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Cluster chemistry

LXXV. * Tetra-, penta- and hepta-nuclear clusters derived from $\{\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{11}\}_2(\mu\text{-dppa})$ [$\text{dppa} = \text{C}_2(\text{PPh}_2)_2$]:
 X-ray structures of $\text{Ru}_4(\mu\text{-H})[\mu_3\text{-HC}_2\text{PPh}_2]\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{11}$] $(\mu\text{-PPh}_2)(\mu\text{-CO})(\text{CO})_9$
 and $\text{Ru}_7(\mu\text{-H})_3(\mu_5\text{-HC}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_{16}$

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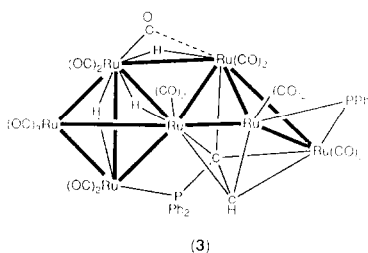
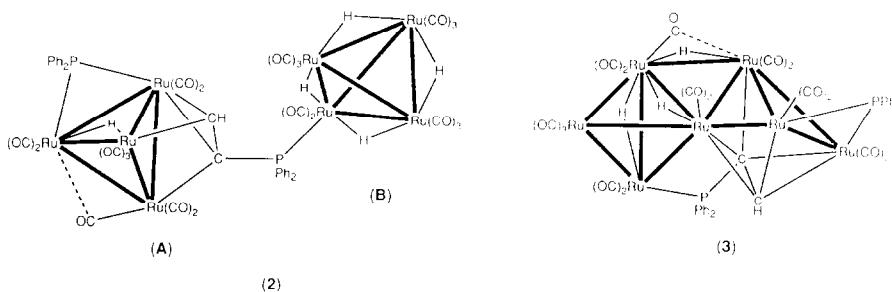
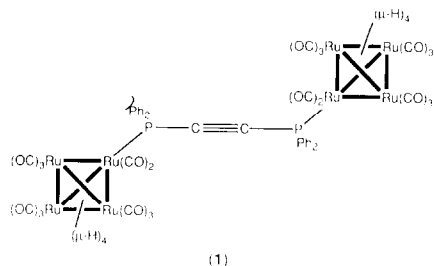
Abstract

The reaction between $\text{C}_2(\text{PPh}_2)_2$ and $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$ gave $\{\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{11}\}_2(\mu\text{-C}_2(\text{PPh}_2)_2)$ (**1**), which on heating formed initially the hydrido- μ_3 -alkyne bis- Ru_4 cluster $\text{Ru}_4(\mu\text{-H})[\mu_3\text{-HC}_2\text{PPh}_2(\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{11})](\mu\text{-PPh}_2)(\mu\text{-CO})(\text{CO})_9$ (**2**) (by cleavage of a P-C(sp) bond in **1** and addition of one cluster H atom to the resulting acetylide), followed by the novel Ru_7 cluster $\text{Ru}_7(\mu\text{-H})_3(\mu_5\text{-HC}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_{16}$ (**3**). The core in **3** has a new geometry, consisting of an Ru_4 tetrahedron sharing an apical Ru atom with a C_2Ru_4 octahedron; there is a further peripheral Ru-Ru interaction linking the two cluster components. By conventional electron counting, **3** is a 108 CVE cluster. Two other minor products isolated from the reaction were $\text{Ru}_5(\mu_4\text{-PPh})(\text{CO})_{15-3n}(\eta\text{-C}_6\text{H}_5\text{Me})_n$ ($n = 0$ and 1).

Introduction

The possibility of using the bis-tertiary phosphine $\text{C}_2(\text{PPh}_2)_2$ (dppa) to synthesise medium-sized cluster complexes was first demonstrated several years ago [2,3]. Coordination of cluster carbonyls to each end of this non-chelating bidentate ligand afforded complexes such as $\{\text{M}_3(\text{CO})_{11}\}_2(\mu\text{-dppa})$ ($\text{M} = \text{Ru}$ [2], Os [4,5]), thermolysis of which resulted in cluster condensation involving cleavage of a

* For Part LXXIV see ref. 1.



P-C(*sp*) bond and coordination of the C≡C triple bond. In this way, the pentanuclear complexes $M_5(\mu_5-C_2PPh_2)(\mu-PPh_2)(CO)_{13}$ were obtained in good to excellent yields ($M = Ru$, 80% [2,3]; $M = Os$, 50% [4]; $M_5 = Os_3Ru_2$, 60% [6]). The chemistry of these interesting complexes is now being explored [7]. This principle of cluster build-up can be applied to other systems and this paper describes the synthesis and characterisation of complexes derived from $Ru_4(\mu-H)_4(CO)_{12}$.

Results

The complex $\{Ru_4(\mu-H)_4(CO)_{11}\}_2(\mu-dppa)$ (**1**) was obtained from the reaction between dppa and two equivalents of either $Ru_4(\mu-H)_4(CO)_{12}$ or $Ru_4(\mu-H)_4(CO)_{11}(NCMe)$ in dichloromethane. In the former case, two equivalents of Me_3NO were added to the solution; both reactions occurred at or below room temperature. Complex **1** was obtained as yellow crystals in about 38% yield from both reactions. It was easily characterised from its IR spectrum, its FAB mass spectrum and by the highfield resonance in the 1H NMR spectra, which was found at $\delta -17.36$ as a doublet ($J(HP) = 6.2$ Hz); as with other complexes of this type, the cluster-bound H atoms are fluxional.

A toluene solution of **1** was heated at $90^\circ C$ for 1.5 h under N_2 flush and gave four major bands when separated by preparative TLC. These were identified as $Ru_4(\mu-H)(\mu_3-HC_2PPh_2[\mu_4(\mu-H)_4(CO)_{11}])(\mu-PPh_2)(\mu-CO)(CO)_9$ (**2**), $Ru_7(\mu-H)_3(\mu_5-HC_2PPh_2)(\mu-PPh_2)(CO)_{16}$ (**3**), $Ru_5(\mu_4-PPh)(CO)_{15}$ (**4**) and $Ru_5(\mu_4-PPh)(CO)_{12}(\eta-PhMe)$ (**5**) by X-ray crystallographic studies. Because of experimental difficulties, the quality of the present X-ray structure determinations has not permitted location and refinement of core hydrogen atoms and the presence and

