

Reactions of  $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)]$  with secondary phosphines  $\text{R}_2\text{PH}$  involving bulky substituents ( $\text{R} = \text{}^t\text{Bu}$ , 1-Ad, Cy); X-ray crystal structures of  $[\text{Ru}_3(\text{CO})_6(\mu\text{-H})_2(\mu\text{-PCy}_2)_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)]$  and the electron-deficient carbonyl cluster  $[\text{Ru}_3(\mu\text{-CO})(\text{CO})_4(\mu_3\text{-H})(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)]$ <sup>1</sup>

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**Abstract**

The reaction of  $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})]$  (**1**) with secondary phosphines  $\text{R}_2\text{PH}$  ( $\text{R} = \text{}^t\text{Bu}$ , 1-Ad) in heptane under reflux leads to the electron-deficient metal cluster complexes  $[\text{Ru}_3(\mu\text{-CO})(\text{CO})_4(\mu_3\text{-H})(\mu\text{-H})(\mu\text{-PR}_2)_2(\mu\text{-dppm})]$  ( $\text{R} = \text{}^t\text{Bu}$  **4**;  $\text{R} = 1\text{-Ad}$  **5**) in good yields. The reactions yield first the monosubstituted compounds  $[\text{Ru}_3(\text{CO})_9(\text{R}_2\text{PH})(\mu\text{-dppm})]$  ( $\text{R} = \text{}^t\text{Bu}$  **2**;  $\text{R} = 1\text{-Ad}$  **3**), which could be isolated in yields up to 85% after 1 h in refluxing THF. The related reaction of **1** with the less bulky phosphine  $\text{Cy}_2\text{PH}$  in heptane under reflux gave the new electronically saturated complex  $[\text{Ru}_3(\text{CO})_6(\mu\text{-H})_2(\mu\text{-PCy}_2)_2(\mu\text{-dppm})]$  (**7**). In this case the intermediate  $[\text{Ru}_3(\text{CO})_9(\text{Cy}_2\text{PH})(\mu\text{-dppm})]$  (**6**) could also be isolated. Compounds **4** and **5** seem to be coordinatively saturated, in that no reaction with carbon monoxide or dihydrogen was observed, either under normal conditions or under elevated pressure. The molecular structures of **4** and **7** were determined by single-crystal X-ray studies (dppm =  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ; Ad = Adamantyl).

**Keywords:** Ruthenium; Carbonyl; Phosphido bridged; Crystal structure

**1. Introduction**

In an earlier publication we reported the synthesis of the electron-deficient dinuclear complex  $[\text{Fe}_2(\text{CO})_3(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-PCy}_2)(\mu\text{-dppm})]$  [**1**]. In this connection we became interested in the analogous ruthenium compound. However, the possible starting material  $\text{Na}[\text{Ru}_2(\mu\text{-CO})(\text{CO})_6(\mu\text{-PR}_2)]$  was not available, and we therefore sought other synthetic approaches. Recently we found that the trinuclear cluster  $[\text{Ru}_3(\text{CO})_{12}]$  is converted into the dinuclear system  $[\text{Ru}_2(\text{CO})_4(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-Bu}_2\text{PH})_2]$  by reaction with excess  $\text{}^t\text{Bu}_2\text{PH}$  [**2**]. Other authors had reported degradation reactions of  $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})]$  (**1**), with formation of the dinuclear system  $[\text{Ru}_2(\text{CO})_7(\mu\text{-dppm})]$  [**3**]. We

thus decided to use **1** as a starting complex for the synthesis of the corresponding dinuclear phosphido-bridged carbonyl compounds.

Recently some studies of the chemistry of  $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})]$  have appeared [4,5]. It was shown that reactions based on **1** proceed more cleanly than analogous reactions of the unsubstituted  $[\text{Ru}_3(\text{CO})_{12}]$ , often giving only one or two products in good yields. In the following we report reactions of  $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})]$  with bulky secondary phosphines  $\text{R}_2\text{PH}$  ( $\text{R} = \text{}^t\text{Bu}$ , 1-Ad, Cy), yielding various products depending on the steric demands of the phosphines used.

**2. Results and discussion**

From reactions of **1** with excess phosphine  $\text{R}_2\text{PH}$  under thermal conditions we hoped to obtain dinuclear electron-precise complexes  $[\text{Ru}_2(\text{CO})_5(\mu\text{-H})(\mu\text{-$

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<sup>1</sup> Dedicated to the memory of Professor H. Takaya.

$\text{PR}_2(\mu\text{-dppm})$ ]. The analogous diiron compounds have been described recently [6]. However, the reaction of  $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})]$  with excess  $\text{R}_2\text{PH}$  ( $\text{R} = \text{}^t\text{Bu}$ , 1-Ad) in heptane under reflux does not lead to degradation of the ruthenium cluster. Instead, the electron-deficient metal cluster complexes  $[\text{Ru}_3(\mu\text{-CO})(\text{CO})_4(\mu_3\text{-H})(\mu\text{-H})(\mu\text{-PR}_2)_2(\mu\text{-dppm})]$  ( $\text{R} = \text{}^t\text{Bu}$  4;  $\text{R} = 1\text{-Ad}$  5) were formed in high yields. It could be shown that the formation of the complexes  $[\text{Ru}_3(\text{CO})_9(\text{R}_2\text{PH})(\mu\text{-dppm})]$  ( $\text{R} = \text{}^t\text{Bu}$ , 2;  $\text{R} = 1\text{-Ad}$  3) is the first step in these reactions. Pure 2 and 3 could be isolated in yields up to 85% if the reactions were carried out in THF in equimolar ratio over 1 h under reflux conditions (Scheme 1).

The identity and composition of compounds 2 and 3 were determined by elemental analysis, IR and NMR spectroscopy, and mass spectrometry. The infrared spectra of the complexes  $[\text{Ru}_3(\text{CO})_9(\text{R}_2\text{PH})(\mu\text{-dppm})]$  ( $\text{R} = \text{}^t\text{Bu}$ , 2;  $\text{R} = 1\text{-Ad}$  3) show only  $\nu(\text{CO})$  absorption bands in the region characteristic of terminal carbonyl ligands. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of 2 (THF,  $\text{D}_2\text{O}$  capillary) consists of a doublet at  $\delta$  14.8 (3 14.6) and a triplet at  $\delta$  61.5 (3 57.9) with  $^3J_{\text{pp}} = 8.0$  Hz (3 8.1 Hz), corresponding to the two equivalent phosphorus nuclei of the bridging dppm ligand, which couple with one phosphorus nucleus coordinated to the remaining unbridged ruthenium atom. In agreement with the  $^{31}\text{P}$  NMR spectrum, the  $^1\text{H}$  NMR spectrum of 2 also contains the expected signals for one  $\text{}^t\text{Bu}_2\text{PH}$  ligand and for the bridging dppm ligand (see Experimental). The mass spectrum of 2 exhibits the molecular ion at  $m/z = 1089$  and fragments resulting from successive loss of the carbonyl ligands.

