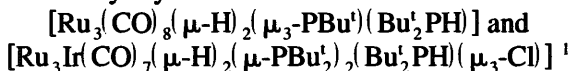




Reactions of $[\text{IrCl}(\text{Bu}_2\text{PH})_3]$ with $[\text{M}_3(\text{CO})_{12}]$ ($\text{M} = \text{Fe}, \text{Ru}$): synthesis and X-ray crystal structures of the metal clusters



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Abstract

The reactions of $[\text{IrCl}(\text{Bu}_2^t\text{PH})_3]$ (**1**) with the metal carbonyls $[\text{M}_3(\text{CO})_{12}]$ ($\text{M} = \text{Fe}, \text{Ru}$) in refluxing toluene have been investigated. By using $[\text{Ru}_3(\text{CO})_{12}]$ the metal cluster $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu_3\text{-PBu}^t)(\text{Bu}_2^t\text{PH})]$ (**2**) and the butterfly configured heterometallic cluster $[\text{Ru}_3\text{Ir}(\text{CO})_7(\mu\text{-H})_2(\mu\text{-PBu}_2^t)_2(\text{Bu}_2^t\text{PH})(\mu_3\text{-Cl})]$ (**3**) were obtained. On the contrary, the reaction of **1** with $[\text{Fe}_3(\text{CO})_{12}]$ leads under cluster degradation beside the mononuclear complex $[\text{Fe}(\text{CO})_5(\text{Bu}_2^t\text{PH})]$ (**5**) to the known compound $[\text{FeIr}(\mu\text{-CO})(\text{CO})_4(\mu\text{-PBu}_2^t)(\text{Bu}_2^t\text{PH})]$ (**4**) in good yields. The molecular structures of **2** and **3** have been determined by single crystal X-ray studies.

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

1. Introduction

Recently, we reported the X-ray crystal structure analyses of the new heterobimetallic complexes $[\text{CoIr}(\text{CO})_5(\mu\text{-H})(\mu\text{-PBu}_2^t)(\text{Bu}_2^t\text{PH})]$ and $[\text{FeIr}(\mu\text{-CO})(\text{CO})_4(\mu\text{-PBu}_2^t)(\text{Bu}_2^t\text{PH})]$ (**4**) obtained from reactions of $[\text{IrCl}(\text{Bu}_2^t\text{PH})_3]$ (**1**) with corresponding metal carbonyl derivatives [1]. With regard to **4**, synthesized by thermolysis of **1** with $[\text{Fe}(\text{CO})_5]$, we were interested in similar reactions, e.g. reactions of metal-halide complexes with neutral metal carbonyls. The reaction principle of the oxidative addition of a reactive bond on a ligand in one complex to a second complex was often used for the synthesis of products containing metal-metal bonds [2]. Especially complexes containing secondary phosphine ligands have been used effectively in this way. In contrast, oxidative addition reactions of metal-halide complexes to metal carbonyls resulting in metal clusters bearing halide ligands are well known, see for instance Ref. [3]. In this paper we describe reactions which include both these principles, e.g. reactions of neutral metal carbonyls $[\text{M}_3(\text{CO})_{12}]$ ($\text{M} = \text{Fe},$

Ru) with complex **1**, which possess a metal-halide bond as well as secondary phosphine ligands. The molecular structures of the products from the reaction with $[\text{Ru}_3(\text{CO})_{12}]$, namely the metal clusters $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu_3\text{-PBu}^t)(\text{Bu}_2^t\text{PH})]$ (**2**) and $[\text{Ru}_3\text{Ir}(\text{CO})_7(\mu\text{-H})_2(\mu\text{-PBu}_2^t)_2(\text{Bu}_2^t\text{PH})(\mu_3\text{-Cl})]$ (**3**) are reported.

2. Results and discussion

Recently, Jones and coworkers [4] described the reaction of $[\text{RhCl}(\text{CO})(\text{Bu}_2^t\text{PH})_2]$ with $[\text{Fe}(\text{CO})_5]$ in refluxing toluene resulting in the phosphido-bridged heteronuclear complex $[\text{FeRh}(\text{CO})_5(\mu\text{-PBu}_2^t)(\text{Bu}_2^t\text{PH})]$ in high yields. In a similar manner we hoped to obtain a heteronuclear phosphido-bridged FeIr cluster by reacting complex **1** with $[\text{Fe}_3(\text{CO})_{12}]$. However, we found that during the latter reaction cluster degradation of the triirondodecacarbonyl occurred and the recently described compound $[\text{FeIr}(\mu\text{-CO})(\text{CO})_4(\mu\text{-PBu}_2^t)(\text{Bu}_2^t\text{PH})]$ (**4**) [1] was formed in yields of about 60% (Scheme 1). Besides **4**, the formation of the mononuclear complex $[\text{Fe}(\text{CO})_5(\text{Bu}_2^t\text{PH})]$ (**5**) could be detected by ³¹P NMR spectroscopy. Up to now, the latter compound was

