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Reaction of $[\{CuCl(Bu^t_2PH)\}_4]$ with $[Ru_3(CO)_{12}]$: X-ray crystal structures of the chloride transfer products $[Ru_3(CO)_7(\mu\text{-}H)(\mu\text{-}PBu^t_2)_2(\mu\text{-}Cl)]$ and the electron-rich 50-electron cluster $[Ru_3(CO)_6(\mu\text{-}PBu^t_2)(\mu\text{-}Cl)_3(Bu^t_2PH)]$†

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Abstract—Treatment of CuCl with Bu^t_2PH in hexane afforded a colourless crystalline material which was characterized as $[\{CuCl(Bu^t_2PH)\}_4]$ (**1**) by an X-ray diffraction study. The reaction of **1** with $[Ru_3(CO)_{12}]$ in refluxing toluene leads to a mixture of products containing the electron-rich chloro-bridged cluster $[Ru_3(CO)_6(\mu\text{-}PBu^t_2)(\mu\text{-}Cl)_3(Bu^t_2PH)]$ (**2**) besides the electron-precise complexes $[Ru_3(CO)_7(\mu\text{-}H)(\mu\text{-}PBu^t_2)_2(\mu\text{-}Cl)]$ (**3**) and $[Ru_3(CO)_8(\mu\text{-}H)_2(\mu_3\text{-}PBu^{\prime})(Bu^t_2PH)]$ (**4**), respectively. No cluster expansion products were observed, therefore, the copper complex acts merely as phosphine and chloride transfer reagent. The molecular structures of the metal clusters **2** and **3** were determined by means of single-crystal X-ray structure analyses. © 1997 Elsevier Science Ltd

Keywords: copper; ruthenium; carbonyl; cluster; phosphido-bridged; chloro-bridged; crystal structure.

Complexes containing heteronuclear metal–metal bonds are of constant interest in view of site-selective reactivity and synergetic effects in catalytic reactions. Previously, we reported a new synthetic route to heteronuclear metal clusters by using oxidative addition reactions of metal halide complexes containing secondary phosphine ligands to neutral metal carbonyl compounds. Thus, the thermolysis of $[IrCl(Bu^t_2PH)_3]$ with $[Ru_3(CO)_{12}]$ in toluene occurs under cluster expansion and affords the butterfly configured cluster $[Ru_3Ir(CO)_7(\mu\text{-}H)_2(\mu\text{-}PBu^t_2)_2(Bu^t_2PH)(\mu_3\text{-}Cl)]$ [1]. This method works also for the analogous $[RhCl(Bu^t_2PH)_3]$, and in this way the tetrametal cluster $[Ru_3Rh(CO)_7(\mu_3\text{-}H)(\mu\text{-}PBu^t_2)_2(Bu^t_2PH)(\mu\text{-}Cl)_2]$ is obtained [2]. At present, we are interested in an expansion of this reaction principle to other transition metal complexes containing 3d metals. For this purpose we prepared the copper complex $[\{CuCl(Bu^t_2PH)\}_4]$ (**1**), and during the course of cluster expansion studies we investigated the reaction of **1** with $[Ru_3(CO)_{12}]$. In this paper we report the synthesis and structural characterization of two novel triruthenium clusters, namely $[Ru_3(CO)_6(\mu\text{-}PBu^t_2)(\mu\text{-}Cl)_3(Bu^t_2PH)]$ (**2**) and $[Ru_3(CO)_7(\mu\text{-}H)(\mu\text{-}PBu^t_2)_2(\mu\text{-}Cl)]$ (**3**), which have been obtained in the reaction mentioned before.

RESULTS AND DISCUSSION

Preparation and structural characterization of $[\{CuCl(Bu^t_2PH)\}_4]$ (**1**)

Treatment of equimolar amounts of Bu^t_2PH with solid CuCl in hexane afforded immediately a colour-

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† Dedicated to Professor Siegfried Engels on the occasion of his 65th birthday.

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less solution from which colourless crystals could be obtained by cooling to $-30°C$. Elemental analysis and the mass spectrum were consistent with the formulation of the compound as 1 : 1 complex. In the ^1H NMR spectrum of this complex a doublet for the equivalent protons of the Bu^t groups at δ 1.28 (d, $^3J_{PH} = 13.9$ Hz) and a doublet for the P–H group at 3.65 (d, $J_{PH} = 297.9$ Hz) were observed. The $^{31}P\{^1H\}$ NMR spectrum exhibits a broad singlet at δ 21.89 (C_6D_6). This value lies close to the chemical shift for the free ligand (Bu$^t_2$PH: δ 19.9 [3]). Such an observation is rare but not unusual, for instance [$Os_3(CO)_{10}$(Bu$^t_2$PH)$_2$] shows a similar effect (δ 21.46 [4]). Moreover, two aspects confirm the coordination of the phosphine: the high value of the PH coupling constant observed in the proton NMR spectrum (Bu$^t_2$PH: $J_{PH} = 197$ Hz [5]) and the line broadening of the signal observed in the $^{31}P\{^1H\}$ NMR spectrum which is interpreted due to the high quadrupol moment of the copper, see for instance Ref. [6].