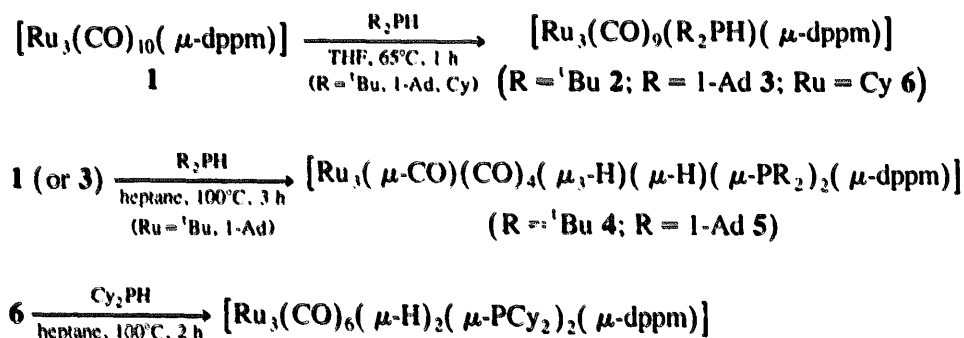
The reaction of 1 with  $\text{R}_2\text{PH}$  ( $\text{R} = \text{}^t\text{Bu}$ , 1-Ad) in molar ratio 1 : 2 in refluxing heptane results after 1 h in the precipitation of purple crystals (compounds 4 and 5 respectively), which were characterized by elemental analysis and spectroscopically ( $^1\text{H}$ ,  $^{31}\text{P}$  NMR, mass spectrometry). In the case of  $\text{R} = \text{}^t\text{Bu}$  the structure  $[\text{Ru}_3(\mu\text{-CO})(\text{CO})_4(\mu_3\text{-H})(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)_2(\mu\text{-dppm})]$  (4) was confirmed by a single-crystal X-ray structure determination (see below). The reaction of 1 with ex-

cess  $\text{}^t\text{Bu}_2\text{PH}$  is closely related to the formation of the bis-phosphido-bridged trinuclear complex  $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-P}^t\text{Bu}_2)_2]$  from  $[\text{Ru}_3(\text{CO})_{12}]$  and  $\text{}^t\text{Bu}_2\text{PH}$  [7]. In this case an electronically saturated trinuclear cluster (48 v.e.) results. We assume that in our case, for steric reasons, the formation of the electron-deficient structure with only 46 v.e. is preferred. Although the hydrides in  $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-P}^t\text{Bu}_2)_2]$  were not located during the X-ray structure determination, it is reasonable to assume that they occupy bridging sites across two Ru–Ru bonds and opposite the two  $\mu\text{-P}^t\text{Bu}_2$  groups. This is clearly indicated by the  $^1\text{H}$  NMR spectrum in solution [7].

The infrared spectra of 4 and 5 are essentially identical in the region of the  $\nu(\text{CO})$  absorptions and exhibit a strong band for a bridging carbonyl ligand at  $1717\text{ cm}^{-1}$  for 4 ( $1712\text{ cm}^{-1}$  for 5, KBr) in the solid and in solution. We therefore assume analogous structures for 4 and 5. The NMR data of the two complexes are consistent with this. The  $^1\text{H}$  NMR spectra show two different (inequivalent) hydride signals in each case. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of 4 and 5 at room temperature consist of four well-separated signals, confirming the chemical inequivalence of all four phosphorus nuclei (see Experimental). The structures of 4 and 5 in solution thus agree well with the solid-state structure determined for 4 by X-ray crystal structure analysis. It is not clear why this unsymmetrical arrangement with one face-capping and one edge-bridging hydride ligand should be preferred in 4. Although the trinuclear cluster complexes 4 and 5 are electronically unsaturated, it seems that they are coordinatively saturated. No reactions were observed with small molecules, e.g. carbon monoxide or dihydrogen, even at elevated pressure (30 bar CO or  $\text{H}_2$ , THF,  $25^\circ\text{C}$ , 6 h).

### 2.1. Molecular structure of $[\text{Ru}_3(\mu\text{-CO})(\text{CO})_4(\mu_3\text{-H})(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)_2(\mu\text{-dppm})]$ (4)

The molecule of 4 is shown in Fig. 1, with selected bond lengths and angles in Table 1. It consists of a  $\mu_3$ -hydride-capped, electron-deficient  $\text{Ru}_3$  cluster with



Scheme 1.

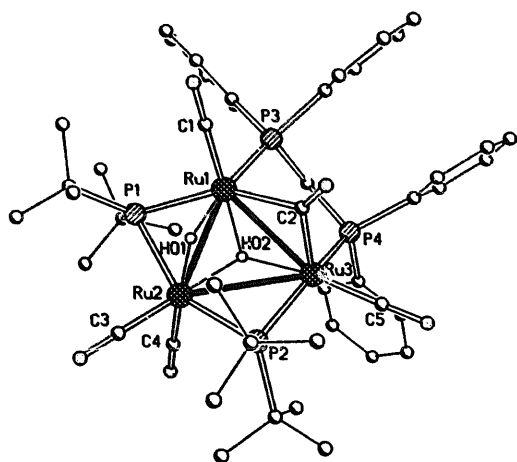


Fig. 1. The structure of complex 4 in the crystal. Radii are arbitrary. Cluster hydrides are shown but other H are omitted for clarity.

three differently substituted Ru atoms. The Ru1 and Ru3 atoms each bear only one terminal carbonyl group; the Ru1–Ru3 bond is dppm- and carbonyl-bridged. The Ru2 atom bears two carbonyl groups and both its Ru–Ru bonds are P<sup>t</sup>Bu<sub>2</sub>-bridged. The Ru1–Ru2 bond is also hydrido-bridged and shows the shortest Ru–Ru bond length of 272.95(4) pm. The longest bond is Ru2–Ru3, at 315.92(4) pm. The angles in the Ru<sub>3</sub> triangle range from 53.393(8)° (Ru1–Ru3–Ru2) to 68.295(8)° (Ru2–Ru1–Ru3). Both phosphorus atoms of the  $\mu$ -dppm group lie on the same side of the Ru<sub>3</sub> plane (P3 by 152, P4 by 185 pm). On the opposite side by –113 pm is C2 of the  $\mu$ -CO group. The phosphorus atoms of the P<sup>t</sup>Bu<sub>2</sub> groups lie on opposite sides of the plane (P1 by 86.9, P2 by –124 pm).