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¹ Dedicated to Professor Rudolf Taube on the occasion of his 65th birthday.

prepared only in situ and not characterized by spectroscopic means [5]. In our laboratory attempts to isolate this complex in a pure state failed, merely an oily residue could be obtained at room temperature. In the mixture of the reaction of $[\text{Fe}_3(\text{CO})_{12}]$ with **1** we found, by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, besides the signals for **4** only a singlet at δ 84.7 (C_6D_6) which we assign to compound **5**. Even attempts at a photochemical initiation of the reaction of ironpentacarbonyl with an equimolar amount of $\text{Bu}'_2\text{PH}$ in hexane resulted in an oily product after removing the solvent. Therefore, a further characterization of **5** was complicated.

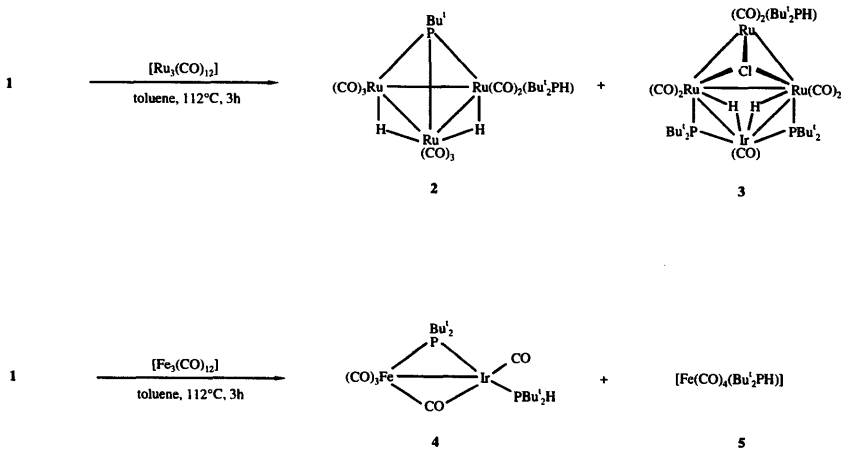
In contrast to this, the analogous reaction of **1** with $[\text{Ru}_3(\text{CO})_{12}]$ leads to a mixture of products containing the homonuclear compound $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu_3\text{-PBu}'_2)(\text{Bu}'_2\text{PH})]$ (**2**) and the heteronuclear cluster $[\text{Ru}_3\text{Ir}(\text{CO})_7(\mu\text{-H})_2(\mu\text{-PBu}'_2)_2(\text{Bu}'_2\text{PH})(\mu_3\text{-Cl})]$ (**3**) as main products. The complexes **2** and **3** were separated by column chromatography on alumina with hexane and hexane/diethylether (5:1) as eluent respectively.

The formation of compound **2** is in agreement with the results of comparable reactions, e.g. pyrolyses of $[\text{Ru}_3(\text{CO})_{12}]$ with secondary phosphines, see for instance Ref. [6]. Therefore, it seems that complex **1** is able to transfer phosphine ligands to the trimetal core under thermal conditions. With respect to the formation of **3**, this cluster can be considered as a product of coupled oxidative addition reactions, namely the oxidative addition of two P–H bonds as well as the addition of an Ir–Cl bond to the neutral Ru_3 metal core. To our knowledge such reaction behavior was observed for the

first time. The identity and composition of compounds **2** and **3** were determined by elemental analysis, IR and NMR spectroscopy, and mass spectrometry. Furthermore, the molecular structures were confirmed by single crystal X-ray analyses.

