO)_8(dppn) \cdot CH_2Cl_2$ (**5**) (10 mg, 9%) as red needles. Drying under vacuum removed the CH_2Cl_2 from the analytical sample. *Anal.* Calc. $C_{67}H_{48}O_8P_4Ru_3$: C, 57.15; H, 3.44. Found: C, 56.70; H, 3.57%. *M*, 1409. IR (CH_2Cl_2): ν(CO) 2028vw, 1979vs, 1953vs (br), 1932(sh), 1903 (sh) cm^{-1}. ^1H NMR: δ 4.04 [t, 2H, *J*(PH) 10Hz, CH_2], 6.98–7.40 and 7.97–7.99 (m, 46H, Ph + nap). ^{31}P NMR: δ 15.98 (s, dppm), 35.97 (s, dppn). ES-MS (positive ion, MeOH, *m/z*): 1409, M^+.

Bands 2 (orange–yellow, R_f 0.47) and 3 (pale orange, R_f 0.57) contained $Ru_3(\mu\text{-dppm})(CO)_{10}$ (23.6 mg, 29.5%) and $Ru_3\{\mu_3\text{-PPhCH}_2\text{PPh}(C_6H_4)\}(CO)_9$ (1.6 mg, 2%), respectively, both identified by comparison of their ν(CO) IR spectrum (cyclohexane) with those of authentic samples.

4.7. Structure determinations

Full spheres of diffraction data were measured at ≈153 K using a Bruker AXS CCD area-detector instrument. N_{tot} reflections were merged to *N* unique (R_{int} cited) after “empirical”/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being used in the full matrix least squares refinements. All data were measured using monochromatic Mo Kα radiation, $\lambda = 0.71073$ Å. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, $(x,y,z,U_{iso})_H$ being constrained at estimates. Conventional residuals *R*, R_w on $|F|$ are quoted [weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$]. Neutral atom complex scattering factors were used; computation used the XTAL 3.7 program system [21]. Pertinent results are given in the figures (which show non-hydrogen atoms with 50% probability amplitude displacement ellipsoids and hydrogen atoms with arbitrary radii of 0.1 Å) and tables.

4.8. Variata

1–**3**. The cluster-bound hydrogens were located and refined in (x,y,z,U_{iso}). The solvent molecules in **1** and **3** were modelled as disordered over two sites, occupancies set at 0.5 after trial refinement, with constrained geometries.

4. All hydrogen atoms were refined in (x,y,z,U_{iso}).

4.9. Supplementary material

Full details of the structure determinations of complexes 1–5 (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre as CCDC 219944-219948, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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