

Synthesis of triruthenium clusters containing mixed bridging phosphido ligands: X-ray crystal structures of $[\text{Ru}_3(\text{CO})_7(\mu\text{-H})(\mu\text{-PBU}_2^t)(\mu\text{-PCy}_2)_2]$ and the electron-deficient complex $[\text{Ru}_3(\mu\text{-CO})(\text{CO})_5(\mu\text{-H})_2(\mu\text{-PBU}_2^t)_2(\text{Bu}_2^t\text{PH})]$ ¹

Marion Graf, Kurt Merzweiler, Clemens Bruhn, Hans-Christian Böttcher *

Institut für Anorganische Chemie der Martin-Luther-Universität Halle-Wittenberg, Kurt-Mothes-Str. 2, D-06120 Halle / Saale, Germany

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Abstract

The reaction of the triruthenium cluster $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-PBU}_2^t)]$ (**1**) with Cy_2PH has been investigated. Complex **1** reacts spontaneously with the phosphine in toluene at room temperature. Subsequent heating under reflux for a short time affords the two novel mixed phosphido-bridged complexes $[\text{Ru}_3(\text{CO})_7(\mu\text{-H})(\mu\text{-PBU}_2^t)(\mu\text{-PCy}_2)_2]$ (**2**) and $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-PBU}_2^t)(\mu\text{-PCy}_2)]$ (**3**) in good yields beside the electron-deficient 46-electron cluster $[\text{Ru}_3(\mu\text{-CO})(\text{CO})_5(\mu\text{-H})_2(\mu\text{-PBU}_2^t)_2(\text{Bu}_2^t\text{PH})]$ (**4**) as minor product. Compound **1** reacts with stoichiometric amounts of Bu_2^tPH to give **4** in nearly quantitative yield. The metal cluster **2** was also synthesized directly by reaction of $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-PCy}_2)_2]$ (**5**) with Bu_2^tPH in refluxing toluene. **5** reacts with $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm) in toluene under reflux to give $[\text{Ru}_3(\text{CO})_6(\mu\text{-H})_2(\mu\text{-PCy}_2)_2(\mu\text{-dppm})]$ (**6**), but is formed only in traces under these conditions. The characterization of the compounds **2**, **3** and **4** was carried out by spectroscopic means and the X-ray crystal structures of **2** and **4** are reported. © 1998 Elsevier Science S.A.

Keywords: Ruthenium; Cluster; Carbonyl; Phosphido-bridged; Crystal structure

1. Introduction

Over the past two decades, there has been increasing interest in the chemistry of transition metal complexes containing phosphido groups because of the favorable bridging characteristics of these ligands for the synthesis of polynuclear compounds, e.g., Refs. [1–25]. Examples of dinuclear complexes containing different types of phosphido bridges, i.e., where the substituents R on each phosphido group are dissimilar, are rare [16–25]. To our knowledge, trinuclear metal clusters which exhibit different bridging phosphido ligands are still unknown. As part of a study of the chemistry of transition metal complexes containing bulky phosphido groups (e.g., $\mu\text{-PBU}_2^t$) we are investigating reactions of the

trimetal cluster $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-PBU}_2^t)]$ (**1**) [26] with phosphine ligands [27]. In the present study we describe reactions of compound **1** with secondary phosphines R_2PH ($\text{R} = \text{Cy}, \text{Bu}^t$). We report a synthetic method for mixed phosphido-bridged triruthenium clusters and the crystal structures of the compounds $[\text{Ru}_3(\text{CO})_7(\mu\text{-H})(\mu\text{-PBU}_2^t)(\mu\text{-PCy}_2)_2]$ (**2**) and the electron-deficient complex $[\text{Ru}_3(\mu\text{-CO})(\text{CO})_5(\mu\text{-H})_2(\mu\text{-PBU}_2^t)_2(\text{Bu}_2^t\text{PH})]$ (**4**).

2. Results and discussion

2.1. Reactions of $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-PBU}_2^t)]$ with Cy_2PH

Treatment of $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-PBU}_2^t)]$ (**1**) with Cy_2PH (molar ratio 1:1.5) in toluene at room temperature affords immediately reaction with a colour change from purple to red-orange. Subsequent heating of the

* Corresponding author.