The infrared spectrum of $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu_3\text{-PBu}'_2)(\text{Bu}'_2\text{PH})]$ shows 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** [hexane, referenced to 85% H_3PO_4 (aq.)] exhibits a doublet at δ 58.0 and a corresponding doublet at δ 373.8 ($^2J(\text{PP}) = 101.3$ Hz). The former value is indicative of a coordinated phosphine whereas the downfield shift is consistent with its assignment to the phosphinidene ligand ($\mu_3\text{-PBu}'_2$) [7]. In agreement with the ^{31}P NMR data, the ^1H NMR spectrum of **2** shows signals corresponding to a phosphine and a phosphinidene ligand in a ratio 1:1 respectively. Furthermore, a hydride resonance signal with a value at high field is found ($\delta = 19.08$, 2H), and the observed ddd pattern is indicative of two chemically equivalent bridging hydride ligands (see Section 3). The mass spectrum of **2** exhibits the molecular ion at $m/z = 766$ and fragments resulting from the successive loss of carbonyl groups.

The infrared spectrum of compound **3** shows only $\nu(\text{CO})$ absorption bands in the region characteristic of terminal carbonyl groups. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (C_6D_6) consists of a triplet at δ 43.3 and a corresponding doublet at δ 318.2 ($^3J(\text{PP}) = 14.9$ Hz) respectively. These shift values are indicative of two chemically equivalent phosphorus nuclei of two phosphido bridges



Scheme 1.

across metal–metal bonds, which couple with a phosphorus nucleus of a phosphine coordinated in a terminal manner. In agreement with the ^{31}P NMR data, the proton NMR spectrum of **3** exhibits the expected signals for one phosphine ligand and two phosphido groups (see Section 3). Furthermore, a resonance at high field ($\delta - 17.40$, 2H) corresponding to two hydride ligands could be detected. The triplet pattern is indicative of an $\text{AA}'\text{XX}'$ spin system, as found in other similar structures [8,9]. However, a further splitting by the phosphorus nucleus of the Bu_2PH ligand to an $\text{AA}'\text{MXX}'$ spin system (dt) is observed. Although the position of the hydride ligands in **3** could not be elucidated during the X-ray analysis (see below), we assume that they occupy bridging sites across the two Ru–Ir bonds and opposite to the two $\mu\text{-PBu}_2$ groups. A bridging position of the other two external Ru–Ru bonds of the metal core cannot be ruled out with certainty, however, with respect to the coordinative saturation of the iridium center it makes sense to assume the former hydride positions. The observed IR and NMR spectra indicate a high molecular symmetry. Furthermore, the mass spectrum of **3** exhibits a molecular ion peak corresponding to the assumed composition at $m/z = 1168$ and fragments resulting from successive loss of carbonyl groups.

2.1. Molecular structure of $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu_3\text{-PBu}'\text{)(Bu}'_2\text{PH})]$ (**2**)

The molecular structure of **2** is shown in Fig. 1, selected bond lengths and angles are summarized in Table 1. The compound crystallizes from hexane in the monoclinic space group $P2_1$ with two molecules in the unit cell.

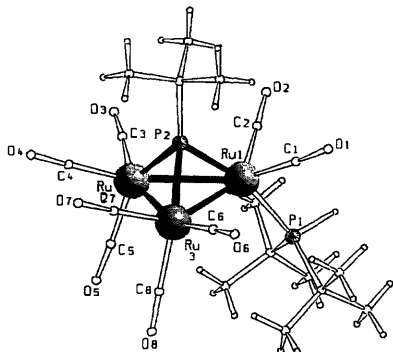


Fig. 1. The molecular structure of $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu_3\text{-PBu}'\text{)(Bu}'_2\text{PH})]$ (**2**).

Table 1
Selected bond lengths [Å] and bond angles [°] for **2**

Ru(1)–Ru(2)	2.989(1)	Ru(1)–P(2)	2.305(2)
Ru(2)–Ru(3)	2.843(1)	Ru(2)–P(2)	2.303(2)
Ru(1)–Ru(3)	2.984(1)	Ru(3)–P(2)	2.304(2)
Ru(1)–P(1)	2.435(2)	Ru(2)–C(3)	1.938(10)
Ru(1)–C(1)	1.898(7)	Ru(2)–C(4)	1.912(8)
Ru(1)–C(2)	1.893(7)	Ru(2)–C(5)	1.943(8)
Ru(3)–C(6)	1.918(10)	Ru(3)–C(8)	1.975(9)
Ru(3)–C(7)	1.915(8)		
Ru(2)–Ru(1)–Ru(3)	56.8(1)	Ru(2)–P(2)–Ru(3)	76.2(1)
Ru(2)–Ru(3)–Ru(1)	61.7(1)	P(1)–Ru(1)–Ru(3)	117.7(1)
Ru(1)–Ru(2)–Ru(3)	61.5(1)	P(1)–Ru(1)–C(1)	93.1(2)
Ru(1)–P(2)–Ru(2)	80.9(1)	P(1)–Ru(1)–C(2)	92.6(2)
Ru(1)–P(2)–Ru(3)	80.7(1)	P(1)–Ru(1)–P(2)	165.1(1)
C(1)–Ru(1)–C(2)	89.4(3)		