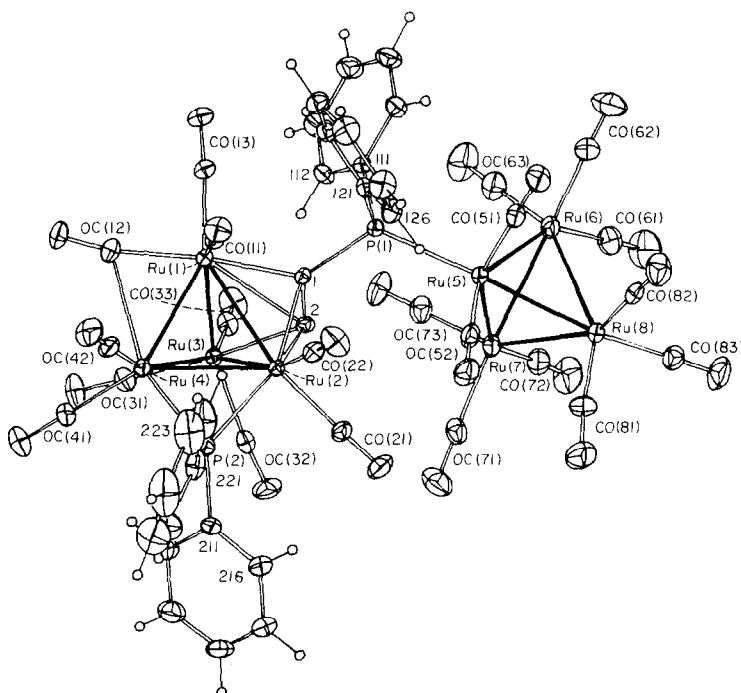
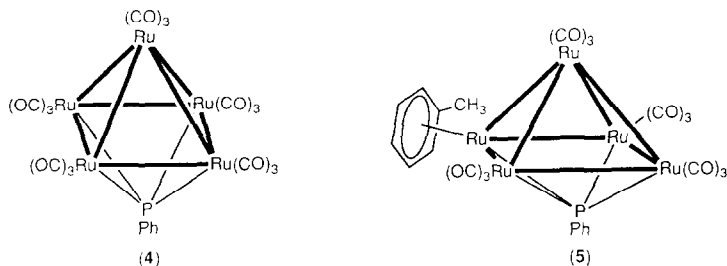


Fig. 1. ORTEP plot of a molecule of $Ru_4(\mu-H)[\mu_3-C_2PPh_2\{Ru_4(\mu-H)_4(CO)_{11}\}](\mu-PPh_2)(CO)_{10}$ (**2**), showing atom numbering scheme. Non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

disposition of the latter must be inferred from other techniques. Complexes **4** and **5** have been obtained on previous occasions and their crystal structures determined [8,9], and so this paper does not include any discussion of their molecular structures.



*Structure of $Ru_4(\mu-H)\{\mu_3-HC_2PPh_2[Ru_4(\mu-H)_4(CO)_{11}]\}(\mu-PPh_2)(\mu-CO)(CO)_9$ (**2**)*

A molecule of **2** is shown in Fig. 1 and selected bond distances are collected in Table 1. Two tetrahedral Ru_4 clusters are linked by a HC_2PPh_2 ligand which is attached to one cluster (**A**) by the alkyne unit bridging a triangular face and to the second cluster (**B**) by a normal *P*-donor interaction. Cluster **A** contains one H atom, which gives a singlet at $\delta -17.98$ in the 1H NMR spectrum, and ten CO groups, one of which semibriges the Ru(1)–Ru(4) vector [Ru(1)–C(12) 1.968(9),

Table 1

Selected bond parameters for **2**

Ru(1)–Ru(2)	2.814(1)	Ru(1)–Ru(3)	2.882(1)
Ru(1)–Ru(4)	2.724(1)	Ru(2)–Ru(3)	2.807(1)
Ru(2)–Ru(4)	2.813(1)	Ru(3)–Ru(4)	2.918(1)
Ru(5)–Ru(6)	2.949(1)	Ru(5)–Ru(7)	2.979(1)
Ru(5)–Ru(8)	2.785(1)	Ru(6)–Ru(7)	2.789(1)
Ru(6)–Ru(8)	2.960(1)	Ru(7)–Ru(8)	2.939(1)
Ru(2)–P(2)	2.324(2)	Ru(4)–P(2)	2.226(2)
Ru(5)–P(1)	2.392(2)	Ru(1)–C(1)	2.125(8)
Ru(2)–C(2)	2.185(7)	Ru(2)–C(1)	2.228(6)
Ru(3)–C(2)	2.104(7)	P(1)–C(1)	1.837(6)
C(1)–C(2)	1.393(9)	Ru(1)–C(12)	1.968(9)
Ru(4)–C(12)	2.610(8)		
Ru–CO	range 1.832–1.956(9), av. 1.892 Å		
C–O	range 1.12–1.16(1), av. 1.14 Å		
P–C(Ph)	range 1.80(1)–1.832(7), av. 1.817 Å		
Ru–C–O	range 170.3(7)–180(1), av. 176.6°		

Ru(4)–C(12) 2.610(8) Å; Ru(1)–C(12)–O(12) 165.1(7)°]. The Ru(2)–Ru(4) vector is bridged by the PPh₂ group [Ru(2)–P(2) 2.324(2), Ru(4)–P(2) 2.226(2) Å]. The Ru–Ru separations range between 2.724(1) and 2.918(1) Å, the shortest being semi-bridged by CO(12) and the longest being bridged by the remaining metal-bonded H atom. The Ru(1)–Ru(2)–Ru(3) face is capped by the alkyne, which is π -bonded to Ru(2) [Ru(2)–C(1) 2.228(6), Ru(2)–C(2) 2.185(7) Å] and σ -bonded to Ru(1) and Ru(3) [Ru(1)–C(1) 2.125(8), Ru(3)–C(2) 2.104(7) Å]. The Ru₃ face forms an equilateral triangle with one long [Ru(1)–Ru(3) 2.882(1) Å] and two short edges [Ru(1)–Ru(2) 2.814(1), Ru(2)–Ru(3) 2.807(1) Å]. The C(1)–C(2) separation is 1.393(9) Å. The \equiv CH resonance occurs at δ 10.56 ($J(\text{HP}) = 17.6$ Hz).

Cluster **B** contains four H atoms and 11 CO ligands and is similar to other derivatives of Ru₄(μ -H)₄(CO)₁₂ containing a tertiary phosphine. The cluster-bound H atoms give rise to a broad resonance between δ –16.9 and –17.5. Within the cluster, the usual pattern of two short [2.785, 2.789(1) Å] and four long [2.939–2.979(1) Å] Ru–Ru separations is found; the latter are bridged by the four hydrogen atoms so that the Ru₄H₄ cluster has C_{2*v*} symmetry. A similar arrangement has been found in other substituted derivatives such as Ru₄(μ -H)₄(CO)_{12–*n*}(L)_{*n*} ($n = 1$, L = P(OMe)₃ [10]; $n = 2$, L = PPh₃ [11,12], L₂ = dpmm [13–15], dppe [16,17]). In **2**, each Ru₄ cluster is electron-precise with a 60-valence electron count.