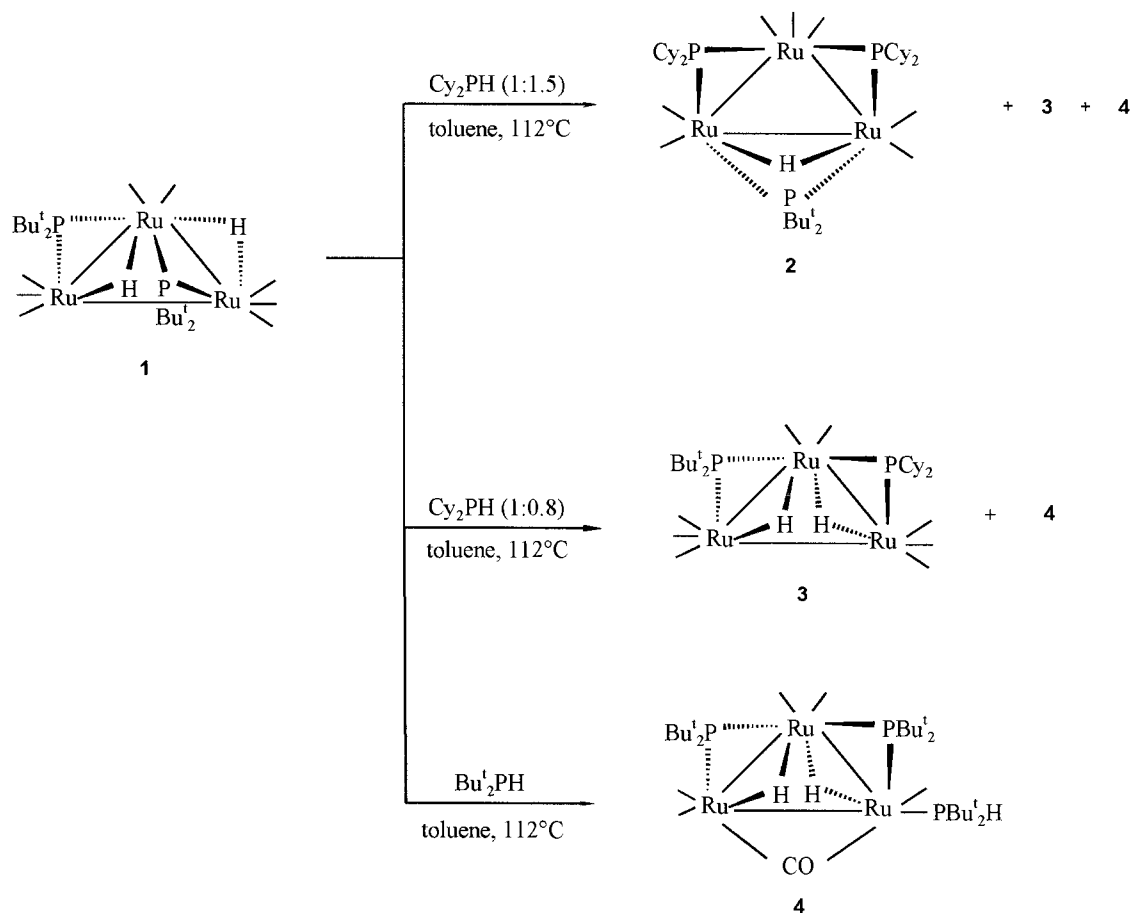
¹ Dedicated to Professor Gottfried Huttner on the occasion of his 60th birthday.

mixture for a few minutes under reflux results in no further significant colour change. These reaction conditions have to be followed, since otherwise other products are formed. Cooling to room temperature, removal of the solvent and subsequent crystallization from hexane affords orange crystals in good yield which could be identified as the mixed phosphido-bridged cluster $[\text{Ru}_3(\text{CO})_7(\mu\text{-H})(\mu\text{-PBU}_2^t)(\mu\text{-PCy}_2)_2]$ (**2**) (Scheme 1).

On the contrary, the reaction of complex **1** with Cy_2PH (molar ratio 1:0.8) under the same conditions, as described before, results in a mixture of two compounds which could be separated by column chromatography on alumina. At first a red band was eluted with hexane containing the mixed phosphido-bridged cluster $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-PBU}_2^t)(\mu\text{-PCy}_2)]$ (**3**). Subsequently, a brown band was obtained with hexane/diethyl ether (1:3) as eluent containing the novel electron-deficient cluster $[\text{Ru}_3(\mu\text{-CO})(\text{CO})_5(\mu\text{-H})_2(\mu\text{-PBU}_2^t)_2(\text{Bu}_2^t\text{PH})]$ (**4**) in low yield (Scheme 1). The complexes **2–4** were fully characterized by microanalyses, spectroscopic means (IR, NMR and MS), and the molecular structures of the compounds **2** and **4** were determined by single crystal X-ray analyses.

The infrared spectrum of complex **2** shows $\nu(\text{CO})$ absorption bands only in the region characteristic of terminal carbonyl ligands, and the band pattern is comparable to that of $[\text{Ru}_3(\text{CO})_7(\mu\text{-H})(\mu\text{-PPh}_2)_3]$ [28,29]. The ^1H NMR spectrum of **2** (C_6D_6) in the region characteristic of metal-hydride resonances exhibits a doublet of triplets centered at $\delta -18.22$ according to the X part of an AM_2X spin system [$^2J(\text{PH}) = 20.5$, $^2J(\text{PH}) = 13.6$ Hz]. These data imply couplings of one hydride ligand to two chemically equivalent and one non-equivalent phosphorus nuclei and are consistent with the found solid state structure (vide infra). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **2** (CDCl_3) shows an AM_2 pattern with resonances centered at δ 246.08 (t, $\mu\text{-PBU}_2^t$) and δ 195.29 (d, $\mu\text{-PCy}_2$) with $^2J(\text{PP}) = 111.2$ Hz, also consistent with the structure in the solid state. In the mass spectrum of **2** (70 eV, EI) no molecular ion peak could be observed (peak with the largest mass: $m/z = 987$, probably $[\text{M}-2\text{CO}]^+$, related to ^{102}Ru).