Since the composition and structure of molecule 4 are new, no structural comparisons with closely related Ru<sub>3</sub> clusters are possible. The above-mentioned [Ru<sub>3</sub>(CO)<sub>8</sub>( $\mu$ -H)<sub>2</sub>( $\mu$ -P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>] is the sole known Ru<sub>3</sub> ring with two bridging P<sup>t</sup>Bu<sub>2</sub> groups, but this cluster core is electronically saturated (48 v.e.). In this case the unbridged Ru–Ru bond is, at 304.6(1) pm, fairly long

and easily broken during dihydrogen addition in the formation of the open framework of [Ru<sub>3</sub>(CO)<sub>8</sub>( $\mu$ -H)<sub>2</sub>(H)<sub>2</sub>( $\mu$ -P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>] [7]. The formal substitution of two carbonyl ligands in [Ru<sub>3</sub>(CO)<sub>8</sub>( $\mu$ -H)<sub>2</sub>( $\mu$ -P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>] by dppm causes, presumably for steric reasons, the loss of a further carbonyl group. An unusual feature of 4 is the very long doubly-bridged Ru2–Ru3 bond. In contrast, the “electron deficient” Ru1–Ru3 bond raises the question of multiple metal–metal bonding character, which can however be ruled out with some confidence in view of the bond length of 289.33(4) pm.

For the interesting electronically and coordinatively unsaturated molecule [Ru<sub>3</sub>(CO)<sub>9</sub>( $\mu$ -H)( $\mu$ -PPh<sub>2</sub>)] (electron count 46 v.e.) the observed Ru–Ru distances between 279.96(5) and 290.49(5) pm also exclude the possibility of an Ru–Ru double bond. However, in this case an unprecedented behaviour was observed, specifically the electron deficiency of one Ru atom is compensated by an “agostic” P–phenyl interaction of the  $\mu$ -PPh<sub>2</sub> ligand [8]. In contrast to this, no such interactions between dppm and Ru1 or Ru3 respectively could be observed for 4 (the shortest Ru...H contact being 314 pm). One might expect for 4 a symmetrical molecular arrangement with two bridging hydrides, however, the “electron deficiency” of the Ru1–Ru3 bond seems to be better compensated by the capping hydride ligand. Further investigations of the unsaturation in the cluster 4 are underway.

## 2.2. Reaction of [Ru<sub>3</sub>(CO)<sub>10</sub>( $\mu$ -dppm)] with Cy<sub>2</sub>PH

The reaction of [Ru<sub>3</sub>(CO)<sub>10</sub>( $\mu$ -dppm)] (1) with equimolar amounts of Cy<sub>2</sub>PH in THF at 65°C for 1 h results, as described for the two phosphines <sup>t</sup>Bu<sub>2</sub>PH and Ad<sub>2</sub>PH, in the formation of the monosubstituted product [Ru<sub>3</sub>(CO)<sub>9</sub>(Cy<sub>2</sub>PH)( $\mu$ -dppm)] (6). The spectroscopic and analytical data (<sup>1</sup>H, <sup>31</sup>P NMR) agree with the proposed composition (see Experimental). 6 was obtained as a red–brown powder in yields up to 80%.

Table 1  
Selected bond lengths (pm) and angles (°) for 4

Ru(1)–C(1)	184.0(3)	Ru(1)–C(2)	217.8(3)
Ru(1)–P(3)	229.71(7)	Ru(1)–P(1)	238.92(7)
Ru(1)–Ru(2)	272.95(4)	Ru(1)–Ru(3)	289.33(4)
Ru(2)–C(3)	184.6(3)	Ru(2)–C(4)	189.1(3)
Ru(2)–P(1)	239.88(7)	Ru(2)–P(2)	240.18(8)
Ru(2)–Ru(3)	315.92(4)	Ru(3)–C(5)	184.5(3)
Ru(3)–C(2)	194.4(3)	Ru(3)–P(4)	233.11(7)
Ru(3)–P(2)	234.84(8)	H(01)–Ru(1)	180(2)
H(01)–Ru(2)	177(2)	H(02)–Ru(1)	194(2)
H(02)–Ru(2)	196(2)	H(02)–Ru(3)	192(2)
Ru(2)–Ru(1)–Ru(3)	68.295(8)	Ru(1)–Ru(2)–Ru(3)	58.312(9)
Ru(1)–Ru(3)–Ru(2)	53.393(8)	Ru(1)–P(1)–Ru(2)	69.51(2)
Ru(3)–P(2)–Ru(2)	83.37(2)	Ru(3)–C(2)–Ru(1)	88.99(10)
C(22)–P(4)–Ru(3)	114.66(8)	Ru(3)–C(2)–Ru(1)	88.99(10)
P(4)–C(22)–P(3)	112.25(13)		

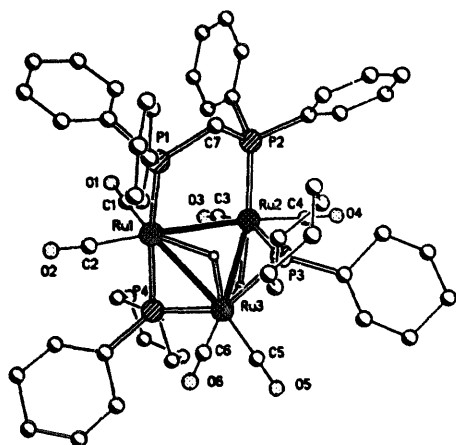


Fig. 2. The structure of complex **7** in the crystal. Radii are arbitrary. Cluster hydrides are shown but other H are omitted for clarity.