The molecule consists of a μ_3 -phosphinidene-capped triruthenium core with a nearly tetrahedral Ru_3P arrangement. Two similar Ru–Ru bond lengths [Ru(1)–Ru(2), 2.989(1); Ru(1)–Ru(3), 2.984(1) Å] and a Ru(2)–Ru(3) bond length of 2.843(1) Å were found. No hydride ligand could be located during the X-ray structure analysis, however, the ^1H NMR data suggest the presence of two chemically equivalent bridging hydride ligands. Therefore, we assume that they occupy bridging sites across the two longer Ru–Ru bonds [Ru(1)–Ru(2), Ru(1)–Ru(3)]. This is in accordance with the known structure of $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu_3\text{-PPh})(\text{PPhH}_2)]$ [10]. Furthermore, a $\text{Bu}'_2\text{PH}$ ligand is coordinated to the Ru(1) atom with a relatively long distance Ru(1)–P(1) of 2.435(2) Å compared with other closely related metal clusters [11,12]. Eight linear carbonyl groups are bound in a terminal coordination mode, while three carbonyls are coordinated to Ru(2) and Ru(3) and two to Ru(1) respectively. Under the assumption of two hydride ligands, the electron counting (EAN) applied to **2** is in agreement with an electronically saturated 48 v.e. trimetal cluster. With respect to **2**, closely related compounds are known, for instance $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu_3\text{-PPh})\text{L}]$ (L = PMePh ; [11]; L = PPhH_2 [10]; L = PPh_3 [12]), which can all be considered as derivatives of the parent cluster type $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu_3\text{-PPh})]$ [13].

2.2. Molecular structure of $[\text{Ru}_3\text{Ir}(\text{CO})_7(\mu\text{-H})_2(\mu_3\text{-PBu}'_2)_2(\text{Bu}'_2\text{PH})(\mu_3\text{-Cl})]$ (**3**)

The molecular structure of **3** is shown in Fig. 2, selected bond lengths and angles are summarized in Table 2. The compound crystallizes from hexane in the triclinic space group $P1$ with two molecules in the unit cell.

Up to now only one Ru_2Ir cluster was structurally investigated, namely $[\text{Ru}_2\text{Ir}(\mu\text{-CO})(\text{CO})_7(\mu\text{-H})_2(\mu_3\text{-PPh})_2(\mu_3\text{-PPhC}_6\text{H}_4)(\text{PPh}_3)]$. In this case the four metal atoms form a tetrahedral arrangement [14]. On the

Table 2
Selected bond lengths [Å] and bond angles [°] for 3

Ir–Ru(1)	2.748(1)	Ru(2)–Ru(3)	2.724(1)
Ir–Ru(2)	2.720(1)	Ru(3)–Ru(1)	2.798(1)
Ru(1)–Cl	2.511(2)	Ru(1)–Ru(2)	2.651(1)
Ru(2)–Cl	2.540(2)	Ru(3)–Cl	2.448(2)
Ir–P(1)	2.290(2)	Ir–P(2)	2.296(2)
Ru(1)–P(1)	2.353(2)	Ru(2)–P(2)	2.347(2)
Ru(1)–C(2)	1.941(7)	Ru(3)–P(3)	2.384(2)
Ru(2)–C(4)	1.839(9)	Ru(1)–C(3)	1.843(9)
Ru(3)–C(6)	1.839(9)	Ru(2)–C(5)	1.943(7)
Ir–C(1)	1.852(8)	Ru(3)–C(7)	1.887(8)
Ir–Ru(1)–Ru(3)	118.9(1)	Ru(1)–Ru(3)–P(3)	163.4(1)
Ru(1)–Ir–Ru(2)	58.0(1)	Ir–Ru(2)–Ru(3)	122.7(1)
Ru(3)–Ru(2)–Ru(1)	62.7(1)	Ru(1)–Ru(3)–Ru(2)	57.4(1)
Ir–Ru(2)–Ru(1)	61.5(1)	Ru(3)–Ru(1)–Ru(2)	59.9(1)
Cl–Ru(2)–Ru(1)	57.8(1)	Ir–Ru(1)–Ru(2)	60.5(1)
Ru(3)–Cl–Ru(1)	68.7(1)	Cl–Ru(1)–Ru(2)	58.9(1)
Ru(1)–Cl–Ru(2)	63.3(1)	Ru(3)–Cl–Ru(2)	66.2(1)
Ru(2)–Ru(1)–P(1)	113.1(1)	Ru(1)–P(1)–Ir	72.6(1)
P(2)–Ir–P(1)	167.6(1)	Ir–Ru(1)–P(1)	52.7(1)
Ir–Ru(2)–P(2)	53.3(1)	Ir–P(2)–Ru(2)	71.7(1)