The mass spectrum of this material contains only the molecular ion peak for the monomeric unit ($m/z = 244$). For Cu^I complexes with the composition [CuXL] (X = Halogen, L = phosphine) the tetrameric 'cubane' structure was found to be the most common in the solid state, although an open 'chair' or ('step') structure was also observed in several cases [7]. Moreover, in the case of very bulky phosphines the 'chair' form tends to break into smaller units, as observed for the halide-bridged dimer [{CuCl(PCy_3)}$_2$] [8]. Studies on complexes containing secondary phosphines are known [9], however, there is no X-ray structural information hitherto on such systems.

Therefore, determination of the structure of our 1 : 1 complex by a single-crystal X-ray diffraction study became desirable. Suitable crystals for a structure analysis were grown by slow cooling of hexane solution to $-30°C$. The results of the X-ray diffraction study showed that the complex possesses the usually observed cubane-type tetrameric structure. Figure 1 shows the molecular structure of [{CuCl(Bu$^t_2$PH)}$_4$] (**1**) while selected interatomic distances and angles are given in Table 1. The complex crystallizes from hexane in the triclinic space group $P\bar{1}$ (No. 2) with two molecules in the unit cell. Closely related molecules are, for instance [{CuCl(PEt_3)}$_4$] [10] and [{CuBr(PBu$^t_3$)}$_4$] [11], while the analogous chloro species of the latter complex was not structurally characterized. Compound **1** possesses a Cu_4Cl_4 core of nearly T_d symmetry. The tetrameric units are separated by normal Van der Waals distances and there are no significant intermolecular contacts. The Cu···Cu separations (av. 3.294 Å) are comparable with those in [{CuCl(PEt_3)}$_4$] (av. 3.211(2) Å). This suggests for **1**—like for the analogous systems—that there are no appreciable Cu···Cu interactions. The Cl···Cl distances of 3.464 Å [Cl(1)···Cl(3)] and

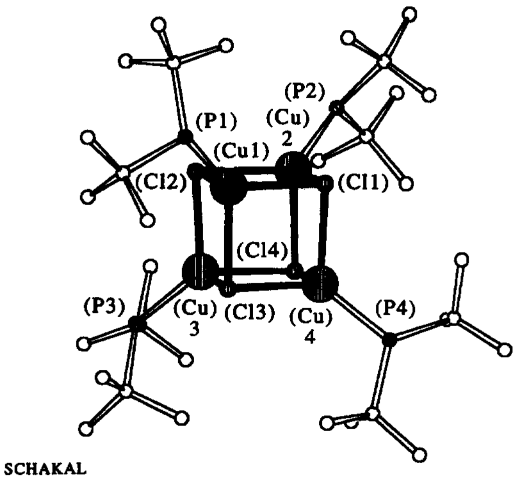


Fig. 1. The molecular structure of [{CuCl(Bu$^t_2$PH)}$_4$] (**1**).

Table 1. Selected bond lengths (Å) and (°) for **1**

Cu(1)–Cl(1)	2.382(1)	Cu(2)–P(2)	2.189(2)
Cu(1)–Cl(2)	2.532(2)	Cu(3)–P(3)	2.187(2)
Cu(2)–Cl(1)	2.473(1)	Cu(4)–P(4)	2.194(2)
Cu(2)–Cl(2)	2.400(1)	Cu(1)···Cu(2)	3.282
Cu(3)–Cl(3)	2.464(2)	Cu(1)···Cu(3)	3.266
Cu(3)–Cl(4)	2.444(2)	Cu(1)···Cu(4)	3.377
Cu(4)–Cl(3)	2.400(2)	Cu(2)···Cu(3)	3.231
Cu(4)–Cl(4)	2.473(2)	Cu(2)···Cu(4)	3.368
Cu(1)–P(1)	2.193(1)	Cu(3)···Cu(4)	3.238
Cl(1)···Cl(3)	3.464	Cl(2)···Cl(4)	3.539
Cl(1)–Cu(1)–Cl(2)	95.2(1)	Cl(1)–Cu(2)–P(2)	117.5(1)
Cl(2)–Cu(2)–Cl(1)	96.3(1)	Cl(2)–Cu(2)–P(2)	126.1(1)
Cl(3)–Cu(3)–Cl(4)	96.8(1)	Cl(3)–Cu(3)–P(3)	119.9(1)
Cl(3)–Cu(4)–Cl(4)	97.8(1)	Cl(4)–Cu(3)–P(3)	119.3(1)
Cl(1)–Cu(1)–P(1)	127.2(1)	Cl(3)–Cu(4)–P(4)	128.9(1)
Cl(2)–Cu(1)–P(1)	114.3(1)	Cl(4)–Cu(4)–P(4)	114.3(1)