Structure of Ru₇(μ -H)₃(μ -HC₂PPh₂)(μ -PPh₂)(CO)₁₆ (**3**)

The molecular structure of **3** is shown in Fig. 2; important bond distances are given in Table 2. In this case, cluster condensation has occurred to give a novel nine-atom C₂Ru₇ cluster consisting of an Ru₄ tetrahedron sharing an apical atom of an octahedron formed from an Ru₄ butterfly and two C atoms of a μ ₄-alkyne ligand; an additional bond is formed between a second Ru atom of the tetrahedron and a hinge atom of the butterfly. The Ru–Ru distances range from 2.695(2) to

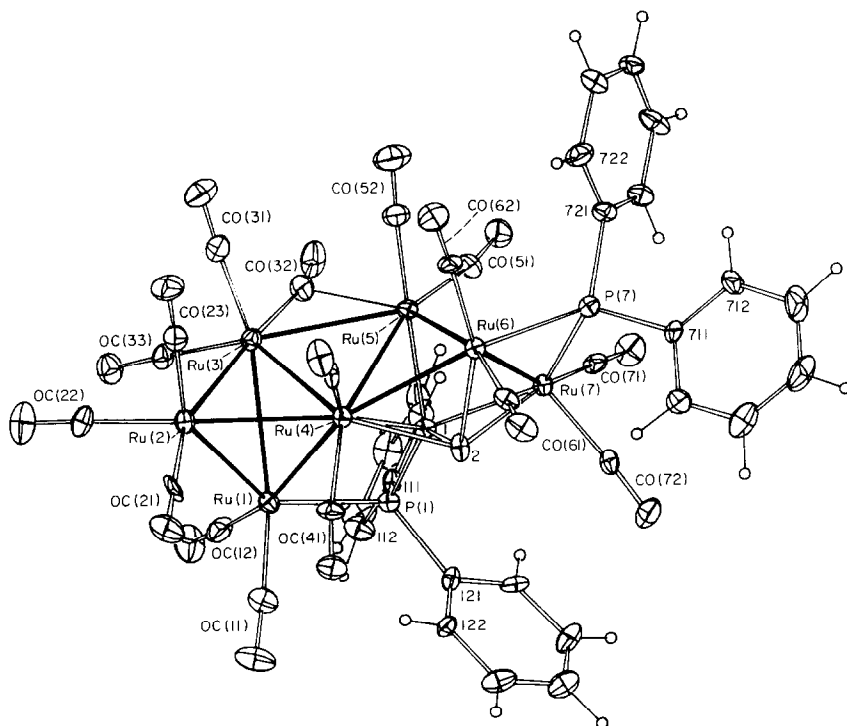


Fig. 2. ORTEP plot of a molecule of $\text{Ru}_7(\mu\text{-H})_3(\mu_5\text{-HC}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_{16}$ (**3**), showing atom numbering scheme. Non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

2.959(2) Å. The shortest is bridged by the PPh_2 group [Ru(6)–P(7) 2.305(4), Ru(7)–P(7) 2.270(4) Å]; three Ru–Ru separations within the butterfly, including the hinge, are essentially equal [2.774–2.793(2) Å], while the fourth is somewhat

Table 2

Selected bond parameters for **3**

Ru(1)–Ru(2)	2.876(2)	Ru(1)–Ru(3)	2.959(2)
Ru(1)–Ru(4)	2.832(2)	Ru(2)–Ru(3)	2.746(2)
Ru(2)–Ru(4)	2.854(2)	Ru(3)–Ru(4)	2.911(2)
Ru(3)–Ru(5)	2.884(2)	Ru(4)–Ru(5)	2.845(2)
Ru(4)–Ru(6)	2.793(2)	Ru(5)–Ru(6)	2.778(2)
Ru(5)–Ru(7)	2.774(3)	Ru(6)–Ru(7)	2.695(2)
Ru(1)–P(1)	2.318(4)	Ru(6)–P(7)	2.305(4)
Ru(7)–P(7)	2.270(4)	P(1)–C(1)	1.79(1)
C(1)–C(2)	1.47(2)	Ru(3)–C(32)	1.94(2)
Ru(5)–C(32)	2.56(1)		
Ru–CO	range 1.84–1.91(2), av. 1.88 Å		
C–O	range 1.11–1.17(2), av. 1.15 Å		
P–C(Ph)	range 1.80–1.83(1), av. 1.81 Å		
Ru–C–O	range 169–180(1), av. 175°		

longer [Ru(4)–Ru(5) 2.845(2) Å]. There is no regular pattern of bond lengths within the Ru₄ tetrahedron, which range from 2.746(2) to 2.959(2) Å; there is also an interaction between Ru(3) and Ru(5) [separation 2.884(2) Å], and this vector is semi-bridged by CO(32) [Ru(3)–C(32) 1.94(2), Ru(5)–C(32) 2.56(1) Å].

The phosphino-alkyne is attached via a normal P-donor bond to Ru(1) [Ru(1)–P(1) 2.318(4) Å] and by the C₂H unit [δ 9.85, $J(\text{HP}) = 10.8$ Hz] which is attached to the four Ru atoms Ru(4)–Ru(7) [Ru–C, 2.16–2.32(1), av. 2.22 Å]. The C–C separation is long at 1.47(2) Å. The values are similar to those found in Ru₄(μ_4 -C₂Ph₂)(CO)₁₂ [18].

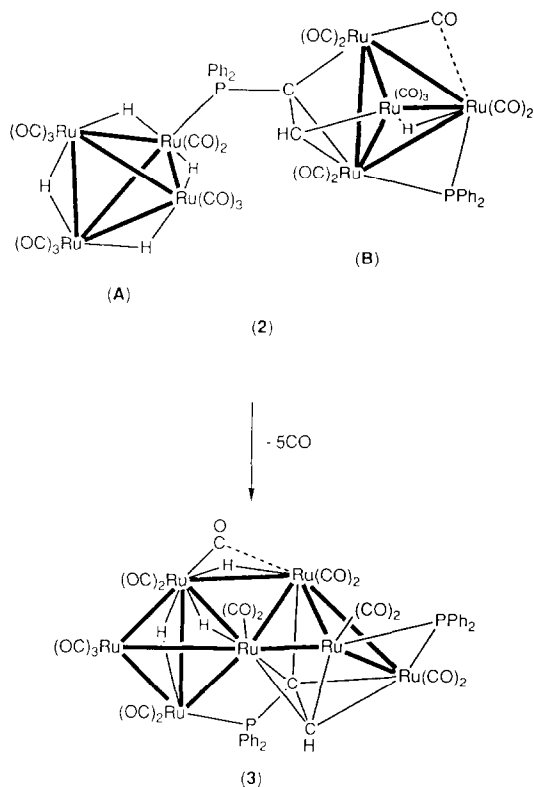
The ¹H NMR spectrum contains three equal intensity Ru–H resonances at δ –12.54 (H_a, d, $J(\text{HP}) = 18.0$ Hz), –17.02 (H_b, d, $J(\text{HP}) = 12.1$ Hz) and –18.74 (H_c, s). None of these cluster-bound H atoms was located in the X-ray structure determination. Applying the usual criterion of lengthening of an H-bridged Ru–Ru bond, two possible locations are Ru(1)–Ru(3) [2.959(2) Å] and Ru(3)–Ru(4) [2.911(2) Å]; the latter is remote from the phosphorus atoms and may be bridged by H_c, and the former by H_a or H_b. The next two longest bonds are Ru(3)–Ru(5) [2.884(2) Å] and Ru(1)–Ru(2) [2.876(2) Å]; the former is semi-bridged by CO(32), so we suggest the third H atom (H_b or H_a) bridges the Ru(1)–Ru(2) vector.