The infrared spectrum of **3** shows $\nu(\text{CO})$ absorption bands corresponding to terminal carbonyl ligands, and the band pattern is comparable to that observed for the



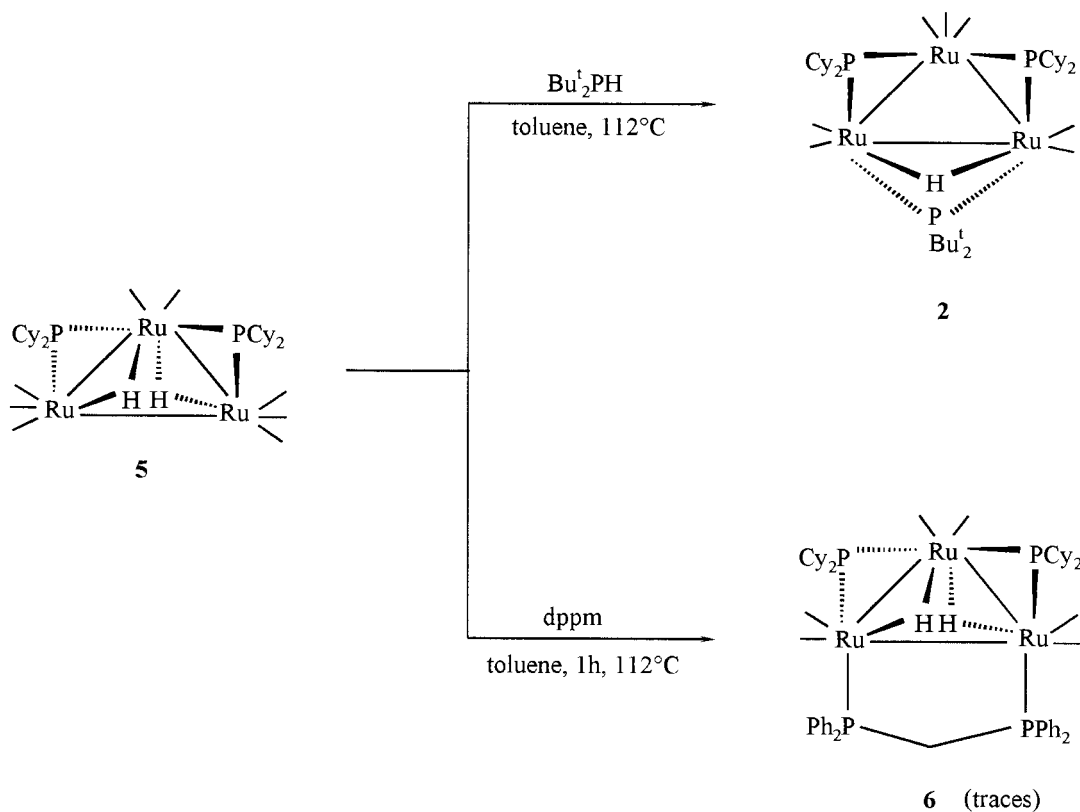
Scheme 1.

complexes $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-PPh}_2)_2]$ [28–30] and $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-PCy}_2)_2]$ [31], respectively. The ^1H NMR spectrum of complex **3** (CDCl_3) in the metal-hydride region shows two complex resonances centered at $\delta -17.13$ (m, 1H) and -17.81 (m, 1H). According to the related structures [28–30], we assume that these two hydride ligands occupy bridging sites across two Ru–Ru bonds and opposite to the phosphido groups. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** (CDCl_3) exhibits two well separated doublets at $\delta 255.98$ and 212.76 with $^2J(\text{PP}) = 98.3$ Hz, consistent with two chemically non-equivalent phosphido groups bridging metal–metal bonds. The complete spin system inclusive both hydrides is probably of AMXX' type. This could be an explanation for the complexity of the two different hydride resonances in the proton NMR spectrum. The mass spectrum of **3** (70 eV, EI) contains the molecular ion peak at $m/z = 874$ corresponding to the formulation as $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-PBu}_2^t)(\mu\text{-PCy}_2)]$.

The infrared spectrum of compound **4** shows, beside strong $\nu(\text{CO})$ absorption bands corresponding to terminal carbonyls, a medium strong band indicating a bridging carbonyl ligand (1740 cm^{-1} , KBr). The ^1H NMR spectrum of **4** (CDCl_3) contains beside the signals for the Bu_2^tPH and the $\mu\text{-PBu}_2^t$ ligands, respectively, two complex multiplets centered at $\delta -14.37$ (m, 1H) and -14.97 (m, 1 H) corresponding to two non-equivalent bridging hydrides. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4**

(C_6D_6) exhibits three well separated signals (spin system AMX) with chemical shifts at $\delta 216.81$ (dd), 178.41 (dd), and 53.82 (dd). The peak pattern at $\delta 216.81$ illustrates couplings of two non-equivalent bridging phosphorus nuclei [$^2J(\text{P}_A\text{P}_M) = 87.9$, $^2J(\text{P}_A\text{P}_X) = 138.4$ Hz]. The signal at $\delta 178.41$ is assigned to the second phosphido bridge [$^2J(\text{P}_A\text{P}_M) = 87.9$, $^3J(\text{P}_M\text{P}_X) = 5.2$ Hz], and the resonance of the Bu_2^tPH at $\delta 53.82$ shows couplings to both bridging phosphorus [$^2J(\text{P}_A\text{P}_X) = 137.1$, $^3J(\text{P}_M\text{P}_X) = 5.2$ Hz].