In the reaction of **1** with  $\text{Cy}_2\text{PH}$  (molar ratio 1 : 2 or excess) in heptane under reflux for 1 h, a dark red solution is formed from which an orange–red powder precipitates on cooling to room temperature. The room temperature  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of this material is complex, showing two different signals for bridging  $\mu\text{-PCy}_2$  groups at lower field and one signal for the bridging dppm ligand at higher field. In the  $^1\text{H}$  NMR spectrum two complex signals in the typical range for hydride ligands are seen. Because of the complexity of the NMR spectra it was desirable to determine the X-ray crystal structure of this material. Single crystals were obtained by slow diffusion of heptane into dichloromethane solutions.

### 2.3. Molecular structure of $[\text{Ru}_3(\text{CO})_6(\mu\text{-H})_2(\mu\text{-PCy}_2)_2(\mu\text{-dppm})]$ (**7**)

The molecule of **7** is shown in Fig. 2; selected bond lengths and angles are listed in Table 2. The molecular geometry of **7** consists of a closed, electronically saturated  $\text{Ru}_3$  cluster with two kinds of Ru–Ru bond length. The longest bond, at 295.47(9) pm, is between the dppm-bridged Ru1 and Ru2. The bond length between

the Ru3 and the two phosphorus- and hydrido-bridged Ru1 and Ru2 is slightly shorter [Ru1–Ru3 290.58(12) pm, Ru2–Ru3 288.94(8) pm]. The angles inside the  $\text{Ru}_3$  ring lie between  $59.07(2)^\circ$  [Ru2–Ru1–Ru3] and  $61.31(2)^\circ$  [Ru1–Ru3–Ru2].

Both phosphorus atoms of the dppm bridge lie on the same side of the  $\text{Ru}_3$  plane (P1 by 188, P2 by 136 pm). The phosphorus atoms of the  $\mu\text{-PCy}_2$  groups and the hydrido atoms each lie one above and one below the  $\text{Ru}_3$  plane (P3 – 169, P4 164.7, H01 – 100, H02 96 pm).

With respect to the  $\text{Ru}_3(\mu\text{-H})_2(\mu\text{-PR}_2)_2$  core, the molecular arrangement of **7** is comparable with the structure of the metal cluster  $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-PPh}_2)_2]$  [**9**]. In this case a nearly equilateral triangle was also observed, whereby the longest Ru–Ru bond is associated with the unbridged edge. Interestingly, this bond is not significantly influenced by the bridging dppm ligand (294.64(3) pm in  $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-PPh}_2)_2]$  vs. 295.47(9) in **7**). The remaining two phosphido-bridged Ru–Ru bonds in **7** are slightly longer because of the higher steric demand of the cyclohexyl substituents. The other structural data (Ru– $\mu\text{-P}$  and Ru–C distances) are in good agreement.

### 3. Experimental

All reactions were carried out under dry nitrogen, using standard Schlenk techniques. Solvents were dried over molecular sieves or sodium/benzophenone ketyl, and were distilled under nitrogen prior to use. Starting materials were either commercially available or were prepared according to literature procedures:  $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})]$  [**10**],  $\text{tBu}_2\text{PH}$  [**11**],  $\text{Ad}_2\text{PH}$  [**12**]. IR spectra were obtained using a Bio-Rad FTS 165 instrument.  $^1\text{H}$  NMR and  $^{31}\text{P}$  NMR spectra were recorded on a Bruker AC 200 spectrometer ( $^1\text{H}$  at 200.132 MHz,  $^{31}\text{P}$  NMR at 81.015 MHz). The mass spectra were obtained on a Hewlett-Packard 5995A instrument ( $\text{M}^+$  referred to  $^{102}\text{Ru}$ ).

Table 2  
Selected bond lengths (pm) and angles ( $^\circ$ ) for **7**

Ru(1)–C(2)	188.3(3)	Ru(1)–C(1)	188.5(4)
Ru(1)–P(1)	235.19(10)	Ru(1)–P(4)	238.13(10)
Ru(1)–Ru(3)	290.58(12)	Ru(1)–Ru(2)	295.47(9)
Ru(2)–C(4)	188.6(3)	Ru(2)–C(3)	189.2(3)
Ru(2)–P(2)	232.82(10)	Ru(2)–P(3)	243.48(11)
Ru(2)–Ru(3)	288.94(8)	Ru(3)–C(5)	185.7(4)
Ru(3)–C(6)	186.9(3)	Ru(3)–P(4)	233.40(10)
Ru(3)–P(3)	235.64(10)		
Ru(3)–Ru(1)–Ru(2)	59.07(2)	Ru(3)–Ru(2)–Ru(1)	59.62(3)
Ru(2)–Ru(3)–Ru(1)	61.31(2)	Ru(3)–P(3)–Ru(2)	74.16(3)
Ru(3)–P(4)–Ru(1)	76.08(4)		

### 3.1. Preparation of $[Ru_3(CO)_9(R_2PH)(\mu-dppm)]$ ( $R = Bu, Ad, Cy; 2, 3, 6$ )

A mixture of **1** (968 mg, 1 mmol) and 1 mmol of the corresponding phosphine  $R_2PH$  ( $^1Bu_2PH$  146 mg,  $Ad_2PH$  302 mg,  $Cy_2PH$  198 mg) was heated in refluxing THF (20 ml) for 1 h. After cooling to room temperature and removal of the solvent the residue was recrystallized from  $CH_2Cl_2$ /heptane to give red-brown powders of **2**, **3** and **6** (yields 931 mg **2**, 86%; 1048 mg **3**, 84%; 910 mg **6**, 80%).

**2**. Anal. Found: C, 46.23; H, 4.19;  $M$ , 1085.91 (Calc.).  $C_{42}H_{41}O_9P_3Ru_3$  Calc.: C, 46.46; H, 3.81%. IR  $\nu(CO)$  (KBr): 2050m, 1984vs, 1963s, 1939s, 1910m, 1887m  $cm^{-1}$ .  $^1H$  NMR  $\delta$  ( $CDCl_3$ ): 7.36 (m, 20H,  $Ph_2PCH_2PPh_2$ ), 4.63 (d,  $J(Ph) = 326.4$  Hz, 1H,  $^1Bu_2PH$ ), 4.22 (t,  $^2J(Ph) = 10.4$  Hz,  $Ph_2PCH_2PPh_2$ ), 1.36 (d,  $^3J(Ph) = 14.5$  Hz, 18H,  $^1Bu_2PH$ ).  $^{31}P\{^1H\}$  NMR  $\delta$  ( $CDCl_3$ ): 61.52 (t,  $^3J(PP) = 8.2$  Hz,  $^1Bu_2PH$ ), 14.78 (d,  $^3J(PP) = 8.2$  Hz,  $Ph_2PCH_2PPh_2$ ). MS: 1089,  $M^+$ ; 1061,  $[M-CO]^+$ ; 1033,  $[M-2CO]^+$ ; 1005,  $[M-3CO]^+$ ; 977,  $[M-4CO]^+$ ; 949,  $[M-5CO]^+$ ; 927,  $[M-6CO]^+$ ; 893,  $[M-7CO]^+$ ; 865,  $[M-8CO]^+$ ; 837,  $[M-9CO]^+$ ; 78,  $[C_6H_6]^+$ , 100%.

