

Synthesis and X-ray crystal structures of phosphido-bridged heterobimetallic complexes: $[\text{FeIr}(\mu\text{-CO})(\text{CO})_4(\mu\text{-P}^t\text{Bu}_2)(^t\text{Bu}_2\text{PH})]$ and $[\text{CoIr}(\text{CO})_5(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(^t\text{Bu}_2\text{PH})]$ ¹

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Abstract

From the reaction of $[\text{IrCl}(^t\text{Bu}_2\text{PH})_3]$ (**1**) with $[\text{Fe}(\text{CO})_5]$ in refluxing toluene, the heterobimetallic complex $[\text{FeIr}(\mu\text{-CO})(\text{CO})_4(\mu\text{-P}^t\text{Bu}_2)(^t\text{Bu}_2\text{PH})]$ (**2**) is obtained. The X-ray structure investigations of **2** show that the Fe–Ir bond is bridged by a carbonyl group; usually in this special type of complex only a semi-bridging carbonyl ligand bound to the electronically saturated metal center is present. The reaction of $[\text{IrCl}(^t\text{Bu}_2\text{PH})_3]/\text{AgPF}_6$ with $\text{K}[\text{Co}(\text{CO})_4]$ in acetone at room temperature results in numerous products. From this reaction the phosphido-bridged heterobimetallic system $[\text{CoIr}(\text{CO})_5(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(^t\text{Bu}_2\text{PH})]$ (**3**) has been isolated. The molecular structures of **2** and **3** were determined by single-crystal X-ray studies: **2** crystallizes in the space group *Pbca* with eight molecules in the unit cell, **3** crystallizes in the space group *P2₁/n* with four molecules per unit cell.

Keywords: Iron; Cobalt; Iridium; Carbonyl; Phosphido-bridged; Crystal structure

1. Introduction

Heterobimetallic complexes are of interest in view of site-selective reactivity and synergetic effects in catalytic reactions involving coordinatively unsaturated species as important key intermediates. It is well known that sterically demanding ligands can be used to induce coordinative unsaturation at a metal center. Recently, we reported a series of binuclear phosphido-bridged complexes containing the sterically demanding $\mu\text{-P}^t\text{Bu}_2$ group [1–4]. Concerning the chemistry of the complexes $[\text{CoRh}(\text{CO})_4(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(^t\text{Bu}_2\text{PH})]$ (**4**) and $[\text{FeRh}(\text{CO})_6(\mu\text{-P}^t\text{Bu}_2)]$ (**5**) [3,4], we were interested in the investigation of analogous iridium compounds. **4** can be prepared in high yields in a reaction of $[\{\text{RhCl}(^t\text{Bu}_2\text{PH})_2\}_2]$ with $\text{K}[\text{Co}(\text{CO})_4]$. Up to now we have no evidence for a similar synthesis of $[\{\text{IrCl}(^t\text{Bu}_2\text{PH})_2\}_2]$, but we could obtain the complex $[\text{IrCl}(^t\text{Bu}_2\text{PH})_3]$ (**1**) by reaction of $[\{\text{IrCl}(\text{COE})_2\}_2]$ ($\text{COE} = \text{cis-cyclooctene}$) with $^t\text{Bu}_2\text{PH}$ under various

molar ratios [5]. In this paper, we describe the preparation and X-ray crystal structure investigations of $[\text{FeIr}(\mu\text{-CO})(\text{CO})_4(\mu\text{-P}^t\text{Bu}_2)(^t\text{Bu}_2\text{PH})]$ (**2**) and $[\text{CoIr}(\text{CO})_5(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(^t\text{Bu}_2\text{PH})]$ (**3**); the latter contains this phosphido-bridged binuclear metal combination for the first time.

2. Results and discussion

Attempts to prepare the analogous iridium compound of $[\text{FeRh}(\text{CO})_5(\mu\text{-P}^t\text{Bu}_2)(^t\text{Bu}_2\text{PH})]$ [3,6] by reaction of **1** with $\text{PPN}[\text{HFe}(\text{CO})_4]$ at room temperature in THF resulted in only a carbonyl transfer with formation of $[\text{IrCl}(\text{CO})(^t\text{Bu}_2\text{PH})_2]$ in low yields. Therefore we proofed the thermal dehalogenation of **1** with an excess of iron pentacarbonyl in refluxing toluene. From this reaction we isolated, after chromatography on alumina with pentane as eluent, the heterobinuclear complex **2** as orange–red crystals in ca. 75% yield (Scheme 1).