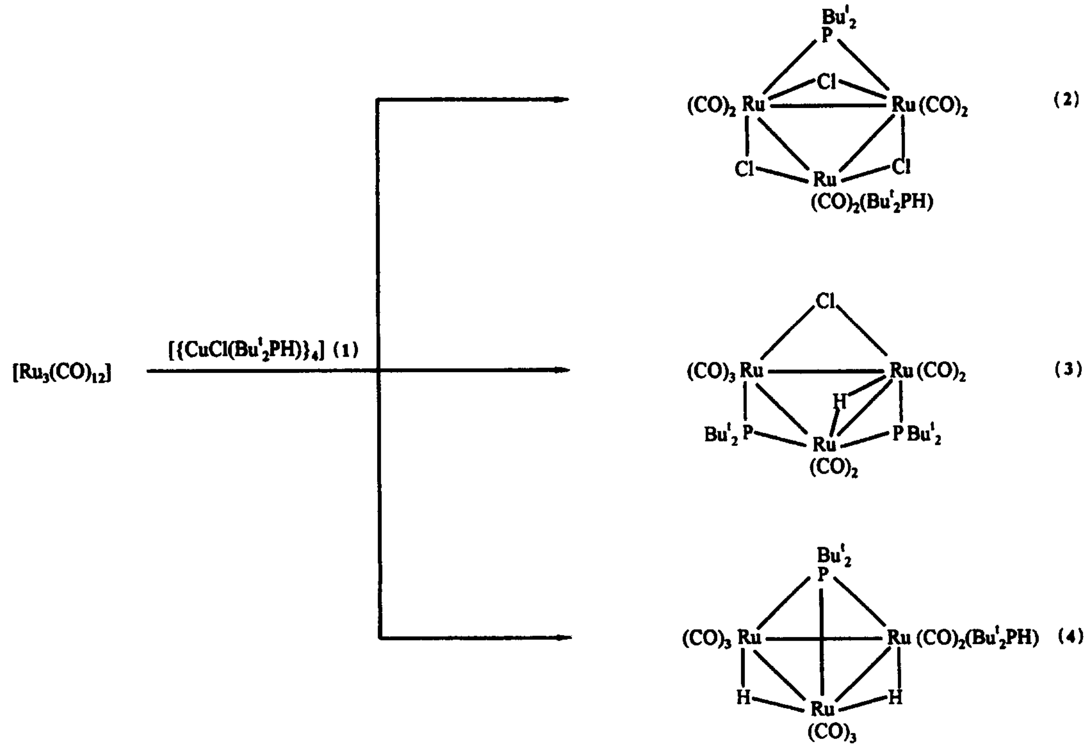
3.539 Å [Cl(2) ··· Cl(4)] are slightly shorter than the expected sum of the van der Waals radii of two Cl atoms (3.60 Å). The Cu–Cl bond lengths (av. 2.454 Å) are in good agreement with those in [{CuCl(PEt$_3$)}$_4$] (2.438(1) Å). A slight elongation in the Cu–P distances compared to the latter is observed (2.191(2) Å in **1** *vs* 2.176(2) Å) probably caused by the higher sterical demands of the Bu^t substituents. Furthermore, the average Cu–P distance agrees better with that found in the tetrameric copper(I) phosphide [{Cu(PBu$^t_2$)}$_4$] (2.209(5) Å [12]).

Reaction of [{CuCl(Bu$^t_2$PH)}$_4$] *with* [Ru$_3$(CO)$_{12}$]

The thermolysis reaction of **1** with [Ru$_3$(CO)$_{12}$] in refluxing toluene (2h) leads, under deposition of metallic copper, to a mixture of products containing the new homonuclear metal clusters [Ru$_3$(CO)$_6$ (μ-PBu$^t_2$)(μ-Cl)$_3$(Bu$^t_2$PH)] (**2**, 35%) and [Ru$_3$(CO)$_7$(μ-PBu$^t_2$)(μ-H)(μ-Cl)] (**3**, 23%), respectively, besides the known complex [Ru$_3$(CO)$_8$ (μ-H)$_2$(μ_3-PBu^t)(Bu$^t_2$PH)] (**4**, 20%) (Scheme 1). No cluster expansion products could be detected, therefore, complex **1** acts only as phosphine and chloride transfer reagent in this reaction. Compounds **2** and **3** were purified by filtration of hexane/diethylether mixtures down alumina and subsequent fractional crystallization from hexane. The complexes **2** and **3** were fully characterized by microanalyses, spectroscopic means (IR, NMR and MS), and by single-crystal X-ray analyses (*vide infra*).

The infrared spectrum of **2** contains only absorption bands in the region characteristic of terminal carbonyl groups. The ^{1}H NMR spectrum of this compound shows signals corresponding to phosphine and phosphido ligands in a ratio of 1 : 1 (see Experimental). No signals corresponding to hydride resonances in the high field region could be detected. In accordance with the proton NMR data, the ^{31}P{^{1}H}NMR spectrum exhibits a signal at δ 288.03 (d, $^2J_{PP} = 7.6$ Hz) indicating a phosphido group bridging a metal–metal bond and a corresponding signal at δ 45.52 (d, $^2J_{PP} = 7.6$ Hz) for a terminal bound phosphine. In the mass spectrum of **2** only the [*M*-CO]$^+$ peak could be detected ($m/z = 841$) and fragments resulting from successive carbonyl loss.

The infrared spectrum of **3** exhibits only ν(CO) absorption bands in the region characteristic of terminal carbonyl ligands. The ^{1}H NMR spectrum of this complex contains signals corresponding to two phosphido ligands in a ratio of 1 : 1, while the Bu^t substituents show four different doublets, i.e., they are all chemically inequivalent. Furthermore, a resonance signal at $\delta -16.37$ was observed (dd, $^2J_{PH} = 25.0$ Hz, $^2J_{PH} = 14.5$ Hz). This signal can be assigned to the bridging hydride ligand found during the X-ray analysis (*vide infra*). The ^{31}P{^{1}H} NMR spectrum of **3** shows a doublet at δ 270.25 and a pertinent doublet at δ 241.36 ($^2J_{PP} = 116.4$ Hz) indicating two chemically non-equivalent phosphido ligands bridging metal–metal bonds. The mass spectrum of **3** exhibits the molecular ion peak at $m/z = 826$ and fragments resulting from successive loss of carbonyl groups.



Scheme. 1.