**3**. Anal. Found: C, 52.17; H, 4.48;  $M$ , 1242.14 (calc.).  $C_{54}H_{53}O_9P_3Ru_3$  Calc.: C, 52.22; H, 4.31%. IR  $\nu(CO)$  (KBr): 2046m, 1986vs, 1968s, 1942s, 1915m,

1890sh  $cm^{-1}$ .  $^1H$  NMR  $\delta$  ( $CDCl_3$ ): 7.30 (m, 20H,  $Ph_2PCH_2PPh_2$ ), 4.18 (d,  $J(Ph) = 319.8$  Hz, 1H,  $Ad_2PH$ ), 4.22 (t,  $^2J(Ph) = 10.3$  Hz, 2H,  $Ph_2PCH_2PPh_2$ ), 2.03–1.70 (m, 30H,  $C_{10}H_{15}$ ).  $^{31}P\{^1H\}$  NMR  $\delta$  ( $CDCl_3$ ): 57.93 (t,  $^3J(PP) = 8.1$  Hz,  $Ad_2PH$ ), 14.56 (d,  $^3J(PP) = 8.1$  Hz,  $Ph_2PCH_2PPh_2$ ). No suitable mass spectrum was obtained.

**6**. Anal. Found: C, 48.93; H, 4.19;  $M$ , 1137.99 (calc.).  $C_{46}H_{45}O_9P_3Ru_3$  Calc.: C, 48.55; H, 3.99%. IR  $\nu(CO)$  (KBr): 2057m, 2019s, 1968s, 1946s, 1920m, 1896sh  $cm^{-1}$ .  $^1H$  NMR  $\delta$  ( $CDCl_3$ ): 7.34 (m, 20H,  $Ph_2PCH_2PPh_2$ ), 4.48 (d,  $J(Ph) = 336.7$  Hz, 1H,  $Cy_2PH$ ), 4.18 (t,  $^2J(Ph) = 10.2$  Hz, 2H,  $Ph_2PCH_2PPh_2$ ), 1.99–0.83 (m, 22H,  $C_6H_{11}$ ).  $^{31}P\{^1H\}$  NMR  $\delta$  ( $CDCl_3$ ): 19.84 (t,  $^3J(PP) = 10.0$  Hz,  $Cy_2PH$ ), 15.74 (d,  $^3J(PP) = 10.3$  Hz,  $Ph_2PCH_2PPh_2$ ). MS: 1113,  $[M-CO]^+$ ; 1085,  $[M-2CO]^+$ ; 1057,  $[M-3CO]^+$ ; 1029,  $[M-4CO]^+$ ; 1001,  $[M-5CO]^+$ ; 973,  $[M-6CO]^+$ ; 945,  $[M-7CO]^+$ ; 917,  $[M-8CO]^+$ ; 889,  $[M-9CO]^+$ ; 78,  $[C_6H_6]^+$ , 100%.

### 3.2. Preparation of $[Ru_3(\mu-CO)(CO)_4(\mu_3-H)(\mu-H)(\mu-PR_2)_2(\mu-dppm)]$ ( $R = ^1Bu$ **4**; $R = Ad$ **5**)

A mixture of **1** (968 mg, 1 mmol) and 2 mmol of the corresponding phosphine  $R_2PH$  ( $^1Bu_2PH$  292 mg;  $Ad_2PH$  605 mg) was heated in refluxing heptane (50

Table 3  
Crystal data and refinement details for complexes **4** and **7**

Complex	<b>4</b> · THF	<b>7</b> · $CH_2Cl_2$
Formula	$C_{50}H_{68}O_6P_4Ru_3$	$C_{56}H_{70}Cl_2O_6P_4Ru_3$
$M_r$	1192.13	1337.11
Crystal habit	red prism	orange tablet
Crystal size ( $mm^3$ )	$0.6 \times 0.2 \times 0.2$	$0.8 \times 0.7 \times 0.2$
Temperature ( $^{\circ}C$ )	–100	–130
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
Cell constants		
$a$ (pm)	1397.17(12)	1185.9(3)
$b$ (pm)	2412.1(3)	1384.5(3)
$c$ (pm)	1621.6(2)	1991.4(5)
$\alpha$ ( $^{\circ}$ )	90	90.02(2)
$\beta$ ( $^{\circ}$ )	106.476(8)	105.71(2)
$\gamma$ ( $^{\circ}$ )	90	114.56(2)
$V$ ( $nm^{-3}$ )	5.2406(10)	2.8388(12)
$Z$	4	2
$D_x$ ( $Mg\ m^{-3}$ )	1.511	1.564
$\mu$ ( $mm^{-1}$ )	1.021	1.043
$F(000)$	2432	1360
$2\theta_{max}$ ( $^{\circ}$ )	55	50
Reflections measured	12097	10165
Independent reflections	12015	10029
$R_{int}$	0.014	0.012
Max. and min. transmission	0.841 and 0.773	0.728 and 1
$wR$ ( $F^2$ , all reflections)	0.059	0.082
$R$ ( $F > 4\sigma(F)$ )	0.030	0.032
No. of parameters	597	648
$S$	0.948	1.041
max. $\Delta/\sigma$	< 0.001	< 0.001
max. $\Delta\rho$ ( $e\ nm^{-3}$ )	403	1231

Table 4  
Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{pm}^2 \times 10^{-1}$ ) for 4