Discussion

The synthesis of **1**, containing an Ru₄(μ -H)₄ cluster attached to each end of the dppa ligand, is straightforward and occasions no special comment. Thermal condensation of the bis-cluster complex afforded two complexes, **2** containing eight Ru atoms, and **3** containing seven Ru atoms. The former is formed by addition of the bisphosphino-acetylene across one Ru₃ face of one of the Ru₄ clusters, to give μ -PPh₂ and μ_3 -C₂PPh₂ groups by cleavage of one of the two C(sp)–P bonds in the coordinated dppa ligand. The phosphino-acetylide group combines with a cluster-bound hydride to give the phosphino-ethyne, as confirmed by observation of the acetylenic proton resonance. A similar transformation has been seen in the hydrogenation of Ru₅(μ_5 -C₂PPh₂)(μ -PPh₂)(CO)₁₃ to Ru₄(μ -H)₃(μ_4 -HC₂PPh₂)(μ -PPh₂)(CO)₁₀ [20]. The second Ru₄ cluster is unchanged, remaining coordinated to the P atom of the phosphino-acetylene.

Further condensation results in elimination of one Ru atom (which is found as Ru₃(CO)₁₂ and Ru₄(μ -H)₄(CO)₁₂) and formation of an Ru₇ cluster, the geometry of which consists of four edge-fused triangles, the end one of which is capped by the seventh Ru atom. The PPh₂ group is attached to the outer edge of the Ru₃ triangle at the other end of the array, while the phosphino-ethyne in **2** has been incorporated into a distorted octahedral C₂Ru₄ cluster. Although it is not possible to label the Ru atoms, a likely route to **3** is further interaction of the acetylene ligand with the second Ru₄ cluster and elimination of the eighth Ru, which is the one not involved in bonding to ligands other than H or CO in **2** (Scheme 1).

There are relatively few Ru₇ clusters known, all of which contain Main Group atoms or ligands as an essential part of the core. The structurally characterised derivatives include Ru₇(μ_4 -PPh₂)₂(CO)_{18–3n}(η^6 -PhMe)_n ($n = 0$ [21], 1 [9]) (two PRu₅ octahedra sharing an Ru₃ triangular face), Ru₇(μ_4 -S)(CO)₂₁ [an octahedral SRu₅ unit with two equatorial edges bridged by Ru(CO)₄ groups] [22], and



Scheme 1

$\text{Ru}_7(\mu_4\text{-S})_2(\text{CO})_{20}$ [a bipyramidal S_2Ru_5 unit, with two Ru–Ru apical-equatorial edges bridged by $\text{Ru}(\text{CO})_4$ units] [23]. In $\text{Ru}_7(\mu_6\text{-H})(\mu\text{-CNMe}_2)(\text{CO})_{19}$, with capped octahedral geometry, the octahedron contains an interstitial H atom [24], while in $\text{Ru}_7(\mu\text{-H})_8(\mu_6\text{-P})(\mu_3\text{-PBu})(\mu\text{-PBu}_2)(\text{CO})_{12}(\text{PBu}_3)_3$, a tricyclo- Ru_6 unit with the boat conformation containing a central P atom has one edge of the central PRu_4 portion bridged by an $\text{Ru}(\text{CO})_3$ group; the resulting Ru_3 triangle is capped by the PBu group [25].

Individual electron counts for the seven metal atoms in **3** leave Ru(1) and Ru(2) electron-deficient unless two hydrogens bridge Ru–Ru vectors involving these atoms, as suggested above. A formal $\text{Ru} \rightarrow \text{Ru}$ donor bond from Ru(4) to Ru(6), together with placement of the third cluster H atom on the Ru(3)–Ru(4) vector allows two of these three Ru atoms to become electronically saturated. The semi-bridging CO(32) also serves to redistribute some electron density within the cluster. However, using Mingos's approach [19], cluster **3** can be considered as an Ru_4 tetrahedron (60 CVE) and a C_2Ru_4 octahedron (66 CVE) sharing the apical Ru(4) atom. The appropriate electron count is thus: $(60 + 66) - 18 = 108$. This count is achieved from: $7\text{Ru}(56) + 2\text{C}(8) + 16\text{CO}(32) + 3\text{H}(3) + \text{PR}_3(2) + \text{PR}_2(3) + 2\text{R}(2) + \text{Ru} - \text{Ru}(2) = 108$, where 2R are the alkyne substituents and Ru–Ru is the further interaction between Ru(3) and Ru(5).

The two minor products, **4** and **5**, contain the familiar octahedral PRu_5 cluster and have been formed by extensive degradation of **1**, resulting in loss of a phenyl

group and the C_2 moiety. Isomerisation of $Ru_5(\mu_5-C_2PPh_2)(\mu-PPh_2)(CO)_{13}$ by migration of PPh to the Ru_5 cluster and concomitant formation of a cluster-bound PhC_2 group has been described [26]; while we have not been able to convert this isomer to **4** (**5** is presumably formed by reaction of **4** with the toluene solvent), it is likely that similar transformations are involved in the formation of these complexes.

Conclusion

Condensation of $\{Ru_4(\mu-H)_4(CO)_{11}\}_2(\mu-dppa)$ (**1**) afforded the bis- Ru_4 cluster **2** by cleavage of one of the $C(sp)-P$ bonds in the dppa ligand and addition of the resulting PPh_2 and C_2PPh_2 groups to one of the Ru_4 clusters. Addition of one cluster H atom to the acetylide carbon gives a $\mu_3-\eta^2-HC_2PPh_2$ ligand. Further condensation resulted in elimination of one Ru atom and formation of **3**, containing an Ru_7 cluster of novel geometry in which an Ru_4 tetrahedron shares an apical Ru atom of a C_2Ru_4 octahedron. The results further illustrate the utility of the acetylenic di-tertiary phosphine dppa in the synthesis of novel cluster complexes.

Experimental

General methods, reaction conditions and instrumentation have been described earlier [27].

Starting materials. $Ru_4(\mu-H)_4(CO)_{12}$ was obtained from $Ru_3(CO)_{12}$ and H_2 [28]; $C_2(PPh_2)_2$ was used as received from Strem Chemicals, Inc. (Newburyport, MA).

Preparation of $Ru_4(\mu-H)_4(CO)_{11}(NCMe)$

A solution of TMNO (30 mg, 0.399 mmol) in MeCN (3 ml) and CH_2Cl_2 (20 ml) was added dropwise over ca. 40 min. to a suspension of $Ru_4(\mu-H)_4(CO)_{12}$ (210 mg, 0.282 mmol) in CH_2Cl_2 (40 ml) and MeCN (5 ml) until no $Ru_4(\mu-H)_4(CO)_{12}$ remained (TLC). After reduction of the solvent volume (to ca. 2 ml MeCN) sufficient CH_2Cl_2 was added to dissolve any precipitated $Ru_4(\mu-H)_4(CO)_{11}(NCMe)$. This solution was purified on a chromatotron (light petroleum/ CH_2Cl_2 /MeCN 20/5/2) to yield a red solution of $Ru_4(\mu-H)_4(CO)_{11}(NCMe)$ [IR: $\nu(CO)$ (5% MeCN in CH_2Cl_2) 2096vw, 2081m, 2066vs, 2058(sh), 2024s, 2008(sh), 1990(sh), 1958vw cm^{-1}].