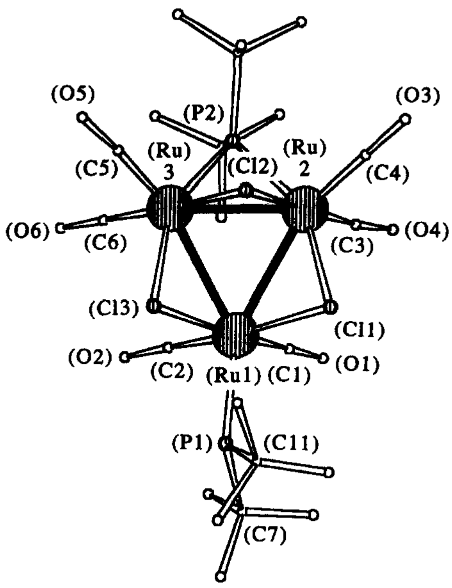


Fig. 2. The molecular structure of [$Ru_3(CO)_6$ (μ-PBu^t_2) (μ-$Cl)_3(Bu^t_2PH)$] (2).

The analytical data and the molecular structure of the third product of this reaction, identified as the metal cluster **4**, were described in an earlier paper [1].

The molecular structure of [$Ru_3(CO)_6$ (μ-PBu^t_2) (μ-$Cl)_3(Bu^t_2PH)$] (**2**)

Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with eight molecules in the unit cell. In the asymmetric unit four crystallographically independent molecules (A–D) are found (see packing scheme in Fig. 3). The molecular structure of **2** is shown in Fig. 2; selected bond lengths and angles for one molecule (molecule A) are summarized in Table 2.

While the metal cores of the molecules A–D are equal within the standard deviations, these molecules differ in rotation of the terminal phosphine ligand around the Ru(1)–P(1) axis. This rotation is well documented in the different torsion angles Ru(2)–Ru(1)–P(1)–C(7); Ru(2)–Ru(1)–P(1)–C(11); Ru(3)–Ru(1)–P(1)–C(7); Ru(3)–Ru(1)–P(1)–C(11), (see Table 3).

Compound **2** consists of a triangular triruthenium core, while each Ru–Ru edge is supported by a chloro ligand. Additionally, the Ru(2)—Ru(3) bond is bridged by a phosphido group and the Ru(1) bears a phosphine ligand. Electron counting reveals this cluster to be a 50-electron species. On the basis of the 18-electron rule, a metal triangle possessing 50 cluster valence electrons (c.v.e.) would be expected to exhibit an open geometry with only two metal–metal bonds. In fact, two Ru–Ru bonds in **2** are slightly elongated

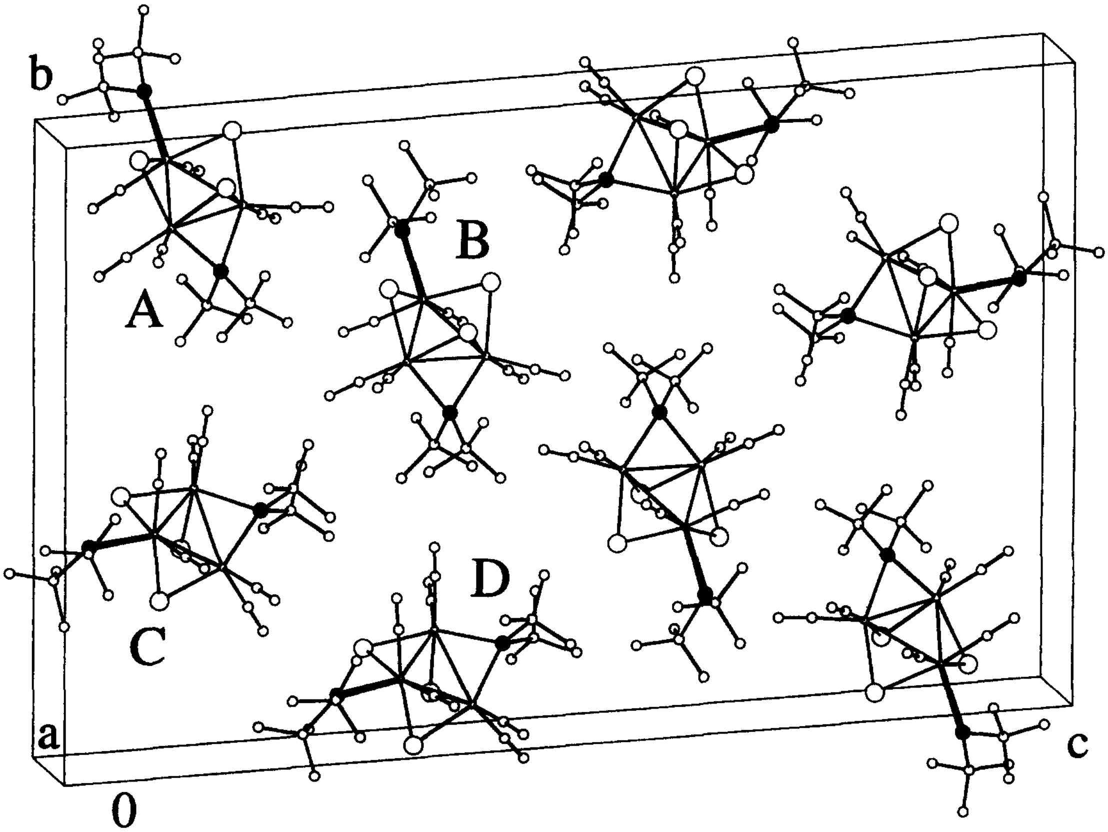


Fig. 3. Packing scheme of [$Ru_3(CO)_6(\mu$-$PBu^t_2)(\mu$-$Cl)_3(Bu^t_2PH)$] (2) in the crystal.