The partial exchange of the $\mu\text{-PBu}_2^t$ groups in **1** towards $\mu\text{-PCy}_2$ ligands during the formation of compounds **2** and **3** is a rare example in the chemistry of phosphido-bridged species. A similar substitution of the bulky ligand Bu_2^tPH by less encumbered phosphines was recently described by Leoni et al., e.g., $[\text{Pd}_2(\mu\text{-PBu}_2^t)(\mu\text{-PBu}_2^t\text{H})(\text{Bu}_2^t\text{PH})_2]\text{X}$ reacts easily with PCy_2H giving $[\text{Pd}_2(\mu\text{-PBu}_2^t)(\text{Cy}_2\text{PH})_4]\text{X}$. Moreover, an interchange of the phosphido and secondary phosphine ligands was observed. So isomerizes $[\text{Pd}_2(\mu\text{-PBu}_2^t)(\text{Cy}_2\text{PH})_3(\text{CO})]\text{X}$ in solution to its thermodynamically more stable isomer $[\text{Pd}_2(\mu\text{-PCy}_2)(\text{Cy}_2\text{PH})_2(\text{Bu}_2^t\text{PH})(\text{CO})]\text{X}$, probably via the intermediate $[\text{Pd}_2(\mu\text{-PBu}_2^t)(\mu\text{-PCy}_2\text{H})(\text{Cy}_2\text{PH})_2]\text{X}$ with a Pd–H–P agostic interaction ($\text{X} = \text{BF}_4^-, \text{CF}_3\text{SO}_3^-$) [32]. Furthermore, a substitution of a $\mu\text{-PCy}_2$ group by a $\mu\text{-PPh}_2$ moiety was also observed during the thermolysis of $[\text{Fe}_2(\mu\text{-CO})(\text{CO})_4(\mu\text{-H})(\mu\text{-PCy}_2)(\mu\text{-dppm})]$ with



Scheme 2.

PPh_2H , whereat the expected compound $[\text{Fe}_2(\text{CO})_4(\mu\text{-PCy}_2)(\mu\text{-PPh}_2)(\mu\text{-dppm})]$ as well as the unexpected complex $[\text{Fe}_2(\text{CO})_4(\mu\text{-PPh}_2)_2(\mu\text{-dppm})]$ were formed [33].

2.2. Synthesis of $[\text{Ru}_3(\mu\text{-CO})(\text{CO})_5(\mu\text{-H})_2(\mu\text{-PBu}'_2)_2(\text{Bu}'_2\text{PH})]$ (**4**)

The very low yield of compound **4** in the synthetic procedure described before, prompted us to investigate the reaction of the compound **1** with $\text{Bu}'_2\text{PH}$. Treatment of equimolar amounts of **1** and the phosphine in toluene at room temperature and subsequent heating under reflux for a short time (ca. 5 min) afforded indeed the electron-deficient metal cluster **4** in nearly quantitative yield (see Section 3). In this context we became interested to prove a similar reaction of the known cluster $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-PCy}_2)_2]$ (**5**) [31] with $\text{Bu}'_2\text{PH}$ in order to obtain the electronically saturated complex $[\text{Ru}_3(\text{CO})_7(\mu\text{-H})_2(\mu\text{-PCy}_2)_2(\text{Bu}'_2\text{PH})]$ (**6**) or the electron-deficient analogue to **4**, respectively. However, we can state that treatment of **5** with equimolar amounts of the phosphine in THF at room temperature afforded no reaction. The same result was even observed in the presence of sodium diphenylketyl and reaction in refluxing THF for 1 h, respectively. Heating an equimolar mixture of complex **5** and $\text{Bu}'_2\text{PH}$ in hexane under reflux for 30 min afforded also no detectable amounts of complex **6**. Furthermore, treatment of the same mixture of compounds in methanol in the presence of equimolar amounts $\text{Me}_3\text{NO}_{x2}\text{H}_2\text{O}$ under reflux for 1 h does even not result in the formation of any traces of complex **6**. Moreover, attempts of a photochemically initiated carbonyl substitution by the phosphine (THF, 3 h, $h\nu$) failed also. Surprisingly, increasing the reaction temperature to 80°C (1 h) in benzene resulted directly in the formation of compound **2** to a considerable extent.

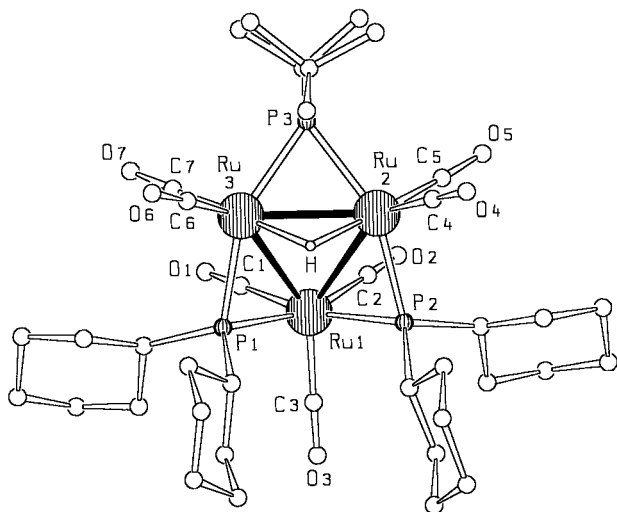


Fig. 1. The molecular structure of $[\text{Ru}_3(\text{CO})_7(\mu\text{-H})(\mu\text{-PBu}'_2)(\mu\text{-PCy}_2)_2]$ (**2**).