*Preparation of $\{Ru_4(\mu-H)_4(CO)_{11}\}_2(\mu-dppa)$ (**1**)*

To a solution of $Ru_4(\mu-H)_4(CO)_{11}(NCMe)$ in a mixture of light petroleum, CH_2Cl_2 and MeCN (from $Ru_4(\mu-H)_4(CO)_{12}$ (260 mg, 0.349 mmol)), cooled to $-64^\circ C$, was added dppa (60 mg, 0.15 mmol) in CH_2Cl_2 (20 ml), dropwise over ca. 25 min. After warming to room temperature solvents were removed and the residue purified by preparative TLC (light petroleum/ CH_2Cl_2 3/1). The major product (R_f 0.5) was recrystallised from CH_2Cl_2 /MeOH to yield yellow crystals of $\{Ru_4(\mu-H)_4(CO)_{11}\}_2(\mu-dppa)$ (**1**) (120 mg, 38%). Anal. Found: C, 31.38; H, 1.48%; M (mass spectrometry), 1827. $C_{48}H_{28}O_{22}P_2Ru_8$ calc.: C, 31.55; H, 1.54; M , 1827. IR: $\nu(CO)$ (cyclohexane) 2095m, 2080w, 2070vs, 2059s, 2029s, 2014(sh), 2010s, 2000(sh), 1995(sh), 1969w cm^{-1} . 1H NMR: $\delta(CDCl_3)$ -17.36 (8H, d, $J(HP)$ 6.2 Hz, Ru-H), 7.40–7.70 (20H, m, Ph). FAB MS (m/z): 1827, $[M]^+$.

Alternatively, a solution of Me₃NO (45 mg, 0.60 mmol) in CH₂Cl₂ (20 ml) was added dropwise to a solution of Ru₄(μ-H)₄(CO)₁₂ (400 mg, 0.54 mmol) and dp₂ppa (113 mg, 0.27 mmol) in CH₂Cl₂ (150 ml). Solvent was removed and the residue chromatographed (Florisil column). Light petroleum eluted Ru₄(μ-H)₄(CO)₁₂ (19 mg, 5%). Light petroleum/CH₂Cl₂ (9/1) eluted a yellow band which was recrystallised (CH₂Cl₂/MeOH) to yield {Ru₄(μ-H)₄(CO)₁₁}₂(μ-dppa) (190 mg, 39%).

Pyrolysis of {Ru₄(μ-H)₄(CO)₁₁}₂(μ-dppa)

Nitrogen was bubbled through a solution of {Ru₄(μ-H)₄(CO)₁₁}₂(μ-dppa) (75 mg, 0.041 mmol) in toluene (40 ml) at 90 °C for 1.5 h. The solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 5/1). Four major bands were collected; a green band (*R_f* 0.6) was recrystallised (CH₂Cl₂/MeOH) to yield Ru₅(μ₄-PPh)(CO)₁₅ (**4**) (5 mg, 12%), m.p. > 300 °C (dec.). Anal. Found: C, 24.33; H, 0.45%; [M + H]⁺, 1035. C₂₁H₅O₁₅PRu₅ calc.: C, 24.40; H, 0.49%; M, 1034. IR: ν(CO) (cyclohexane) 2094vw, 2056vs, 2032s, 2009vw, 1992w cm⁻¹ (lit. [8]: ν(CO) (toluene) 2095w, 2056s, 2030s cm⁻¹). FAB MS (*m/z*): 1035, [M + H]⁺; 1006–614 ([M - *n*CO]⁺, *n* = 1–8, 15). A red band (*R_f* 0.5) was recrystallised (CH₂Cl₂/MeOH) to yield Ru₄(μ-H)(μ₃-HC₂PPh₂[Ru₄(μ-H)₄(CO)₁₁])(μ-PPh₂)(μ-CO)(CO)₉ (**2**) (12 mg, 16%), m.p. 152–153 °C (dec.). This complex is unstable on the TLC plate, the IR spectrum of the crude mixture indicating that it is present in much larger amount; however, we were unable to find a satisfactory method of separating **2** in higher yield. Anal. Found: C, 31.21; H, 1.53%; M (mass spectrometry), 1799. C₄₇H₂₈O₂₁P₂Ru₈ calc.: C, 31.38; H, 1.54%; M, 1799. IR:

Table 3

Crystal data and refinement details for **2** and **3**

	2	3
Formula	C ₄₇ H ₂₈ O ₂₁ P ₂ Ru ₈	C ₄₂ H ₂₃ O ₁₀ P ₂ Ru ₇ ·0.78CH ₂ Cl ₂
M.W.	1799	1525
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$; No. 2	<i>P</i> 2 ₁ /c; No. 14
<i>a</i> , Å	18.967(5)	15.357(4)
<i>b</i> , Å	14.964(3)	13.639(11)
<i>c</i> , Å	11.279(2)	24.815(9)
α, deg.	107.36(2)	–
β, deg.	101.58(2)	104.97(1)
γ, deg.	102.43(2)	–
<i>U</i> , Å ³	2861	5021
<i>Z</i>	2	4
<i>D_c</i> , g cm ⁻³	2.08	2.02
<i>F</i> (000)	1720	2906.4
Crystal size, mm	0.07 × 0.26 × 0.20	0.05 × 0.20 × 0.15
<i>A</i> * (min, max)	1.13, 1.57	1.23, 1.30
μ, cm ⁻¹	19.8	20.5
2 θ _{max} , deg.	60	50
<i>N</i>	10041	8833
<i>N_o</i>	7763	4800
<i>R</i>	0.038	0.051
<i>R_w</i>	0.043	0.049

$\nu(\text{CO})$ (cyclohexane) 2094m, 2079w, 2066w, 2057(sh), 2036m, 2024(sh), 2019s, 2012m, 2007(sh), 1992m, 1986(sh), 1963(sh), 1957m cm^{-1} . $^1\text{H NMR}$: $\delta(\text{CDCl}_3)$ – 17.98 (1H, s Ru–H), – 17.54 (4H, m (br), Ru–H), 7.38–7.67 (20H, m, Ph), 10.56 (1H, d $J(\text{HP})$ 17.6 Hz, CCH). FAB MS (m/z): 1799, $[\text{M}]^+$; 1771–1211 ($[\text{M} - n\text{CO}]^+$, $n = 1, 4-13$); 1134 $[\text{M} - 21\text{CO} - \text{Ph}]^+$. A black band (R_f 0.35) was recrystallised ($\text{CH}_2\text{Cl}_2/\text{MeOH}$) to yield $\text{Ru}_7(\mu\text{-H})_3(\mu_3\text{-HC}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_{16}$