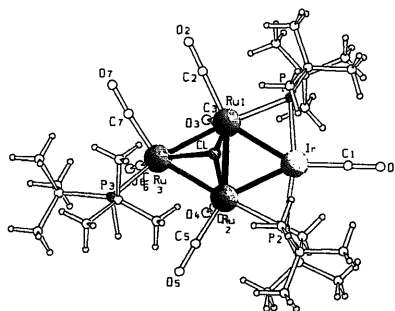


Fig. 2. The molecular structure of $[Ru_3Ir(CO)_7(\mu-H)_2(\mu-PBu_2)_2(Bu_2PH)(\mu_3-Cl)]$ (3).

contrary, the ‘butterfly’ configured tetrametal cluster 3 is characterized by a nearly planar Ru_3Ir core with a dihedral angle of 166° between the planes $[Ru(1)-$

$Ru(2)-Ru(3)]$ and $[Ru(1)-Ru(2)-Ir]$. The three $Ru-Ru$ bond lengths are 2.651(1), 2.798(1) and 2.742(1) Å respectively, and the two $Ru- Ir$ bond lengths were determined to be 2.748(1) and 2.720(1) Å.

The closed Ru_3 triangle is μ_3 -capped by a chloride ligand and the Ru_2Ir wing is edge-bridged by two

Table 3
Crystal data and structure refinement for 2 and 3

	2	3
Identification code	2	3
Empirical formula	$C_{20}H_{12}O_8P_2Ru_3$	$C_{31}H_{37}ClIrO_7P_3Ru_3$
Formula weight	765.59	1165.54
Crystal habit	orange needle	dark red prism
Temperature	RT	RT
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	$P2_1$	$P\bar{1}$
Unit cell dimensions (Å)	$a = 8.907(1)$ $b = 17.088(3)$ $c = 9.886(2)$ $\beta = 96.77(14)^\circ$	$a = 12.523(2)$ $b = 12.966(2)$ $c = 15.907(4)$ $\alpha = 97.94(2)^\circ$ $\beta = 108.77(2)^\circ$ $\gamma = 113.45(14)^\circ$
Volume (Å ³)	1494.2(4)	2135.6(7)
Z	2	2
Density (calc.) (g cm ⁻³)	1.697	1.813
Absorption coefficient (mm ⁻¹)	1.640	4.359
$F(000)$	752	1140
θ range for data collection	3.15 to 30.48°	2.7 to 28.14°
Index ranges	$-12 \leq h \leq 12$, $-24 \leq k \leq 24$, $-14 \leq l \leq 14$	$-16 \leq h \leq 16$, $-17 \leq k \leq 17$, $-21 \leq l \leq 21$
Reflections collected	24219	28259
Independent reflections	8995	9611
Refinement method		F^2 for all non-hydrogen atoms
Data/restraints/parameters	8995/1/313	9611/0/419
Goodness-of-fit on F^2	1.028	1.025
Flack parameter	-0.03(5)	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0436$, $wR_2 = 0.0965$	$R_1 = 0.0541$, $wR_2 = 0.1342$
R indices (all data)	$R_1 = 0.0825$, $wR_2 = 0.1136$	$R_1 = 0.0715$, $wR_2 = 0.1468$
Largest difference peak and hole (e Å ⁻³)	0.726 and -0.906	1.426 and -2.775