Table 2. Selected bond lengths (Å) and angles (°) for **2** (molecule A)

Ru(1)–Ru(2)	2.997(2)	Ru(1)–Cl(1)	2.442(3)
Ru(1)–Ru(3)	3.016(2)	Ru(2)–Cl(1)	2.448(3)
Ru(2)–Ru(3)	2.835(2)	Ru(2)–Cl(2)	2.417(5)
Ru(1)–P(1)	2.419(4)	Ru(3)–Cl(2)	2.419(5)
Ru(2)–P(2)	2.334(3)	Ru(1)–Cl(3)	2.441(3)
Ru(3)–P(2)	2.318(3)	Ru(3)–Cl(3)	2.442(3)
Ru(1)–C(1)	1.860(14)	Ru(2)–C(4)	1.879(14)
Ru(1)–C(2)	1.844(14)	Ru(3)–C(5)	1.837(13)
Ru(2)–C(3)	1.806(15)	Ru(3)–C(6)	1.860(12)
Ru(1)–Ru(2)–Ru(3)	62.2(1)	P(2)–Ru(3)–Ru(1)	102.7(1)
Ru(2)–Ru(3)–Ru(1)	61.5(1)	P(2)–Ru(2)–Ru(1)	102.8(1)
Ru(2)–Ru(1)–Ru(3)	56.3(1)	Ru(1)–Cl(1)–Ru(2)	75.6(1)
P(1)–Ru(1)–Ru(2)	148.3(1)	Ru(1)–Cl(3)–Ru(3)	76.3(1)
P(1)–Ru(1)–Ru(3)	138.6(1)	Ru(2)–Cl(2)–Ru(3)	71.8(1)
Cl(2)–Ru(2)–P(2)	86.8(2)	Cl(2)–Ru(2)–Ru(1)	85.2(1)
Ru(2)–P(2)–Ru(3)	75.1(1)	Cl(2)–Ru(3)–Ru(1)	84.7(1)

Table 3. Selected torsion angles (°) for **2**

Torsion angles	A	B	C	D
Ru(2)–Ru(1)–P(1)–C(7)	−113.49(47)	−137.32(45)	−145.33(36)	−114.19(38)
Ru(2)–Ru(1)–P(1)–C(11)	26.11(54)	82.79(50)	74.76(44)	77.81(40)
Ru(3)–Ru(1)–P(1)–C(7)	142.76(46)	114.23(46)	106.87(38)	108.75(40)
Ru(3)–Ru(1)–P(1)–C(11)	−77.63(51)	−25.67(53)	−33.04(46)	−32.26(43)

[Ru(1)–Ru(2) = 2.997(2), Ru(1)–Ru(3) = 3.016(2) Å], however, the third [Ru(2)–Ru(3) = 2.835(2) Å] lies in the range expected for Ru–Ru single bonds (2.70–2.95 Å [13]). The shortening of the latter is caused due to the doubly-bridged nature of this bond. Therefore, the slightly expanded metal framework of **2** is indicative of an excess of electrons, and this trimetal cluster can be considered as an electron-rich species. Recently, the class of electron-rich clusters received more attention, and only few examples of such trinuclear complexes are known [14]. The average values of the metal–metal distances are 3.011(2) and 3.039(2) Å, respectively, for the longer, and 2.855(2) Å for the shorter ones. By inspection of these Ru–Ru distances [av. 2.968(2) Å], all the intermetallic distances in **2** are short enough to be considered as bonding interactions.

The molecular structure of complex **2** is related to that of the 50-electron cluster [$\text{Ru}_3(\text{CO})_7(\mu\text{-PPh}_2)_3(\mu\text{-Cl})$] [15]. Compared to **2**, in the latter two chloride-bridges are substituted formally by two phosphido bridges, and the third Ru center bears only carbonyl ligands. Even two elongated Ru–Ru distances were determined for this compound [3.2222(7) and 3.1288(8) Å], however, the doubly-bridged Ru—Ru bond was found to be longer than in **2** (2.9293(8) Å). The chloro bridges in **2** are symmetrically arranged (see Table 2), whereas the phosphido-bridge is slightly asymmetric (i.e. Ru(2)–P(2), 2.334 (3); Ru(3)–P(2), 2.318(3) Å). Following Ru–Cl distances were found (average on all eight molecules): Ru(1)–Cl(1), 2.449(3); Ru(2)–Cl(1); 2.461(3); Ru(1)–Cl(3), 2.442(3); Ru(3)–Cl(3), 2.450(3); Ru(2)–Cl(2), 2.456(5); Ru(3)–Cl(2), 2.400(5) Å. These values are in accordance with the Ru–Cl bond length observed for the 50e-cluster [$\text{Ru}_3(\text{CO})_7(\mu\text{-PPh}_2)_3(\mu\text{-Cl})$] mentioned before (Ru(1)–Cl(1), 2.453(2); Ru(2)–Cl(1), 2.450(1) Å [15]).