Table 4

Non-hydrogen atomic coordinates and equivalent isotropic thermal parameters for **2**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}} (\text{\AA}^2)$
Ru(1)	0.85092(3)	0.55141(4)	0.59148(5)	0.0324(2)
Ru(2)	0.75178(3)	0.57583(4)	0.38986(5)	0.0325(2)
Ru(3)	0.69024(3)	0.47220(4)	0.53371(5)	0.0350(2)
Ru(4)	0.77938(3)	0.39506(4)	0.36775(5)	0.0391(3)
Ru(5)	0.76475(3)	0.90201(4)	0.62900(6)	0.0363(2)
Ru(6)	0.71511(4)	1.00545(5)	0.84869(6)	0.0518(3)
Ru(7)	0.60990(4)	0.84066(5)	0.65387(7)	0.0499(3)
Ru(8)	0.66739(4)	1.01157(4)	0.58548(6)	0.0464(3)
C(11)	0.9286(4)	0.5982(5)	0.5224(7)	0.044(3)
O(11)	0.9744(3)	0.6213(4)	0.4780(6)	0.067(3)
C(12)	0.8771(4)	0.4304(6)	0.5876(8)	0.051(4)
O(12)	0.8956(3)	0.3700(4)	0.6136(5)	0.065(3)
C(13)	0.9120(4)	0.6070(5)	0.7708(7)	0.045(3)
O(13)	0.9507(3)	0.6347(4)	0.8718(5)	0.068(3)
C(21)	0.6715(5)	0.6156(6)	0.3155(7)	0.054(4)
O(21)	0.6227(4)	0.6395(5)	0.2749(6)	0.089(4)
C(22)	0.8170(5)	0.6547(6)	0.3301(7)	0.053(4)
O(22)	0.8573(4)	0.7021(4)	0.2977(6)	0.080(3)
C(31)	0.6742(5)	0.3325(6)	0.5024(8)	0.056(4)
O(31)	0.6602(4)	0.2542(4)	0.4979(7)	0.086(4)
C(32)	0.5930(5)	0.4522(5)	0.4235(8)	0.055(4)
O(32)	0.5353(3)	0.4454(5)	0.3662(6)	0.077(3)
C(33)	0.6580(4)	0.4949(5)	0.6881(8)	0.052(4)
O(33)	0.6403(4)	0.5063(5)	0.7802(6)	0.084(3)
C(41)	0.7430(5)	0.2581(6)	0.2944(8)	0.060(4)
O(41)	0.7225(4)	0.1756(4)	0.2509(7)	0.094(4)
C(42)	0.8617(5)	0.3834(6)	0.3078(7)	0.058(4)
O(42)	0.9143(4)	0.3787(5)	0.2739(6)	0.083(3)
C(51)	0.8514(4)	1.0048(6)	0.6710(8)	0.051(4)
O(51)	0.9050(3)	1.0685(4)	0.7002(7)	0.081(3)
C(52)	0.7571(5)	0.8614(6)	0.4516(8)	0.057(4)
O(52)	0.7526(4)	0.8400(5)	0.3447(5)	0.084(4)
C(61)	0.6438(6)	1.0612(7)	0.911(1)	0.087(5)
O(61)	0.6001(5)	1.0929(7)	0.9475(9)	0.148(6)
C(62)	0.8015(6)	1.1167(7)	0.9466(9)	0.086(5)
O(62)	0.8519(5)	1.1819(6)	1.0033(8)	0.144(5)
C(63)	0.7228(6)	0.9453(7)	0.9751(9)	0.076(5)
O(63)	0.7242(5)	0.9120(6)	1.0521(7)	0.120(5)
C(71)	0.5433(5)	0.7357(6)	0.5006(9)	0.062(4)
O(71)	0.5008(4)	0.6746(5)	0.4148(7)	0.101(4)
C(72)	0.5328(5)	0.8759(7)	0.719(1)	0.076(5)
O(72)	0.4818(4)	0.8951(6)	0.7512(8)	0.112(5)
C(73)	0.6248(5)	0.7616(7)	0.7552(9)	0.068(4)

Table 4 (continued)

Atom	x	y	z	U_{eq} (Å ²)
O(73)	0.6329(4)	0.7136(5)	0.8149(7)	0.091(4)
C(81)	0.6379(5)	0.9546(6)	0.4037(7)	0.057(4)
O(81)	0.6125(5)	0.9232(6)	0.2935(7)	0.126(5)
C(82)	0.7444(5)	1.1064(6)	0.5794(9)	0.068(4)
O(82)	0.7944(4)	1.1651(5)	0.5702(7)	0.094(4)
C(83)	0.6002(5)	1.0883(6)	0.5995(9)	0.064(4)
O(83)	0.5573(4)	1.1324(5)	0.6133(8)	0.103(4)
P(1)	0.8369(1)	0.7986(1)	0.6798(2)	0.0328(7)
C(111)	0.8552(4)	0.8122(5)	0.8509(6)	0.036(3)
C(112)	0.8166(4)	0.7417(5)	0.8902(7)	0.044(3)
C(113)	0.8292(5)	0.7559(6)	1.0203(8)	0.064(4)
C(114)	0.8801(6)	0.8402(7)	1.1122(8)	0.072(4)
C(115)	0.9179(5)	0.9104(6)	1.0744(7)	0.064(4)
C(116)	0.9051(4)	0.8980(5)	0.9448(7)	0.050(3)
C(121)	0.9310(4)	0.8289(5)	0.6582(7)	0.039(3)
C(122)	0.9943(4)	0.8193(5)	0.7380(7)	0.048(3)
C(123)	1.0637(4)	0.8403(6)	0.7147(8)	0.059(4)
C(124)	1.0716(5)	0.8719(7)	0.613(1)	0.075(5)
C(125)	1.0109(5)	0.8810(7)	0.5356(9)	0.074(5)
C(126)	0.9427(5)	0.8617(6)	0.5600(8)	0.052(4)
C(1)	0.7991(4)	0.6649(5)	0.6005(6)	0.033(3)
C(2)	0.7217(4)	0.6237(5)	0.5707(6)	0.034(3)
P(2)	0.7207(1)	0.4348(1)	0.2081(2)	0.0443(8)
C(211)	0.6226(5)	0.3779(6)	0.1172(7)	0.056(4)
C(212)	0.5797(5)	0.2929(6)	0.1214(8)	0.063(4)
C(213)	0.5059(5)	0.2513(7)	0.0461(9)	0.082(5)
C(214)	0.4755(6)	0.2938(8)	-0.033(1)	0.101(5)
C(215)	0.5168(7)	0.3793(8)	-0.036(1)	0.112(6)
C(216)	0.5898(6)	0.4214(7)	0.0380(9)	0.084(5)
C(221)	0.7661(5)	0.4266(6)	0.0810(8)	0.062(4)
C(222)	0.8401(7)	0.4809(8)	0.102(1)	0.100(7)
C(223)	0.8762(8)	0.4668(9)	0.008(1)	0.123(8)
C(224)	0.837(1)	0.395(1)	-0.113(1)	0.143(9)
C(225)	0.7679(8)	0.340(1)	-0.135(1)	0.133(9)
C(226)	0.7305(7)	0.3524(7)	-0.0441(9)	0.091(6)