μ -PBu₂ ligands. In agreement with the hydride resonance signal found in the ¹H NMR spectrum (see above) and electron counting (62 v.e. for a butterfly configured tetrametal core, EAN), we assume two hydride ligands occupying bridging sites across the two Ru–Ir bonds and opposite to the two phosphido ligands. In accordance with the observed infrared spectrum, only terminal carbonyl groups were found, while each ruthenium atom bears two CO ligands and the iridium center merely one. Furthermore, as indicated by the ³¹P NMR data, a terminal Bu₂PH is coordinated to the Ru(3). An inclination of this phosphine ligand from the Ru₂ plane was observed [Ru(1)–Ru(3)–P(3), 163.4(1); Ru(2)–Ru(3)–P(3), 111.8(1)°]. The μ -Cl ligand was found to have an asymmetric arrangement with two comparable Ru–Cl distances [Ru(1)–Cl, 2.51(2); Ru(2)–Cl, 2.540(2) Å] and with a shorter Ru–Cl bond length [Ru(3)–Cl, 2.448(2) Å]. The two bridging phosphorus atoms lie nearly in the plane of the Ru₂Ir triangle [Ru(3)–Ru(1)–P(1), 165.7(1); Ru(3)–Ru(2)–P(2), 165.6(1)°]. As expected for a heterobimetallic system, the two phosphido bridges are somewhat asymmetric, but surprisingly the Ir–(μ -P) distances are on average shorter by 0.057 Å than the Ru–(μ -P) distances. However, these bonding characteristics are typical for such butterfly configured clusters with two phosphido groups and are often observed in similar systems [15].

3. Experimental

All reactions were carried out under dry argon, 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. The synthesis of [IrCl(Bu₂PH)₃] was described elsewhere [16]. IR spectra were obtained using a Mattson 5000 instrument. ¹H NMR and ³¹P NMR spectra were recorded on a Bruker AC 200 spectrometer (¹H NMR at 200.1 MHz, referenced to Me₄Si; ³¹P NMR at 81.0 MHz, referenced to 85% H₃PO₄ aq.). The mass spectra were obtained on a Hitachi Perkin–Elmer RMU 6, Nermag R30-10 instrument. Elemental analyses: Analytisches Laboratorium des Pharmazeutischen Institutes der Martin-Luther-Universität Halle-Wittenberg. Crystal data for 2 and 3 are given in Table 3, atomic coordinates and equivalent isotropic displacement parameters in Tables 4 and 5.

3.1. Reaction of 1 with [Fe₃(CO)₁₂]

A mixture of 1 (666 mg, 1 mmol) and [Fe₃(CO)₁₂] (504 mg, 1 mmol) was heated in refluxing toluene (40 ml) for 3 h. After cooling to room temperature and

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 2

Atom	x	y	z	U_{eq}
Ru(1)	2969(1)	3489(1)	7367(1)	45(1)
Ru(2)	–194(1)	3426(1)	5974(1)	56(1)
Ru(3)	513(1)	4545(1)	8080(1)	59(1)
P(1)	3833(2)	2462(1)	8981(2)	56(1)
P(2)	1570(2)	4415(1)	6075(2)	51(1)
C(1)	4692(8)	4123(4)	7879(7)	63(2)
C(2)	3973(7)	3040(4)	5971(7)	61(2)
C(3)	14(10)	2768(5)	4411(10)	84(2)
C(4)	–1844(9)	3996(5)	5030(10)	85(2)
C(5)	–1462(8)	2801(5)	7027(9)	74(2)
C(6)	1568(10)	5358(5)	9141(12)	91(3)
C(7)	–1082(9)	5234(5)	7366(9)	76(2)
C(8)	–606(9)	4041(6)	9456(10)	87(2)
C(9)	2190(8)	5134(4)	4834(8)	70(2)
C(10)	3348(16)	5688(7)	5549(13)	138(5)
C(11)	2868(16)	4713(7)	3728(11)	135(5)
C(12)	820(13)	5597(8)	4230(15)	140(5)
C(13)	4096(10)	2712(6)	10857(8)	82(2)
C(14)	4776(11)	3537(8)	11005(8)	113(4)
C(15)	5203(20)	2147(10)	11680(11)	185(8)
C(17)	3038(9)	1448(5)	8645(9)	80(2)
C(16)	2620(14)	2758(7)	11447(11)	116(4)
C(20)	1394(11)	1429(8)	8918(12)	118(4)
C(18)	3105(13)	1303(6)	7118(12)	121(4)
C(19)	3902(19)	838(7)	9472(18)	179(8)
O(1)	5737(6)	4495(4)	8144(6)	97(2)
O(2)	4600(7)	2785(4)	5117(6)	97(2)
O(3)	58(10)	2370(5)	3493(7)	129(3)
O(4)	–2814(7)	4317(4)	4454(9)	133(3)
O(5)	–2258(7)	2461(5)	7619(8)	117(2)
O(6)	2124(9)	5848(5)	9765(10)	150(4)
O(7)	–2023(7)	5644(4)	6911(8)	109(2)
O(8)	–1241(8)	3766(6)	10247(9)	136(3)

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

removal of the solvent the residue was extracted three times with 20 ml portions of pentane. The volume of the combined extracts was reduced to 10 ml and separated by column chromatography on alumina with hexane as eluent. At first a yellow band containing [Fe(CO)₅(Bu₂PH)] (detected by ³¹P NMR) was obtained. Further elution with hexane yielded a red–orange fraction which afforded 4 as orange crystals after reducing the solvent to 10 ml and cooling at –30 °C (yield 410 mg, 60%); for spectroscopic data see Ref. [1].