The molecular structure of [$\text{Ru}_3(\text{CO})_7(\mu\text{-H})(\mu\text{-PBu}^t_2)_2(\mu\text{-Cl})$] (**3**)

The molecular structure of complex **3** is shown in Fig. 4, selected bond lengths and angles are summarized in Table 4. The compound crystallizes from hexane/diethylether in the triclinic space group $P\bar{1}$ with two molecules in the unit cell.

The metal cluster **3** consists of a triangle of ruthenium atoms with the Ru(1)–Ru(3) and Ru(1)–Ru(2) edges bridged by PBu^t_2 groups and the Ru(2)–Ru(3) edge bridged by a chloro ligand. Additionally, the Ru(1)–Ru(3) edge is bridged by a hydrido ligand which have been found during the refinement by difference fourier analysis. Two nearly similar Ru–Ru distances [Ru(1)–Ru(2), 3.001(1); Ru(2)–Ru(3), 2.963(1) Å] were determined, whereas the doubly-bridged Ru(1)—Ru(3) bond was found to be 2.787(1)

Table 4. Selected bond lengths (Å) and angles (°) for **3**

Ru(1)–Ru(2)	3.001(1)	Ru(2)–P(2)	2.443(1)
Ru(2)–Ru(3)	2.963(1)	Ru(2)–Cl	2.451(1)
Ru(1)–Ru(3)	2.787(1)	Ru(3)–Cl	2.482(1)
Ru(1)–P(1)	2.371(1)	Ru(1)–H(1)	1.738(5)
Ru(3)–P(1)	2.310(1)	Ru(3)–H(1)	1.860(5)
Ru(1)–P(2)	2.360(1)	Ru(2)–C(4)	1.923(3)
Ru(1)–C(1)	1.899(3)	Ru(2)–C(5)	1.879(3)
Ru(1)–C(2)	1.855(3)	Ru(3)–C(6)	1.866(3)
Ru(2)–C(3)	1.947(3)	Ru(3)–C(7)	1.880(3)
Ru(3)–Ru(1)–Ru(2)	61.5(1)	Ru(2)–Ru(3)–H(1)	77.59(3)
Ru(1)–Ru(2)–Ru(3)	55.7(1)	Ru(2)–Ru(1)–H(1)	78.07(3)
Ru(2)–Ru(3)–Ru(1)	62.8(1)	Ru(1)–Ru(2)–Cl	94.4(1)
P(1)–Ru(1)–P(2)	151.9(1)	Ru(2)–Ru(3)–P(1)	105.5(1)
Ru(3)–P(1)–Ru(1)	73.1(1)	Ru(2)–Ru(1)–P(1)	102.8(1)
Ru(1)–P(2)–Ru(2)	77.3(1)	Ru(1)–Ru(3)–Cl	99.3(1)
Ru(2)–Cl–Ru(3)	73.8(1)	Ru(3)–Ru(1)–P(2)	99.9(1)
Ru(1)–H(1)–Ru(3)	101.44(3)	Ru(3)–Ru(2)–P(2)	93.3(1)

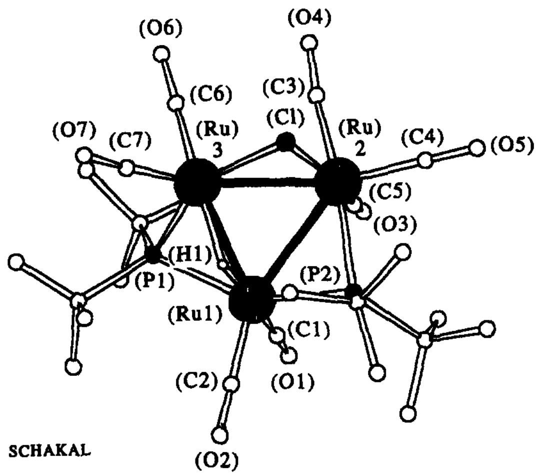


Fig. 4. The molecular structure of $[Ru_3(CO)_7(\mu\text{-}H)(\mu\text{-}PBu^t_2)_2(\mu\text{-}Cl)]$ (**3**).

Å. The phosphido bridges and the hydrido bridge are asymmetrically arranged [Ru(1)–P(1), 2.371(1); Ru(3)–P(1), 2.310(1) and Ru(1)–P(2), 2.360(1); Ru(2)–P(2), 2.443(1) and Ru(1)–H(1), 1.738(5); Ru(3)–H(1), 1.860(5) Å]. On the contrary, the chloro bridge is nearly symmetric with distances Ru(2)–Cl = 2.451(1) and Ru(3)–Cl = 2.482(1) Å. Seven carbonyl ligands complete the coordination sphere of the metal cluster core, three are attached to Ru(2), two to Ru(1) and Ru(3), respectively.

The molecular structure of complex **3** is related to that of $[Ru_3(CO)_7(\mu\text{-}H)(\mu\text{-}PPh_2)_3]$ (**5**) [16, 17], merely one diorganophosphido bridge is formally substituted towards a bridging chloro ligand. A comparison of structure **3** with that of **5** shows a good agreement of the metal–metal bond lengths, e.g. the hydrido supported Ru—Ru bond in **5** (doubly-bridged) is shorter than the other two Ru—Ru distances (2.807(1) *vs* 2.971(1) and 2.999(1) Å, average on the two crystallographically-independent molecules [17]). As in **3**, the hydrido bridge in **5** is also asymmetrically arranged [Ru(1)–H, 1.738(5); Ru(3)–H, 1.860(5) Å in **3** *vs* Ru(3)–H, 1.79; Ru(2)–H, 1.84 Å in **5**]. The Ru—Cl bond lengths found in molecule **3** (Table 3) are in good agreement with those observed for **2** and $[Ru_3(CO)_7(\mu\text{-}PPh_2)_3(\mu\text{-}Cl)]$ (*vide supra*). By electron counting, the trimetal cluster **3** possess 48 c.v.e. and exhibits an electronically saturated species.