Table 1
Selected bond lengths [\AA] and bond angles [$^\circ$] for **2**

Ru(1)–Ru(3)	3.096(1)	Ru(2)–Ru(3)	2.788(1)
Ru(1)–Ru(2)	3.105(1)	Ru(3)–H	1.91
Ru(1)–P(1)	2.430(2)	Ru(1)–C(1)	1.94(1)
Ru(1)–P(2)	2.420(2)	Ru(1)–C(2)	1.94(1)
Ru(2)–P(2)	2.341(2)	Ru(1)–C(3)	1.89(1)
Ru(2)–P(3)	2.370(2)	Ru(2)–C(4)	1.87(1)
Ru(3)–P(1)	2.329(2)	Ru(2)–C(5)	1.86(1)
Ru(3)–P(3)	2.365(2)	Ru(3)–C(6)	1.84(1)
Ru(2)–H	1.92	Ru(3)–C(7)	1.86(1)
Ru(1)–Ru(2)–Ru(3)	63.10(2)	P(1)–Ru(1)–C(2)	163.5(3)
Ru(1)–Ru(3)–Ru(2)	63.45(2)	C(1)–Ru(1)–C(2)	84.7(4)
Ru(3)–Ru(1)–Ru(2)	53.44(2)	P(1)–Ru(1)–C(3)	94.7(3)
Ru(1)–P(1)–Ru(3)	81.12(7)	P(2)–Ru(1)–C(3)	91.9(3)
Ru(1)–P(2)–Ru(2)	81.41(7)	C(3)–Ru(1)–C(2)	100.3(4)
Ru(2)–P(3)–Ru(3)	72.16(7)	C(3)–Ru(1)–C(1)	98.2(4)
Ru(2)–H–Ru(3)	93.7	C(4)–Ru(2)–C(5)	87.1(5)
P(1)–Ru(1)–P(2)	100.26(8)	C(4)–Ru(2)–P(2)	99.2(3)
P(1)–Ru(3)–P(3)	152.67(8)	H–Ru(2)–C(5)	175.3
P(2)–Ru(2)–P(3)	153.24(8)	H–Ru(2)–C(4)	89.2
C(7)–Ru(3)–H	178.1	C(6)–Ru(3)–H	89.9
P(2)–Ru(2)–H	88.6	P(3)–Ru(2)–C(5)	96.4(4)
P(1)–Ru(3)–H	84.1	P(3)–Ru(2)–C(4)	105.5(3)
P(1)–Ru(1)–C(1)	86.5(3)		

Under these conditions there was also no evidence for complex **6** as an intermediate. Further elevation of the temperature by refluxing in toluene allowed us to develop a high yield synthesis of **2** (Scheme 2).

To examine if any carbonyl substitution towards phosphines in compound **5** is possible at all, we investigated the reaction of **5** with $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm), whereat the known complex $[\text{Ru}_3(\text{CO})_6(\mu\text{-H})_2(\mu\text{-PCy}_2)_2(\mu\text{-dppm})]$ (**7**) [34] should result. However, **5** does not react with dppm in THF even in the presence of catalytic amounts of sodium diphenylketyl at 50°C . Furthermore, heating in toluene for 1 h under reflux afforded compound **7** only in detectable traces (Scheme 2), i.e., the synthesis of **7** by reaction of $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})]$ with Cy_2PH [34] is clearly favoured. These results have been somewhat frustrating, but they confirm the observation by Keister and co-workers of a complete lack of reactivity of complex **5** [31].

2.3. Molecular structure of $[\text{Ru}_3(\text{CO})_7(\mu\text{-H})(\mu\text{-PBu}'_2)(\mu\text{-PCy}_2)_2]$ (**2**)

Compound **2** crystallizes from dichloromethane in the orthorhombic space group $Pcab$ with eight molecules in the unit cell. The molecular structure of **2** is shown in Fig. 1, selected bond lengths and angles are summarized in Table 1.

The molecule consists of a triruthenium core bridged by two PCy_2 groups and one PBu'_2 group. Furthermore, a bridging hydride between Ru(2) and Ru(3) could be localized. Two similar Ru–Ru bond lengths with $\text{Ru}(1)\text{--Ru}(3) = 3.096(1)$ and $\text{Ru}(1)\text{--Ru}(2) = 3.105(1)$ \AA

and a shorter hydride-bridged bond $\text{Ru}(2)\text{--Ru}(3) = 2.788(1) \text{ \AA}$ were determined. Relative to 'normal' Ru–Ru bond distances (2.70–2.95 \AA [35]), the only phosphido-bridged bonds are substantially lengthened. However, these bonding characteristics are in good agreement with those found for the closely related molecules $[\text{Ru}_3(\text{CO})_7(\mu\text{-H})(\mu\text{-PPh}_2)_3]$ [28,29] and $[\text{Ru}_3(\text{CO})_7(\mu\text{-H})(\mu\text{-PCy}_2)_3]$ (3.034(1) and 3.013(1) vs. 2.808(1) \AA) [36]. The hydride ligand in **2** was found to be symmetrically arranged ($\text{Ru}(2)\text{--H}$, 1.92; $\text{Ru}(3)\text{--H}$, 1.91 \AA). The Ru–P distances for the bridging phosphorus atoms which are situated *trans* to the carbonyl ligands [$\text{Ru}(1)\text{--P}(1)$ and $\text{Ru}(1)\text{--P}(2)$, av. 2.425(2) \AA] are substantially longer than the other Ru–P bonds (av. 2.351(2) \AA), and this trend was also observed for $[\text{Ru}_3(\text{CO})_7(\mu\text{-H})(\mu\text{-PPh}_2)_3]$ [28,29] and $[\text{Ru}_3(\text{CO})_7(\mu\text{-H})(\mu\text{-PCy}_2)_3]$ [36].

2.4. Molecular structure of $[\text{Ru}_3(\mu\text{-CO})(\text{CO})_5(\mu\text{-H})_2(\mu\text{-PBu}_2)_2(\text{Bu}_2\text{PH})]$ (**4**)

Compound **4** crystallizes from dichloromethane/hexane in the monoclinic space group $P2_1/a$ with four molecules in the unit cell. The molecular structure of **4** is shown in Fig. 2, selected bond lengths and angles are summarized in Table 2.