3.2. Reaction of 1 with [Ru₃(CO)₁₂], synthesis of 2 and 3

A mixture of 1 (666 mg, 1 mmol) and [Ru₃(CO)₁₂] (640 mg, 1 mmol) was heated in refluxing toluene (40 ml) for 3 h. After cooling to room temperature and removal of the solvent the residue was extracted three times with 20 ml portions of pentane. The volume of the combined extracts was reduced to 10 ml and separated

Table 5

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3**

Atom	x	y	z	U_{eq}
Ru(1)	1239(1)	2100(1)	2675(1)	41(1)
Ru(2)	51(1)	3294(1)	3016(1)	39(1)
Ru(3)	-917(1)	1015(1)	3042(1)	45(1)
Ir	1770(1)	4198(1)	2276(1)	41(1)
P(1)	2685(2)	3030(2)	2039(1)	44(1)
P(2)	578(2)	5033(2)	2590(1)	43(1)
P(3)	-3011(2)	290(2)	3004(2)	51(1)
Cl	-1019(2)	1497(2)	1593(1)	48(1)
Cl(1)	2537(9)	5276(7)	1731(7)	61(2)
Cl(2)	1293(9)	617(7)	2433(7)	60(2)
Cl(3)	2417(8)	2582(7)	3890(6)	54(2)
Cl(4)	1093(8)	3973(7)	4270(6)	52(2)
Cl(5)	-1395(7)	3287(6)	3230(5)	49(2)
Cl(6)	-20(8)	1474(7)	4314(6)	54(2)
Cl(7)	-1065(10)	-514(8)	2837(8)	71(3)
Cl(8)	4445(8)	3607(8)	2808(7)	61(2)
Cl(9)	4829(9)	4612(8)	3651(7)	72(2)
Cl(10)	5297(9)	4128(10)	2302(8)	85(3)
Cl(11)	4693(9)	2627(9)	3113(8)	75(3)
Cl(12)	2267(9)	2276(7)	780(6)	58(2)
Cl(13)	2852(12)	3147(9)	306(7)	79(3)
Cl(14)	792(9)	1704(8)	273(6)	72(3)
Cl(15)	2662(11)	1295(9)	705(8)	78(3)
Cl(16)	1464(10)	6499(6)	3570(6)	61(2)
Cl(17)	1705(11)	7554(7)	3197(8)	79(3)
Cl(18)	2787(9)	6638(7)	4167(7)	72(3)
Cl(19)	711(11)	6481(8)	4164(7)	75(3)
Cl(20)	-709(8)	5061(7)	1570(7)	60(2)
Cl(21)	-1601(11)	5416(10)	1871(9)	88(3)
Cl(22)	-142(10)	5863(8)	1041(7)	72(2)
Cl(23)	-1494(10)	3786(8)	897(7)	78(3)
Cl(24)	-3437(10)	-3658(7)	3764(7)	67(2)
Cl(25)	-2256(11)	-219(8)	4667(7)	79(3)
Cl(26)	-3873(12)	-1960(7)	3283(9)	91(4)
Cl(27)	-4503(13)	-548(11)	4006(9)	101(4)
Cl(28)	-4345(8)	-304(8)	1802(7)	66(2)
Cl(29)	-4156(9)	770(8)	1431(7)	69(2)
Cl(30)	-5707(9)	-821(9)	1774(9)	85(3)
Cl(31)	-4238(11)	-1226(9)	1169(7)	82(3)
O(1)	3028(8)	5952(6)	1418(5)	87(2)
O(2)	1389(8)	-216(6)	2320(6)	91(2)
O(3)	3102(7)	2825(6)	4641(4)	73(2)
O(4)	1712(6)	4364(5)	5058(4)	69(2)
O(5)	-2180(6)	3355(6)	3406(5)	73(2)
O(6)	585(7)	1769(6)	5106(5)	73(2)
O(7)	-1084(9)	-1395(6)	2723(7)	109(3)

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

by column chromatography on alumina with hexane as eluent. At first a yellow band containing **2** was obtained. Further elution with a mixture of hexane/diethylether (5:1) yielded a red-brown fraction of **3**. The complexes **2** and **3** were crystallized from hexane at -30°C (yields 191 mg **2**, 25%; 643 mg **3**, 55%).