Atom	x	y	z	$U_{\text{eq}}$
Ru(1)	8498.6(2)	2861.0(1)	3241.1(1)	15.0(1)
Ru(2)	7754.6(2)	3914.3(1)	3082.2(1)	16.3(1)
Ru(3)	7092.8(2)	3018.0(1)	4231.7(1)	16.9(1)
H(01)	8822(21)	3543(8)	3685(20)	47(10)
H(02)	7183(16)	3175(7)	3097(14)	22(7)
P(1)	8375.7(5)	3449.9(3)	2030.8(4)	17.3(1)
P(2)	7532.0(5)	3954.6(3)	4496.2(4)	18.7(1)
P(3)	7880.7(5)	1998.0(3)	2776.8(4)	17.0(1)
P(4)	6196.4(5)	2242.8(3)	3579.0(4)	17.1(1)
O(1)	10594.0(14)	2439.6(9)	3622.2(14)	36.9(5)
O(2)	9017.3(14)	2543.8(8)	5180.0(12)	27.8(4)
O(3)	8687(2)	5038.3(8)	3182.2(14)	38.5(5)
O(4)	5781.4(15)	4376.5(9)	1992.3(14)	37.1(5)
O(5)	6419(2)	2850.8(10)	5815.8(14)	41.9(6)
C(1)	9780(2)	2595.8(11)	3451(2)	22.2(6)
C(2)	8438(2)	2715.8(10)	4551(2)	19.0(5)
C(3)	8327(2)	4607.8(11)	3133(2)	23.4(6)
C(4)	6530(2)	4210.9(11)	2406(2)	23.4(6)
C(5)	6683(2)	2919.0(11)	5208(2)	24.9(6)
C(6)	9617(2)	3705.5(12)	1914(2)	25.6(6)
C(7)	9507(2)	4211.9(13)	1325(2)	38.3(8)
C(8)	10297(2)	3876.5(12)	2798(2)	29.9(7)
C(9)	10155(2)	3238.0(13)	1578(2)	34.7(7)
C(10)	7453(2)	3377.6(11)	924(2)	20.7(6)
C(11)	7855(2)	3040.8(12)	296(2)	30.2(7)
C(12)	7098(2)	3944.4(11)	512(2)	26.6(6)
C(13)	6541(2)	3075.6(11)	1038(2)	24.6(6)
C(14)	6402(2)	4373.0(12)	4572(2)	26.8(6)
C(15)	6307(2)	4402.0(14)	5490(2)	40.4(8)
C(16)	5470(2)	4069.1(13)	4029(2)	33.4(7)
C(17)	6409(2)	4959.1(12)	4208(2)	36.4(7)
C(18)	8664(2)	4171.7(12)	5407(2)	25.7(6)
C(19)	8732(2)	4807.2(12)	5531(2)	36.5(7)
C(20)	8636(2)	3881.0(14)	6237(2)	39.0(8)
C(21)	9626(2)	3995.5(12)	5210(2)	28.4(6)
C(22)	6526(2)	1990.4(11)	2626(2)	19.3(5)
C(31)	8001(2)	1756.7(10)	1737(2)	19.2(5)
C(32)	8953(2)	1736.5(12)	1628(2)	28.1(6)
C(33)	9089(2)	1561.0(13)	859(2)	35.4(7)
C(34)	8292(2)	1403.5(12)	190(2)	33.8(7)
C(35)	7339(2)	1419.1(13)	288(2)	35.4(7)
C(36)	7198(2)	1594.5(12)	1056(2)	27.7(6)
C(41)	8303(2)	1385.5(10)	3454(2)	19.5(5)
C(42)	7811(2)	883.0(11)	3205(2)	26.9(6)
C(43)	8059(2)	421.4(12)	3722(2)	30.7(7)
C(44)	8813(2)	448.1(12)	4479(2)	31.7(7)
C(45)	9325(2)	935.2(12)	4726(2)	28.9(6)
C(46)	9067(2)	1406.8(11)	4213(2)	25.3(6)
C(51)	4882(2)	2428.7(11)	3166(2)	21.3(6)
C(52)	4444(2)	2578(2)	2326(2)	45.6(9)
C(53)	3457(3)	2747(2)	2070(2)	65.5(13)
C(54)	2907(2)	2774(2)	2643(2)	54.1(10)
C(55)	3334(2)	2633.9(14)	3481(2)	40.0(8)
C(56)	4313(2)	2459.6(13)	3740(2)	32.2(7)
C(61)	6165(2)	1602.4(11)	4171(2)	21.1(6)
C(62)	5435(2)	1202.1(12)	3852(2)	31.1(7)
C(63)	5464(3)	702.4(13)	4275(2)	42.5(8)
C(64)	6226(3)	597.0(13)	5013(2)	43.2(9)
C(65)	6949(3)	992.7(13)	5339(2)	39.4(8)
C(66)	6917(2)	1493.9(12)	4915(2)	27.3(6)
C(91)	1526(4)	1137(2)	2904(3)	80.1(14)
C(92)	2527(4)	886(3)	3225(3)	92(2)
O(93)	2376(6)	356(3)	3583(5)	98(2)

Table 4 (continued)

Atom	x	y	z	$U_{\text{eq}}$
C(94)	1481(5)	168(3)	3049(5)	41(3)
C(95)	841(4)	650(2)	2843(4)	97(2)
O(93')	2475(7)	329(4)	2959(6)	128(3)

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

ml) over 3 h. After cooling to room temperature the volume was reduced to 20 ml and 4 and 5 were filtered off as purple crystals, washed three times with 10 ml portions of pentane, and dried in vacuo (yields 840 mg 4, 75%; 1031 mg 5, 72%).