(3) (5 mg, 8%). Anal. Found: C, 32.11; H, 1.84%; $[M + H]^+$, 1555. $C_{42}H_{26}O_{16}P_2Ru_7$ calc.: C, 32.46; H, 1.56%; M , 1554. $\nu(\text{CO})$ (cyclohexane) 2085s, 2047s, 2036vs, 2013s, 1990w, 1970m cm^{-1} . $^1\text{H NMR}$: $\delta(\text{CDCl}_3)$ -18.74 (1H, s, RuH), -17.02 (1H, d, $J(\text{HP})$ 12.0 Hz, Ru-H), -12.54 (1H, d, $J(\text{HP})$ 18.1 Hz, Ru-H), 7.28-7.88 (20H, m, Ph), 9.85 (1H, d, $J(\text{HP})$ 10.8 Hz). FAB MS (m/z): 1555, $[M]^+$; 1499-1107, $[M - n\text{CO}]^+$ ($n = 2-16$); 1030, $[M - 16\text{CO} - \text{Ph}]^+$. A green band (R_f 0.20) was recrystallised ($\text{CH}_2\text{Cl}_2/\text{MeOH}$) to yield $Ru_5(\mu_4\text{-PPh})(\text{CO})_{12}(\eta\text{-PhMe})$ (5) (5 mg, 12%), m.p. > 300 °C (dec.). Anal. Found: M (mass spectrometry), 1043. $C_{38}H_{24}O_{12}P_2Ru_5$ calc.: M , 1043. IR: $\nu(\text{CO})$ (cyclohexane) 2071m, 2034vs, 2013s, 1993m, 1969m, 1949vw cm^{-1} [lit. [9] $\nu(\text{CO})$ (cyclohexane) 2071m, 2035vs, 2012s, 1994w (br), 1975(sh), 1967w (br), cm^{-1}]. FAB MS (m/z): 1043, M^+ ; 1015-707 ($[M - n\text{CO}]^+$, $n = 1-12$). Four other trace bands were not identified.

Crystallography

Unique data sets were measured at *ca.* 295 K within the specified $2\theta_{\max}$ limits using an Enraf–Nonius CAD4 diffractometer ($2\theta/\theta$ scan mode; monochromatic Mo- K_{α} radiation, λ 0.7107₃ Å); N independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered ‘observed’ and used in the full matrix least squares refinement after gaussian absorption correction. Anisotropic thermal parameters

Table 5

Non-hydrogen atomic coordinates and equivalent isotropic thermal parameters for **3**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (Å ²)
Ru(1)	0.74595(7)	0.28952(9)	0.81543(5)	0.0351(6)
Ru(2)	0.61887(8)	0.15761(9)	0.74605(5)	0.0392(6)
Ru(3)	0.77603(7)	0.19079(9)	0.71561(5)	0.0361(6)
Ru(4)	0.64674(7)	0.34960(8)	0.70785(4)	0.0308(6)
Ru(5)	0.79199(7)	0.36980(8)	0.65705(5)	0.0324(6)
Ru(6)	0.63742(7)	0.48295(8)	0.62112(4)	0.0314(6)
Ru(7)	0.79348(7)	0.57106(8)	0.67335(5)	0.0319(6)
C(11)	0.6853(9)	0.332(1)	0.8682(6)	0.06(1)
O(11)	0.6515(8)	0.352(1)	0.9017(5)	0.093(9)
C(12)	0.835(1)	0.233(1)	0.8735(6)	0.06(1)
O(12)	0.8911(8)	0.1975(9)	0.9076(5)	0.087(8)
C(21)	0.509(1)	0.183(1)	0.7642(6)	0.054(9)
O(21)	0.4427(7)	0.1989(9)	0.7751(4)	0.077(8)
C(22)	0.6312(9)	0.030(1)	0.7772(6)	0.054(9)
O(22)	0.6414(7)	−0.0436(8)	0.7975(5)	0.086(8)
C(23)	0.5584(9)	0.113(1)	0.6732(6)	0.049(9)
O(23)	0.5233(8)	0.0831(9)	0.6303(4)	0.074(7)
C(31)	0.743(1)	0.110(1)	0.6516(6)	0.06(1)
O(31)	0.7232(8)	0.0646(8)	0.6118(5)	0.080(8)
C(32)	0.889(1)	0.222(1)	0.6984(6)	0.06(1)
O(32)	0.9634(7)	0.2161(8)	0.6959(5)	0.078(8)
C(33)	0.8135(9)	0.086(1)	0.7621(6)	0.044(8)
O(33)	0.8424(7)	0.0231(8)	0.7935(4)	0.067(7)
C(41)	0.5770(9)	0.384(1)	0.7561(5)	0.046(9)
O(41)	0.5314(6)	0.4144(8)	0.7828(4)	0.060(7)
C(42)	0.540(1)	0.325(1)	0.6509(6)	0.047(8)
O(42)	0.4696(6)	0.3092(8)	0.6223(4)	0.067(7)
C(51)	0.8931(9)	0.419(1)	0.6385(6)	0.050(9)
O(51)	0.9599(7)	0.4333(8)	0.6270(4)	0.066(7)
C(52)	0.764(1)	0.315(1)	0.5861(6)	0.055(9)
O(52)	0.7436(9)	0.2845(9)	0.5411(5)	0.091(9)
C(61)	0.5313(9)	0.553(1)	0.6180(5)	0.041(8)
O(61)	0.4648(6)	0.5902(8)	0.6145(4)	0.059(7)
C(62)	0.5805(9)	0.418(1)	0.5531(5)	0.044(8)
O(62)	0.5413(7)	0.3788(8)	0.5140(4)	0.073(7)
C(71)	0.9108(9)	0.617(1)	0.6774(6)	0.042(8)
O(71)	0.9816(6)	0.6489(8)	0.6786(5)	0.070(7)
C(72)	0.7723(8)	0.691(1)	0.7024(5)	0.039(7)
O(72)	0.7552(7)	0.7640(7)	0.7223(5)	0.067(7)
C(1)	0.7753(7)	0.4466(9)	0.7298(5)	0.029(7)
C(2)	0.6931(8)	0.505(1)	0.7104(5)	0.040(8)
P(1)	0.8208(2)	0.4323(3)	0.8036(1)	0.033(2)

Table 5 (continued)