The molecule of **4** consists of a trimetal core with three differently substituted Ru atoms and three very different metal–metal distances were observed (see Table 2). The most remarkable difference between the structures of **1** and **4** is that in **4** one carbonyl ligand on Ru(1) has been replaced by Bu_2PH . The substitution is accompanied by the loss of a terminal carbonyl group on another Ru atom, namely Ru(3), probably by sterical reasons. Therefore, the overall molecular structure ex-

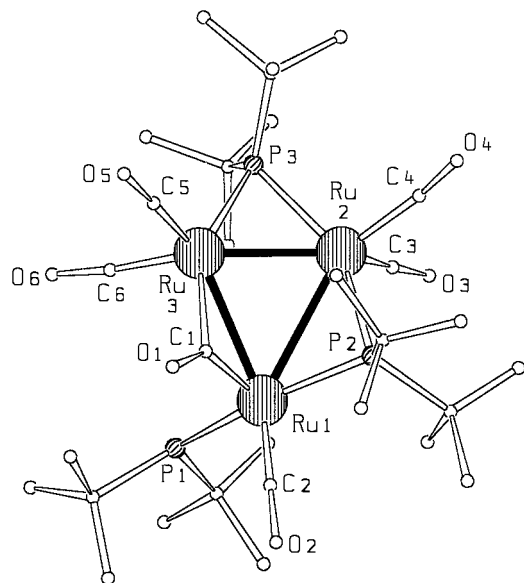


Fig. 2. The molecular structure of $[\text{Ru}_3(\mu\text{-CO})(\text{CO})_5(\mu\text{-H})_2(\mu\text{-PBu}_2)_2(\text{Bu}_2\text{PH})]$ (**4**).

Table 2
Selected bond lengths [\AA] and bond angles [$^\circ$] for **4**

Ru(1)–Ru(2)	3.154(3)	Ru(1)–C(1)	1.91(4)
Ru(2)–Ru(3)	2.722(3)	Ru(1)–C(2)	1.81(3)
Ru(1)–Ru(3)	2.965(3)	Ru(2)–C(3)	1.83(3)
Ru(1)–P(1)	2.425(8)	Ru(2)–C(4)	1.83(4)
Ru(1)–P(2)	2.352(7)	Ru(3)–C(5)	1.81(4)
Ru(2)–P(2)	2.407(6)	Ru(3)–C(6)	1.80(3)
Ru(2)–P(3)	2.426(7)	Ru(3)–C(1)	2.15(3)
Ru(3)–P(3)	2.401(7)		
Ru(1)–Ru(2)–Ru(3)	60.07(8)	Ru(2)–Ru(1)–P(2)	49.3(2)
Ru(2)–Ru(1)–Ru(3)	52.73(7)	Ru(1)–P(2)–Ru(2)	83.0(2)
Ru(1)–Ru(3)–Ru(2)	67.20(8)	Ru(2)–P(3)–Ru(3)	68.7(2)
Ru(1)–Ru(3)–C(1)	39.9(10)	P(3)–Ru(2)–Ru(3)	55.2(2)
Ru(3)–Ru(1)–C(1)	46.2(8)	Ru(3)–P(3)–Ru(2)	68.7(2)
Ru(1)–C(1)–Ru(3)	94.0(2)	Ru(2)–Ru(1)–P(1)	121.4(2)
Ru(3)–C(1)–O(1)	129.0(2)	P(1)–Ru(1)–P(2)	159.5(3)
Ru(1)–C(1)–O(1)	137.0(2)	P(1)–Ru(1)–C(2)	91.9(9)
P(3)–Ru(2)–P(2)	150.3(3)	P(1)–Ru(1)–C(1)	104.8(9)
Ru(1)–Ru(2)–P(2)	47.7(2)		

hibits only 46 c.v.e. (cluster valence electrons) and compound **4** can be considered as an 'electron-deficient' trinuclear species. Normally, the replacement of one carbonyl on Ru(1) by the bulky phosphine might be expected to result in a further loss of CO from the same metal center. However, the increased electron density on Ru(1), due to the presence of the σ -donating phosphine ligand, may increase the Ru(1)–CO π -backbonding strength and therefore prevent the loss of carbonyls. As a further consequence of the electronical unsaturation [formally 16 electrons on Ru(3)] a semibridging carbonyl ligand [C(1)–O(1)] across Ru(1)–Ru(3) is formed ($\alpha = 0.126$, criterion for semibridging carbonyls [37]), which is clearly indicated in the infrared spectra. The composition of **4** is closely related to $[\text{Os}_3(\text{CO})_6(\mu\text{-H})_2(\mu\text{-PBu}_2)_2(\text{Bu}_2\text{PH})]$ (46 c.v.e.) [38], however, in the molecular structure of the latter no semibridging carbonyl group could be found. This lack of bridging carbonyls, compared with the situation in the structure of **4**, confirms the tendency of the carbonyl-bridging ability of the higher elements to decrease. The hydrogen of the secondary phosphine on P(1) could not be localized during the X-ray diffraction study.

Although two different hydrides, which have been unambiguously detected in the proton NMR spectrum of **4**, were not located in the X-ray analysis, it is reasonable to assume that one hydride occupies a bridging site across the shortest Ru–Ru bond [$\text{Ru}(2)\text{--Ru}(3) = 2.722(3) \text{ \AA}$] and opposite to the phosphido group P(3). The location of the second hydride remains uncertain, an assignment across the second shortest Ru–Ru bond [$\text{Ru}(1)\text{--Ru}(3)$] seems to be possible, however the bridging position on $\text{Ru}(1)\text{--Ru}(2)$ cannot be ruled out with certainty.