EXPERIMENTAL

General considerations

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 prepared according to literature procedures. IR spectra were obtained using a Mattson 5000 instrument. ^1H NMR and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC 200 spectrometer (^1H at 200.1 MHz, referenced to Me_4Si; ^{31}P NMR at 80.1 MHz, referenced to 85% H_3PO_4 aq). 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, Martin-Luther-Universität Halle-Wittenberg.

Synthesis of $[\{CuCl(Bu^t_2PH)\}_4]$ (**1**)

Solid CuCl (990 mg, 10 mmol) was stirred in 50 cm^3 hexane and Bu^t_2PH (1460 mg, 10 mmol) was added.

Immediately a colourless solution was obtained which was stirred for 1 h at room temperature. About half the solvent was removed *in vacuo* and the solution cooled to −30°C overnight. During this period colourless needles deposited. These were filtered off, washed with a small amount cold hexane and dried *in vacuo*. Yield: *ca* 2080 mg, (85%). Found: C, 39.4, H, 7.7, Cl, 14.4, P, 12.3; Calc. for $C_8H_{19}ClCuP$; C, 39.2, H, 7.8, Cl, 14.5, P, 12.6%. ^1H NMR (C_6D_6): δ 1.28 (d, $^3J_{PH}$ = 13.9 Hz, 18H, PBu^t_2), 3.65 (d, J_{PH} = 297.9 Hz, 1H, Bu^t_2PH); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 21.89 (s, br); MS: 244, M^+ (monomer), 208 $[M-Cl]^+$.

Synthesis of complexes $[Ru_3(CO)_6(\mu\text{-}PBu^t_2)(\mu\text{-}Cl)_3(Bu^t_2PH)]$ (**2**) *and* $[Ru_3(CO)_7(\mu\text{-}H)(\mu\text{-}PBu^t_2)_2(\mu\text{-}Cl)]$ (**3**)

A mixture of $[Ru_3(CO)_{12}]$ (1278 mg, 2 mmol) and $[\{CuCl(Bu^t_2PH)\}_4]$ (1952 mg, 2 mmol) was heated in toluene (40 cm^3) under reflux for 2 h. After cooling to room temperature and removal of the solvent, the residue was extracted three times with 20 cm^3 hexane. The volume of the combined extracts was reduced to 10 cm^3 *in vacuo* and passed down on alumina (3 × 10 cm). An orange band containing complexes **2**, **3** and **4** with a mixture of hexane/diethylether (3 : 1) as eluent was obtained. These compounds were separated by fractional crystallization from hexane at −30°C. Yield: 609 mg **2** (35%), 380 mg **3** (23%), 305 mg **4** (20%), based on $[Ru_3(CO)_{12}]$.

Analytical data for **2**. Found: C, 30.4, H, 4.5, Cl, 11.6, P, 7.4; Calc. for $C_{22}H_{37}Cl_3O_6P_2Ru_3$; C, 30.4, H, 4.3, Cl, 12.2, P, 7.1%. IR (KBr pellet, cm^{-1}): ν(CO): 2037(w), 2002(vs), 1949(s). ^1H NMR (C_6D_6): δ 4.84 (d, J_{PH} = 343.2 Hz, 1H, Bu^t_2PH), 1.37 (d, $^3J_{PH}$ = 14.2 Hz, 18H, $\mu\text{-}PBu^t_2$), 1.22 (d, $^3J_{PH}$ = 14.6 Hz, 18H, Bu^t_2PH). ^{31}P $\{^1H\}$ NMR (C_6D_6): δ 288.03 (d, $^3J_{PP}$ = 7.6 Hz, $\mu\text{-}PBu^t_2$), 45.52 (d, $^3J_{PP}$ = 7.6 Hz, $HPBu^t_2$). MS: 841 $[M\text{-}CO]^+$, 805 $[M\text{-}CO, \text{-}Cl]^+$, 777 $[M\text{-}2CO, \text{-}Cl]^+$, 749 $[M\text{-}3CO, \text{-}Cl]^+$, 721 $[M\text{-}4CO, \text{-}Cl]^+$, 693 $[M\text{-}5CO, \text{-}Cl]^+$, 665 $[M\text{-}6CO, Cl]^+$.

Analytical data for **3**. Found: C, 33.4; H, 4.4; Cl, 4.2, P, 7.3; Calc. for $C_{23}H_{37}ClO_7P_2Ru_3$; C, 33.4, H, 4.5, Cl, 4.3, P, 7.5%. IR (KBr pellet, cm^{-1}): ν(CO): 2065 (m), 2003 (vs), 1954(m). ^1H NMR (C_6D_6): δ 1.46 (d, 9H, $^3J_{PH}$ = 14.6 Hz, $\mu\text{-}PBu^t_2$), 1.40 (d, 9H, $^3J_{PH}$ = 14.0 Hz, $\mu\text{-}PBu^t_2$), 1.31 (d, 9H, $^3J_{PH}$ = 14.3 Hz,

Table 5. Crystal data and details of X-ray analyses for complexes **1**, **2** and **3**