Atom	x	y	z	U_{eq} (Å ²)
C(111)	0.9418(8)	0.4175(9)	0.8233(5)	0.035(7)
C(112)	0.986(1)	0.395(1)	0.8775(6)	0.06(1)
C(113)	1.079(1)	0.381(1)	0.8939(6)	0.07(1)
C(114)	1.1258(9)	0.383(1)	0.8550(7)	0.07(1)
C(115)	1.085(1)	0.402(1)	0.8007(7)	0.07(1)
C(116)	0.9909(9)	0.419(1)	0.7837(6)	0.046(8)
C(121)	0.8005(9)	0.5458(9)	0.8350(5)	0.037(8)
C(122)	0.7208(8)	0.5690(9)	0.8468(6)	0.037(7)
C(123)	0.7037(9)	0.659(1)	0.8651(6)	0.06(1)
C(124)	0.767(1)	0.735(1)	0.8683(7)	0.06(1)
C(125)	0.847(1)	0.715(1)	0.8580(7)	0.06(1)
C(126)	0.8609(9)	0.622(1)	0.8387(6)	0.049(9)
P(7)	0.7143(2)	0.5990(3)	0.5839(2)	0.036(2)
C(711)	0.6655(8)	0.7199(9)	0.5640(5)	0.033(7)
C(712)	0.676(1)	0.769(1)	0.5172(6)	0.054(9)
C(713)	0.639(1)	0.862(1)	0.5045(7)	0.08(1)
C(714)	0.593(1)	0.903(1)	0.5379(8)	0.09(1)
C(715)	0.579(1)	0.853(1)	0.5818(7)	0.07(1)
C(716)	0.6134(9)	0.762(1)	0.5962(6)	0.050(9)
C(721)	0.7672(8)	0.570(1)	0.5286(5)	0.039(8)
C(722)	0.723(1)	0.516(1)	0.4829(6)	0.06(1)
C(723)	0.767(1)	0.498(1)	0.4411(6)	0.07(1)
C(724)	0.853(1)	0.531(1)	0.4444(6)	0.07(1)
C(725)	0.897(1)	0.581(1)	0.4898(6)	0.07(1)
C(726)	0.8534(9)	0.601(1)	0.5315(6)	0.047(9)
Cl(11) ^a	1.1464(9)	-0.470(1)	1.0162(5)	0.27(1)
Cl(12) ^a	1.019(2)	-0.359(3)	0.9751(6)	0.77(5)
C(01) ^a	1.085(3)	-0.376(3)	0.964(2)	0.21(2)

^a Population = 0.78.

were refined for the non-hydrogen atoms; $(x, y, z, U_{\text{iso}})_{\text{H}}$ were included constrained at estimated values for the non-core hydrogens. Conventional residuals R , R' on $|F|$ are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{\text{diff}}) + 0.0004\sigma^4(I_{\text{diff}})$ being used. Computation used the XTAL 2.6 program system [28] implemented by S.R. Hall; neutral atom complex scattering factors were employed.

Abnormal features / variations in procedure. In the case of **2**, despite the acquisition of an extensive data set and tolerable precision in residuals and other refinement variables, core hydrogen atoms could not be confidently assigned from consideration of difference map residues. For **3**, the quality of crystals left much to be desired, the available specimen being small, twinned and, seemingly, partly desolvated. Core hydrogen atoms could not be confidently assigned from consideration of difference map residues. From the latter, larger fragments were indicative of solvation by dichloromethane; refinement of the population of the latter model led to a final occupancy of 0.78.

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References

- 1 Part LXXIV: C.J. Adams, M.I. Bruce, M.J. Liddell and B.K. Nicholson, *J. Organomet. Chem.*, 420 (1991) 105.
- 2 M.I. Bruce, M.L. Williams, J.M. Patrick and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1985) 1229.
- 3 J.-C. Daran, O. Kristiansson and Y. Jeannin, *C. R. Acad. Sci. Paris*, 300 (1985) 943.
- 4 J.-C. Daran, E. Cabrera, M.I. Bruce and M.L. Williams, *J. Organomet. Chem.*, 319 (1987) 239.
- 5 B.F.G. Johnson, J. Lewis, A.D. Massey, P.R. Raithby and W.T. Wong, *J. Organomet. Chem.*, 397 (1990) C28.
- 6 C.J. Adams, M.I. Bruce, B.W. Skelton and A.H. White, unpublished work.
- 7 M.I. Bruce, *J. Organomet. Chem.*, 394 (1990) 365.
- 8 K. Natarajan, L. Zsolnai and G. Huttner, *J. Organomet. Chem.*, 209 (1981) 85.
- 9 K.J. Edwards, J.S. Field, R.J. Haines and F. Mulla, *J. Organomet. Chem.*, 402 (1991) 113.
- 10 R.D. Wilson and R. Bau, *J. Am. Chem. Soc.*, 98 (1976) 4687.
- 11 R.D. Wilson, S.M. Wu, R.A. Love and R. Bau, *Inorg. Chem.*, 17 (1978) 1271.
- 12 K. Sasvari, P. Main, F.H. Cano, M. Martinez-Ripoll and P. Frediani, *Acta Crystallogr., Sect. B*, 35 (1979) 87.
- 13 F. Mansilla, G. Lavigne and J.-J. Bonnet, *Acta Crystallogr., Sect. C*, 42 (1986) 1011.
- 14 M.I. Bruce, E. Horn, O. bin Shawkataly, M.R. Snow, E.R.T. Tiekink and M.L. Williams, *J. Organomet. Chem.*, 316 (1986) 187.
- 15 J. Puga, A. Arce, D. Braga, N. Centritto, F. Grepioni, R. Castillo and J. Ascanio, *Inorg. Chem.*, 26 (1987) 867.
- 16 J.R. Shapley, S.I. Richter, M.R. Churchill and R.A. Lashewycz, *J. Am. Chem. Soc.*, 99 (1977) 7384; M.R. Churchill and R.A. Lashewycz, *Inorg. Chem.*, 17 (1978) 1950.
- 17 M.R. Churchill, R.A. Lashewycz, J.R. Shapley and S.I. Richter, *Inorg. Chem.*, 19 (1980) 1277.
- 18 B.F.G. Johnson, J. Lewis, B.E. Reichert, K.T. Schorpp and G.M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, (1977) 1417.
- 19 D.M.P. Mingos and A.S. May, in D.F. Shriver, H.D. Kaesz and R.D. Adams (Eds.), *The Chemistry of Metal Cluster Complexes*, VCH, New York, 1990, p. 11.
- 20 M.I. Bruce, M.L. Williams, B.W. Skelton and A.H. White, *J. Organomet. Chem.*, 282 (1985) C53.
- 21 F. van Gestel, N.J. Taylor and A.J. Carty, *J. Chem. Soc., Chem. Commun.*, (1987) 1049.
- 22 R.D. Adams, J.E. Babin and M. Tasi, *Organometallics*, 7 (1988) 503.
- 23 R.D. Adams, J.E. Babin and M. Tasi, *Inorg. Chem.*, 26 (1987) 2807.
- 24 R.D. Adams, J.E. Babin and J.T. Tanner, *Organometallics*, 7 (1988) 2027.
- 25 P. Frediani, M. Bianchi, A. Salvini, F. Piacenti, S. Ianelli and M. Nardelli, *J. Chem. Soc., Dalton Trans.*, (1990) 1705.
- 26 C.J. Adams, M.I. Bruce, B.W. Skelton and A.H. White, *J. Organomet. Chem.*, 420 (1991) 87.
- 27 M.I. Bruce, M.J. Liddell, B.W. Skelton and A.H. White, *Organometallics*, 10 (1991) 3282.
- 28 S.A.R. Knox, J.W. Koepke, M.A. Andrews and H.D. Kaesz, *J. Am. Chem. Soc.*, 97 (1975) 3942; M.I. Bruce and M.L. Williams, *Inorg. Synth.*, 26 (1989) 262; 28 (1990) 219.
- 29 S.R. Hall and J.M. Stewart (Eds.), *XTAL Users' Manual*, Version 2.6, Universities of Western Australia and Maryland, 1989.