2. Anal. Found: C, 31.73; H, 4.17; *M*, 763.61 (calc.). $\text{C}_{20}\text{H}_{30}\text{O}_7\text{P}_2\text{Ru}_3$. Calc.: C, 31.46; H, 3.96%. IR $\nu(\text{CO})$ (CsBr): 2066m; 2025vs, sh; 1990s; 1961s cm^{-1} . ^1H

NMR δ (C_6D_6): 4.21 (d, $J(\text{PH}) = 326.5$ Hz, 1H, $\text{Bu}'_2\text{PH}$), 1.59 (d, $^3J(\text{PH}) = 18.8$ Hz, 9H, $\mu_2\text{-PBu}'$), 1.01 (d, $^3J(\text{PH}) = 14.2$ Hz, 18H, $\text{Bu}'_2\text{PH}$), -19.08 (ddd, $^2J(\text{PH}) = 14.7$ Hz, $^2J(\text{PH}) = 11.8$ Hz, $^3J(\text{HH}) = 2.0$ Hz, 2H, $\mu\text{-H}$). $^{31}\text{P}\{^1\text{H}\}$ NMR δ (D_2O capillary/hexane): 373.8 (d, $^2J(\text{PP}) = 101.3$ Hz, $\mu_2\text{-PBu}'$); 58.0 (d, $^2J(\text{PP}) = 101.2$ Hz ($\text{Bu}'_2\text{PH}$)). MS: 766, M^+ ; 738, $[\text{M-CO}]^+$; 710, $[\text{M-2CO}]^+$; 682, $[\text{M-3CO}]^+$; 654, $[\text{M-4CO}]^+$; 626, $[\text{M-5CO}]^+$; 598, $[\text{M-6CO}]^+$; 57, $[\text{C}_4\text{H}_9]^+$, 100%.

3. Anal. Found: C, 31.63; H, 5.37; Cl, 2.63; *M*, 1165.59 (calc.). $\text{C}_{31}\text{H}_{57}\text{ClIrO}_7\text{P}_3\text{Ru}_3$. Calc.: C, 31.85; H, 4.92, Cl, 2.99%. IR $\nu(\text{CO})$ (CsBr): 2035vs; 2007s; 1985m; 1949s, sh cm^{-1} . ^1H NMR δ (C_6D_6): 4.62 (d, 335.0 Hz, 1H, $\text{Bu}'_2\text{PH}$), 1.46 (dt, $N = 14.7$ Hz, 36H, $\mu\text{-PBu}'_2$), 1.20 (d, $^3J(\text{PH}) = 14.5$ Hz, $\text{Bu}'_2\text{PH}$), -17.40 (dt, $^2J(\text{PH}) = 11.9$ Hz, $^3J(\text{PH}) = 1.6$ Hz, 2H, $\mu\text{-H}$). $^{31}\text{P}\{^1\text{H}\}$ NMR δ (C_6D_6): 318.2 (d, $^3J(\text{PP}) = 14.9$ Hz, $\mu\text{-PBu}'_2$), 43.3 (t, $^3J(\text{PP}) = 14.9$ Hz, $\text{Bu}'_2\text{PH}$). MS: 1168, M^+ ; 1140, $[\text{M-CO}]^+$; 1112, $[\text{M-2CO}]^+$; 1084, $[\text{M-3CO}]^+$; 1056, $[\text{M-4CO}]^+$; 1028, $[\text{M-5CO}]^+$; 1000, $[\text{M-6CO}]^+$; 972, $[\text{M-7CO}]^+$; 57, $[\text{C}_4\text{H}_9]^+$, 100%.

4. X-ray structure determinations

Crystals of **2** and **3** suitable for X-ray diffraction were grown by cooling of hexane solutions (-40°C). For the data collection the diffractometer Stoe-IPDS was used. The structures were solved by direct methods and refined on F^2 (program systems SHELXS-86, SHELXL-93 [17]). A summary of crystal data along with details of the structure determinations is given in Table 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 numbers CSD-59332 (**2**) and (**3**).

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