4. Anal. Found: C, 48.84; H, 5.10;  $M$ , 1120.08 (calc.).  $\text{C}_{46}\text{H}_{60}\text{O}_5\text{P}_4\text{Ru}_3$  Calc.: C, 49.33; H, 5.41%. IR  $\nu(\text{CO})$  (KBr): 2001vs, 1944vs, 1929vs, 1899vs, 1717vs  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR  $\delta$  ( $\text{CDCl}_3$ ): 7.29 (m, 20H,  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ), 3.26 (dt,  $^2J(\text{PH}) = 9.3$  Hz, 2H,  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ), 1.19 (d,  $^3J(\text{PH}) = 13.6$  Hz, 18H,  $\mu\text{-P}^i\text{Bu}_2$ ), 1.12 (d,  $^3J(\text{PH}) = 14.0$  Hz, 18H,  $\mu\text{-P}^i\text{Bu}_2$ ), -14.40 (m, 1H,  $\mu\text{-H}$ ), -14.80 (m, 1H,  $\mu_3\text{-H}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR  $\delta$  (THF,  $\text{D}_2\text{O}$  cap.): 203.35 [ddd,  $^2J(\text{PP}) = 152.4$ ,  $^2J(\text{PP}) = 81.1$ ,  $^3J(\text{PP}) = 3.1$  Hz,  $\mu\text{-P}(1)$ ], 144.68 [ddd,  $^2J(\text{PP}) = 81.3$ ,  $^2J(\text{PP}) = 10.8$ ,  $^3J(\text{PP}) = 5.1$  Hz,  $\mu\text{-P}(2)$ ], 48.37 (ddd,  $^2J(\text{PP}) = 90.1$ ,  $^2J(\text{PP}) = 11.1$ ,  $^3J(\text{PP}) = 3.4$  Hz, dppm), 27.15 (ddd,  $^2J(\text{PP}) = 152.3$ ,  $^2J(\text{PP}) = 89.9$ ,  $^3J(\text{PP}) = 5.1$  Hz, dppm). MS: 1123,  $M^+$ , 1095, [ $M\text{-CO}$ ] $^+$ ; 1067, [ $M\text{-2CO}$ ] $^+$ ; 1039, [ $M\text{-3CO}$ ] $^+$ ; 1011, [ $M\text{-4CO}$ ] $^+$ ; 983, [ $M\text{-5CO}$ ] $^+$ ; 57 [ $\text{C}_4\text{H}_9$ ] $^+$ , 100%.

5. Anal. Found: C, 58.80; H, 6.02;  $M$ , 1432.54 (calc.).  $\text{C}_{70}\text{H}_{84}\text{O}_5\text{P}_4\text{Ru}_3$  Calc.: C, 58.69; H, 5.92%. IR  $\nu(\text{CO})$  (KBr): 1997vs, 1938vs, 1930vs, 1896vs, 1716vs  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR  $\delta$  ( $\text{CDCl}_3$ ): 7.38 (m, 20 H,  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ), 3.22 (dt,  $^2J(\text{PH}) = 9.1$  Hz, 2H,  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ), 2.53–0.82 (m, 60H,  $\text{C}_{10}\text{H}_{15}$ ), -14.58 (m, 1H,  $\mu\text{-H}$ ), -14.99 (m, 1H,  $\mu_3\text{-H}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR  $\delta$  (THF,  $\text{D}_2\text{O}$  cap.): 200.84 [ddd,  $^2J(\text{PP}) = 149.3$ ,  $^2J(\text{PP}) = 78.9$ ,  $^3J(\text{PP}) = 3.4$  Hz,  $\mu\text{-P}(1)$ ], 139.57 [ddd,  $^2J(\text{PP}) = 79.3$ ,  $^2J(\text{PP}) = 11.5$ ,  $^3J(\text{PP}) = 4.2$  Hz,  $\mu\text{-P}(2)$ ], 49.47 (ddd,  $^2J(\text{PP}) = 93.5$ ,  $^2J(\text{PP}) = 11.3$ ,  $^3J(\text{PP}) = 3.8$  Hz, dppm), 29.42 (ddd,  $^2J(\text{PP}) = 148.8$ ,  $^2J(\text{PP}) = 93.6$ ,  $^3J(\text{PP}) = 4.7$  Hz, dppm). MS: 1435,  $M^+$ ; 1407, [ $M\text{-CO}$ ] $^+$ ; 1379, [ $M\text{-2CO}$ ] $^+$ ; 1351, [ $M\text{-3CO}$ ] $^+$ ; 1323, [ $M\text{-4CO}$ ] $^+$ ; 1295, [ $M\text{-5CO}$ ] $^+$ .

### 3.3. Preparation of $[\text{Ru}_3(\text{CO})_6(\mu\text{-H})_2(\mu\text{-PCy}_2)_2(\mu\text{-dppm})]$ (7)

A mixture of 1 (968 mg, 1 mmol) and  $\text{Cy}_2\text{PH}$  (396 mg, 2 mmol) was heated in refluxing heptane (50 ml) for 1 h. From the deep red solution orange-red crystals precipitated on cooling to room temperature. The volume was reduced to 20 ml, the crystals were filtered off, washed three times with 10 ml of pentane and dried in vacuo (yield 751 mg, 60%). Anal. Found: C, 52.48; H,

Table 5  
Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{pm}^2 \times 10^{-1}$ ) for 7