3. Experimental

All manipulations were performed under oxygen-free argon using conventional Schlenk techniques. Solvents were dried over molecular sieves or sodium/benzophenone ketyl and were distilled under argon prior to use. Starting materials were either commercially available or were prepared according to literature procedures. IR spectra were obtained using a Mattson 5000 instrument. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on the spectrometer WP 200 (^1H at 199.975 MHz, $^{31}\text{P}\{^1\text{H}\}$ NMR at 80.950 MHz). The mass spectra were obtained on a Hitachi Perkin Elmer RMU 6, Nermag R30-10 instrument. The elemental analyses were performed by the Analytisches Laboratorium des Pharmazeutischen Institutes der Martin-Luther-Universität Halle-Wittenberg.

3.1. Reaction of $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-P}Bu_2^t)_2]$ (**1**) with C_y_2PH

A solution of C_y_2PH (18 mg, 0.09 mmol) in 20 ml of toluene was added slowly to a solution of **1** (50 mg, 0.06 mmol) in 20 ml of toluene at room temperature. The colour of the solution changes immediately from violet to red-orange. The mixture was heated under reflux for ca. 2 min. After cooling to room temperature and removal of the solvent the residue was dissolved in 30 ml of hexane. The volume of the solution was reduced to 10 ml in vacuo, compound **2** crystallizes as orange powder at room temperature and a second fraction from the filtrate by cooling to -30°C overnight (total yield: 43 mg, 68%).

2: Anal. Found: C, 45.49; H, 6.02, P, 8.76%; M, 1040.06 (calc.). $\text{C}_{39}\text{H}_{63}\text{O}_7\text{P}_3\text{Ru}_3$ calc.: C, 45.04; H, 6.11 P, 8.93%. IR $\nu(\text{CO})$ (KBr): 2043s, 1990vs, 1972vs, 1947s cm^{-1} . ^1H NMR (C_6D_6): 2.30–0.80 (m, 44H, C_6H_{11}), -18.22 (m, 1H, $\mu\text{-H}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): 246.08 (t, $^2J(\text{PP}) = 111.2$ Hz, $\mu\text{-P}Bu_2^t$), 195.29 (d, $^2J(\text{PP}) = 111.2$ Hz, $\mu\text{-PCy}_2$). MS: 987, $[\text{M}-2\text{CO}]^+$.

3.2. Synthesis of $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-P}Bu_2^t)(\mu\text{-PCy}_2)]$ (**3**) and $[\text{Ru}_3(\mu\text{-CO})(\text{CO})_5(\mu\text{-H})_2(\mu\text{-P}Bu_2^t)_2(\text{Bu}_2^t\text{PH})]$ (**4**) from **1** and C_y_2PH

A solution of C_y_2PH (10 mg, 0.05 mmol) in 20 ml of toluene was added slowly to a solution of **1** (50 mg, 0.06 mmol) in 20 ml of toluene at room temperature. The colour of the solution changed from violet to red-orange. The mixture was heated under reflux for ca. 2 min. After cooling to room temperature and removal of the solvent the residue was dissolved in 20 ml of hexane and separated by column chromatography on alumina with hexane as eluent. At first a red band containing **3** was obtained (27 mg, 52%). Further elu-

tion with a mixture of hexane-diethyl ether (1:3) afforded an orange fraction containing **4** (11 mg, 17%).

3: Anal. Found: C, 38.55; H, 4.78; P, 7.38%; M, 871.79 (calc.). $\text{C}_{28}\text{H}_{42}\text{O}_8\text{P}_2\text{Ru}_3$; C, 38.45; H, 4.84; P, 7.09%. IR $\nu(\text{CO})$ (KBr): 2066s, 2025sh, 2016vs, 1995vs, 1957s, 1937s cm^{-1} . ^1H NMR (CDCl_3): 1.67–1.12 (m, 22H, C_6H_{11}), 1.00 (d, $^3J(\text{PH}) = 14.3$ Hz, 18H, $\mu\text{-P}Bu_2^t$), -17.13 (m, 1H, $\mu\text{-H}$), -17.81 (m, 1H, $\mu\text{-H}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): 255.98 (d, $^2J(\text{PP}) = 98.3$ Hz); 212.76 (d, $^2J(\text{PP}) = 98.3$ Hz). MS: 874, M^+ ; 846, $[\text{M}-\text{CO}]^+$; 818, $[\text{M}-2\text{CO}]^+$; 790, $[\text{M}-3\text{CO}]^+$; 762, $[\text{M}-4\text{CO}]^+$; 734, $[\text{M}-5\text{CO}]^+$; 706, $[\text{M}-6\text{CO}]^+$; 678, $[\text{M}-7\text{CO}]^+$; 650, $[\text{M}-8\text{CO}]^+$.