Complex	1	2	3
Empirical formula	$C_{32}H_{76}Cl_4Cu_4P_4$	$C_{22}H_{37}Cl_3O_6P_2Ru_3$	$C_{23}H_{37}ClO_7P_2Ru_3$
Formula weight	980.85	869.05	826.15
Crystal habit	prisms	needles	prisms
Temperature	R.T.	R.T.	R.T.
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions	a = 12.237(3)	a = 8.984(4)	a = 8.758(3) (Å)
	b = 13.508(3)	b = 21.124(9)	b = 11.941(4) (Å)
	c = 15.975(3)	c = 34.54(2)	c = 15.829(5) (Å)
	α = 86.69(2)	α = 85.03(4)	α = 99.45(3)°
	β = 78.59(2)	β = 82.92(4)	β = 96.52(3)°
	γ = 72.52(2)	γ = 81.60(3)	γ = 106.57(3)°
V (Å^3)	2469.0(8)	6419(5)	1542.4(8)
Z	2	8	2
Density (calculated) (g/cm^3)	1.250	1.796	1.779
Absorption coefficient (mm^{-1})	2.062	1.775	1.677
F(000)	922	3432	820
θ range for data collection (°)	2.39–25	1.79–22.50	2.89–28
Index ranges	$-16 \leqslant h \leqslant 16$	$-10 \leqslant h \leqslant 10$,	$-10 \leqslant h \leqslant 10$
	$-17 \leqslant k \leqslant 17$	$-24 \leqslant l \leqslant 24$	$-14 \leqslant l \leqslant 15$
	$-21 \leqslant h \leqslant 19$	$-39 \leqslant k \leqslant 39$	$-20 \leqslant h \leqslant 20$
Reflections collected	17911	53572	13294
Independent reflections	8178	15959	6792
Refinement method		Full-matrix least-squares on F^2	
Data/restraints/parameters	8178/0/413	15957/0/1297	6792/0/473
Goodness-of-fit on F^2	1.015	1.031	1.058
Final R indices [I > 2σ(I)]	$R1$ = 0.0461	$R1$ = 0.0508	$R1$ = 0.0260
	$wR2$ = 0.1115	$wR2$ = 0.1301	$wR2$ = 0.0639
R indices (all data)	$R1$ = 0.0881	$R1$ = 0.0887	$R1$ = 0.0335
	$wR2$ = 0.1326	$wR2$ = 0.1513	$wR2$ = 0.0675
Largest diff. peak and hole (Å^{-3})	0.554/−0.326	1.650/−1.363	0.809/−0.577

μ-P*Bu*$^t_2$), 1.28 (d, 9H, $^3J_{PH} = 13.7$ Hz, μ-P*Bu*$^t_2$), -16.37 (dd, 1H, $^2J_{PH} = 25.0$ Hz, $^2J_{PH} = 14.5$ Hz, μ-H). ^{31}P {^{1}H} NMR (C_6D_6): δ 270.25 (d, $^2J_{PP} = 116.4$ Hz, μ-PBu$^t_2$), 241.36 (d, $^2J_{PP} = 116.4$ Hz, μ-*P*Bu$^t_2$). MS: 826 [*M*]$^+$, 798 [*M*-CO]$^+$, 770 [*M*-2CO]$^+$, 742 [*M*-3CO]$^+$, 714 [*M*-4CO]$^+$, 686 [*M*-5CO]$^+$, 658 [*M*-6CO]$^+$, 630 [*M*-7CO]$^+$, 594 [*M*-7CO, -Cl]$^+$.

Analytical data for **4**. See Ref. [1].

X-ray crystal structure determinations of **1**, **2** *and* **3**

Crystal data, data collection and refinement parameters are summarized in Table 5. Crystals of **1**, **2** and **3**, respectively, suitable for X-ray diffraction studies were grown by slow diffusion of hexane into CH_2Cl_2 solutions. For data collection at room temperature the diffractometer Stoe-IPDS was used. 200 frames were taken with a rotation of 1°. Cell refinement was carried out with 2000 reflections. The structures were solved by direct methods (SHELXS-86) and refined on F^2 (SHELXL-93) [18]. 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 ordered on quoting the full literature citation and the reference number CSD 391052 (**1**), CSD 391053 (**2**) and CSD 391054 (**3**).

CONCLUSION

The copper complex [{CuCl(Bu$^t_2$PH)}$_4$] (**1**) has been prepared and the crystal structure of this compound determined by means of X-ray diffraction methods. **1** represents the first structurally characterized tetrameric 'cubane'-like type [$Cu_4Cl_4L_4$] where L is a secondary phosphine. The thermolysis reaction of **1** with [$Ru_3(CO)_{12}$] in refluxing toluene afforded the two novel triruthenium clusters [$Ru_3(CO)_6$(μ-PBu$^t_2$)(μ-Cl)$_3$(Bu$^t_2$PH)] (**2**) and [$Ru_3(CO)_7$(μ-H)(μ-PBu$^t_2$)(μ-Cl)] (**3**). Their crystal structures have been determined by single-crystal X-ray structure analyses. **2** exhibits one of the rare known electron-rich trimetal clusters containing 50 cluster valence electrons. A slight elongation of the metal–metal bonds in this molecule was observed, however, these intermetallic distances are short enough to be considered as bonding interactions. A triruthenium cluster containing chloro, phosphido and hydrido ligands on the same metal core, as found therein in the molecular structure of **3**, was described for the first time.

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