Atom	x	y	z	$U_{\text{eq}}$
Ru(1)	6857.8(2)	7176.7(2)	2341.9(1)	18.1(1)
Ru(2)	8872.6(2)	8835.2(2)	1837.6(1)	18.2(1)
Ru(3)	9283.8(2)	8693.3(2)	3325.0(1)	17.6(1)
P(1)	5356.6(7)	7772.6(6)	1682.3(4)	20.4(2)
P(2)	7360.7(8)	9081.9(6)	917.3(4)	21.4(2)
P(3)	9190.1(8)	10163.2(6)	2757.7(4)	20.2(2)
P(4)	8508.1(8)	6835.3(6)	3141.4(4)	19.8(2)
C(1)	6416(3)	6140(3)	1585(2)	28.8(7)
O(1)	6110(3)	5497(2)	1121.6(15)	44.1(7)
C(2)	5586(3)	6326(3)	2757(2)	27.6(7)
O(2)	4754(3)	5800(2)	2973(2)	47.3(7)
C(3)	8903(3)	7624(3)	1417(2)	26.1(7)
O(3)	9073(3)	6959(2)	1180.7(13)	36.8(6)
C(4)	10305(3)	9729(3)	1567(2)	25.3(7)
O(4)	11160(2)	10299(2)	1365.0(15)	40.2(6)
C(5)	11036(3)	9185(3)	3809(2)	29.7(7)
O(5)	12109(3)	9472(3)	4116(2)	53.4(8)
C(6)	8967(3)	8790(3)	4186(2)	25.9(7)
O(6)	8791(3)	8825(2)	4722.9(13)	42.1(6)
C(7)	5882(3)	8867(3)	1145(2)	24.5(7)
C(11)	4499(3)	8290(3)	2114(2)	27.6(7)
C(12)	3570(5)	8572(4)	1684(2)	54.9(12)
C(13)	2915(6)	8992(5)	1976(3)	77(2)
C(14)	3151(5)	9124(4)	2689(3)	60.9(13)
C(15)	4044(4)	8821(3)	3117(2)	46.6(10)
C(16)	4733(3)	8412(3)	2828(2)	33.0(8)
C(21)	3950(3)	6671(3)	1072(2)	23.4(6)
C(22)	3908(3)	6409(3)	389(2)	28.0(7)
C(23)	2859(3)	5542(3)	-44(2)	31.1(7)
C(24)	1828(4)	4914(3)	196(2)	35.6(8)
C(25)	1869(4)	5149(3)	877(2)	42.6(9)
C(26)	2916(3)	6018(3)	1313(2)	36.9(8)
C(31)	6721(3)	8316(3)	37(2)	27.0(7)
C(32)	6007(4)	8642(3)	-513(2)	46.2(10)
C(33)	5442(5)	8052(4)	-1169(2)	60.3(13)
C(34)	5590(4)	7146(4)	-1296(2)	47.7(10)
C(35)	6297(4)	6819(3)	-766(2)	43.9(9)
C(36)	6868(4)	7405(3)	-104(2)	35.0(8)
C(41)	7854(3)	10436(3)	656(2)	25.9(7)
C(42)	8840(4)	10801(3)	334(2)	39.9(9)
C(43)	9251(4)	11808(3)	124(2)	47.4(10)
C(44)	8682(4)	12468(3)	219(2)	46.0(10)
C(45)	7700(4)	12116(3)	527(2)	39.1(9)
C(46)	7278(3)	11102(3)	739(2)	30.5(7)
C(51)	10778(3)	11340(3)	2886(2)	27.9(7)
C(52)	11456(4)	11942(3)	3607(2)	43.0(9)
C(53)	12904(4)	12648(4)	3670(3)	56.5(12)
C(54)	13013(5)	13399(4)	3110(3)	65.5(14)
C(55)	12267(4)	12841(4)	2391(3)	56.1(12)
C(56)	10856(3)	12102(3)	2323(2)	29.9(7)
C(61)	8056(3)	10666(3)	2959(2)	29.5(7)
C(62)	8038(4)	11655(3)	2633(2)	32.7(8)
C(63)	7021(4)	11940(3)	2801(2)	41.3(9)
C(64)	7283(4)	12169(3)	3578(2)	43.1(9)
C(65)	7334(4)	11221(3)	3934(2)	44.7(10)
C(66)	8290(4)	10877(3)	3764(2)	40.4(9)
C(71)	9460(3)	6260(3)	2810(2)	25.7(7)
C(72)	8676(4)	5113(3)	2434(2)	40.2(9)
C(73)	9489(4)	4783(3)	2087(2)	46.6(10)
C(74)	10755(4)	4928(3)	2599(2)	40.2(9)
C(75)	11521(4)	6063(3)	2972(2)	42.9(9)
C(76)	10719(4)	6378(3)	3340(2)	37.1(8)
C(81)	8010(3)	6139(2)	3882(2)	24.1(7)

Table 5 (continued)

Atom	x	y	z	$U_{\text{eq}}$
C(82)	9119(4)	6351(3)	4560(2)	34.5(8)
C(83)	8567(4)	5936(3)	5172(2)	43.0(9)
C(84)	7645(4)	4745(3)	5005(2)	44.3(10)
C(85)	6573(4)	4518(3)	4320(2)	38.8(9)
C(86)	7131(3)	4931(3)	3716(2)	31.8(8)
C(99)	4091(5)	1563(4)	5141(3)	58.6(12)
Cl(98)	5352(2)	1488.7(14)	4865.8(9)	86.6(5)
Cl(99)	4603.9(13)	2827.9(11)	5593.0(7)	64.6(3)

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

5.39;  $M$ , 1252.25 (calc.).  $\text{C}_{55}\text{H}_{68}\text{O}_6\text{P}_4\text{Ru}_3$  Calc.: C, 52.75; H, 5.49%. IR  $\nu(\text{CO})$  (KBr): 2006vs, 1987vs, 1959vs, 1929s, 1905vs  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR  $\delta$  ( $\text{CDCl}_3$ ): 7.42 (m, 20H,  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ), 3.48 (dt,  $^2J(\text{PH}) = 12.6$  Hz, 2H,  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ), 2.32–0.80 (m, 44H,  $\text{C}_6\text{H}_{11}$ ), -15.62 (m, 1H,  $\mu\text{-H}$ ), -17.56 (m, 1H,  $\mu\text{-H}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR  $\delta$  ( $\text{CDCl}_3$ ): 199.3 (m,  $\mu\text{-PCy}_2$ ), 177.7 (m,  $\mu\text{-PCy}_2$ ), 28.4 (m,  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ). MS: 1171,  $[\text{M}-3\text{CO}]^+$ ; 1143,  $[\text{M}-4\text{CO}]^+$ ; 1115,  $[\text{M}-5\text{CO}]^+$ ; 1087,  $[\text{M}-6\text{CO}]^+$ .

#### 4. X-ray structure determinations

See Table 3 for crystal data and refinement details.

##### 4.1. Data collection and reduction

Crystals were mounted on glass fibres in inert oil and transferred to the cold gas stream of the diffractometer (Siemens R4 for 4, Stoe STADI-4 for 7, both with Siemens LT-2 low temperature attachment). Monochromated Mo K  $\alpha$  radiation was employed. The orientation matrix for 4 was refined from setting angles of 65 reflections in the  $2\theta$  range 10–23°. The cell constants for 7 were refined from  $\pm\omega$  angles of 48 reflections in the  $2\theta$  range 20–23°. Absorption corrections based on  $\psi$ -scans were applied.

##### 4.2. Structure solution and refinement

The structures were solved by direct methods and refined anisotropically on  $F^2$  (program system SHELXL-93 [13]). For 4 the oxygen atom of THF was disordered over two sites. Non-hydridic H atoms were included using a riding model or rigid methyl groups. Despite the presence of crystal solvent, cluster H atoms could be located directly in difference syntheses; they were refined with Ru–H restrained equal (in two classes for  $\mu_2$ - and  $\mu_3$ -H). The weighting schemes were of the form  $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ , with  $P = (F_o^2 + 2F_c^2)/3$ . Full details of the structure determinations have been deposited at the Fachinformationszentrum

Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, from where this material may be obtained on quoting the full literature citation and the reference number CSD 404361 (4), 404362 (7).

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