4: Anal. Found: C, 39.76; H, 6.47; P, 9.93%; M, 909.91 (calc.). $\text{C}_{30}\text{H}_{57}\text{O}_6\text{P}_3\text{Ru}_3$; C, 39.47; H, 6.30; P, 10.19%. IR $\nu(\text{CO})$ (KBr): 2025s, 2006vs, 1957vs, 1907s, 1740m cm^{-1} . ^1H NMR (CDCl_3): 4.47 (d, $J(\text{PH}) = 301.5$ Hz, 1H, Bu_2^tPH), 1.39 (m, $N = 87.1$ Hz, 36H, $\mu\text{-P}Bu_2^t$), 0.86 (d, $^3J(\text{PH}) = 13.6$ Hz, 18H, Bu_2^tPH), -14.37 (m, 1H, $\mu\text{-H}$), -14.97 (m, 1H, $\mu\text{-H}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): 216.81 (dd, $^2J(\text{PP}) = 87.9$ Hz, $^2J(\text{PP}) = 138.4$ Hz); 178.41 (dd, $^2J(\text{PP}) = 91.5$ Hz, $^3J(\text{PP}) = 5.2$ Hz); 53.82 (dd, $^2J(\text{PP}) = 137.1$ Hz; $^3J(\text{PP}) = 5.2$ Hz). MS: 856 $[\text{M}-2\text{CO}]^+$, 828 $[\text{M}-3\text{CO}]^+$, 800 $[\text{M}-4\text{CO}]^+$.

3.3. Synthesis of **2** from **5** and Bu_2^tPH

A mixture of **5** (325 mg, 0.33 mmol) and Bu_2^tPH (48 mg, 0.33 mmol) was heated in refluxing toluene (30 ml) for 2 h. After cooling to room temperature and removal of the solvent the remaining residue was dissolved in 30 ml of hexane. The volume of the solution was reduced to 10 ml in vacuo, complex **2** crystallizes as orange powder by cooling to -30°C overnight (yield: 344 mg, 72%).

3.4. Synthesis of **4** from **1** and Bu_2^tPH

A mixture of **1** (100 mg, 0.12 mmol) and Bu_2^tPH (18 mg, 0.12 mmol) was heated in toluene (20 ml) under reflux for ca. 5 min. The colour of the solution turns from purple to dark brown. After cooling to room temperature and removal of the solvent the remaining residue was dissolved in 20 ml of hexane. The volume of the solution was reduced to ca. 5 ml in vacuo, complex **4** crystallizes as dark brown powder by cooling to -30°C overnight (yield: 110 mg, nearly quantitative).

4. X-ray crystal structure determinations

Crystal data, data collection and refinement parameters for compounds **2** and **4** are summarized in Table 3. Crystals of **2** and **4** suitable for X-ray diffraction were grown from dichloromethane and from a dichloromethane/hexane mixture, respectively.

Table 3
Crystal data and structure refinement for **2** and **4**

Identification code	2	4
Empirical formula	C ₃₉ H ₆₃ O ₇ P ₃ Ru ₃ ·xCH ₂ Cl ₂	C ₃₀ H ₅₇ O ₆ P ₃ Ru ₃
Formula weight	1124.94	909.88
Temperature	R.T.	R.T.
Wavelength	0.71073 Å	0.71073 Å
Crystal system	orthorhombic	monoclinic
Space group	<i>Pcab</i> ^a	<i>P2</i> ₁ / <i>a</i>
Unit cell dimensions	<i>a</i> = 16.143(3) Å <i>b</i> = 17.269(2) Å <i>c</i> = 34.158(5) Å $\alpha = \beta = \gamma = 90.0^\circ$	<i>a</i> = 9.836(3) Å <i>b</i> = 37.327(12) Å <i>c</i> = 11.203(3) Å $\alpha = \gamma = 90.0^\circ; \beta = 105.48(3)$
Volume	9522(3) Å ³	3964(2) Å ³
Z	8	4
Density (calculated)	1.569 g cm ⁻³	1.525 g cm ⁻³
Absorption coefficient	1.196 mm ⁻¹	1.284 mm ⁻¹
<i>F</i> (000)	4576	1848
θ range for data collection	1.83 to 24.04°	1.96 to 22.50°
Index ranges	-18 ≤ <i>h</i> ≤ 18 -18 ≤ <i>k</i> ≤ 19 -38 ≤ <i>l</i> ≤ 38	-11 ≤ <i>h</i> ≤ 10 -44 ≤ <i>k</i> ≤ 44 -13 ≤ <i>l</i> ≤ 13
Reflections collected	54 689	12 397
Independent reflections	7448	4694
<i>R</i> _{int}	0.0797	0.2624
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data/restraints/parameters	7442/0/473	4694/0/199
Goodness-of-fit on <i>F</i> ²	1.066	0.830
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.065 <i>wR</i> 2 = 0.2337	<i>R</i> 1 = 0.0823 <i>wR</i> 2 = 0.1571
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0854 <i>wR</i> 2 = 0.2550	<i>R</i> 1 = 0.2433 <i>wR</i> 2 = 0.2303
Largest diff. peak and hole	4.303 and -0.462 e Å ⁻³	0.959 and -1.608 e Å ⁻³

^aStandard cell setting and transformation matrix for **2**: *Pbca* (1000 – 1010).

For data collection the diffractometer Stoe-IPDS was used. The structures were solved by direct methods and refined on *F*² (program systems: SHELXS-86 [39], SHELXL-93 [40]). The remaining high residual electron density for **2** is caused by a solvent molecule in the unit cell which was not further refinable. Due to the very small size of the crystals of **4** (approximately 0.05 × 0.05 × 0.10 mm³) only a low quality intensity data set could be obtained which yielded a relative high, but just tolerable *R*1 value of 8.23%. Full details of the structure determinations have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information, D-76344 Eggenstein-Leopoldshafen, Germany, from where this material may be ordered on quoting the full literature citation and the reference numbers CSD-407948 (**2**) and CSD-407947 (**4**).

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