The composition of complex $[\text{FeIr}(\mu\text{-CO})(\text{CO})_4(\mu\text{-P}^t\text{Bu}_2)(^t\text{Bu}_2\text{PH})]$ is closely related to some other binuclear electronically unsaturated Fe–Ir compounds, like $[\text{FeIr}(\text{CO})_4(\mu\text{-PCy}_2)(\text{COD})]$ ($\text{COD} = 1.5\text{-cyclooctadiene}$) [7] or $[\text{FeIr}(\text{CO})_4(\mu\text{-PPh}_2)(\text{PPh}_3)_2]$ pre-

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¹ Dedicated to Professor Max Herberhold on the occasion of his 60th birthday.

pared by thermal or photochemical loss of a carbonyl ligand from $[\text{FeIr}(\text{CO})_5(\mu\text{-PPh}_2)(\text{PPh}_3)_2]$ [8], but especially for these two compounds no X-ray data for comparison purposes are available. In this case the electronic unsaturation at the Ir center is relatively rare [7,8], normally three terminal ligands bound to the iridium were observed. In contrast, in the case of rhodium the unsaturation in such complexes is the rule, for example see Refs. [3,4,6,8]. The bonding situation in these heterobimetallic complexes can be formulated as containing a dative bond from the electronically saturated to the unsaturated metal center. An often observed semi-bridging carbonyl group bound to the electronically saturated metal center compensates for increased electron density from the rhodium d orbitals (as a consequence of the dative bond).

Attempts to prepare the analogous iridium compound $[\text{CoRh}(\text{CO})_4(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(^t\text{Bu}_2\text{PH})]$ [3] by room temperature reaction of **1** with $\text{K}[\text{Co}(\text{CO})_4]$ in THF failed. Also in this case the formation of the carbonyl transfer product $[\text{IrCl}(\text{CO})(^t\text{Bu}_2\text{PH})_2]$ in low yield could be detected by NMR spectroscopy. A similar result was observed by thermal reaction of **1** with $[\text{Co}_2(\text{CO})_8]$ in refluxing toluene for 3 h. In this case the Vaska-type carbonylation product is formed nearly quantitatively (see Scheme 1). Therefore treatment of **1** with AgPF_6 in acetone for the formation of $[\text{Ir}(^t\text{Bu}_2\text{PH})_3]\text{PF}_6$ in situ was necessary. However, also under these conditions the new phosphido-bridged heterobimetallic complex $[\text{CoIr}(\text{CO})_5(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(^t\text{Bu}_2\text{PH})]$ (**3**) has been obtained only in low yields as orange crystals.

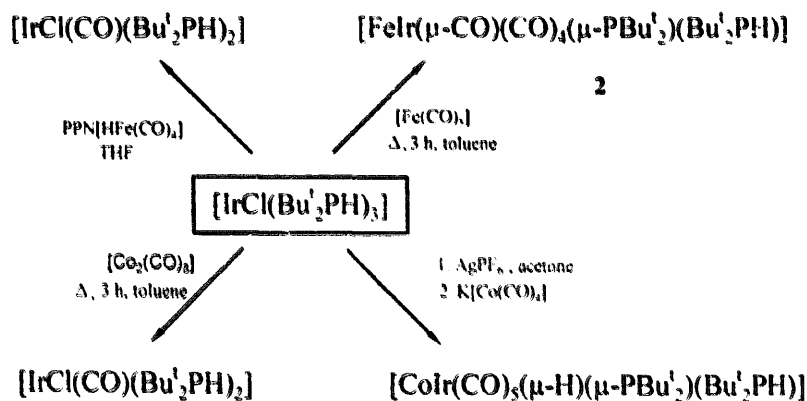
The identity of compounds **2** and **3** was determined by elemental analysis, IR and NMR spectra, and by mass spectrometry. The infrared spectrum of **2** shows $\nu(\text{CO})$ absorption bands in the region characteristic of terminal carbonyl ligands and one strong band for a bridging carbonyl group (1813s, KBr). The bridging carbonyl group of **2** was confirmed by the X-ray diffraction study (see below) and compared with other known

phosphido-bridged heterobimetallic rhodium and iridium complexes; such an arrangement was observed for the first time. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** (CDCl_3) consists of a doublet at δ 182.9 ($\mu\text{-P}^t\text{Bu}_2$) and a doublet at δ 55.8 ($^t\text{Bu}_2\text{PH}$) with the large coupling constant $^2J(\text{PP}) = 171$ Hz corresponding to the *trans* orientation for phosphido and phosphine ligands.

The infrared spectrum of **3** shows only $\nu(\text{CO})$ absorptions in the region characteristic of terminal carbonyl ligands. The ^1H NMR spectrum consists of – in addition to the signals for phosphido and phosphine ligands in a ratio of 1:1 (see Experimental section) – a resonance at δ –12.67 (ddd) corresponding to a hydride ligand bridging the metal–metal bond. This hydride could not be located during the X-ray structure determination. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CDCl_3) shows a doublet at δ 30.6 for the phosphine ligand with a large *trans* coupling to the phosphorus nucleus of the phosphido-bridge. The resonance for the latter is observed at δ 265.8 as a small broad doublet [$^2J(\text{PP}) = 117$ Hz] due to coupling with the ^{59}Co nucleus ($I = 7/2$, 100%), the same effect was observed for **4** [3]. Currently, the achievement of only very low yields during the preparation of **3** is not well understood, and we are searching for an improved synthesis. Studies on the reactivity of **2** and **3** are under way.

2.1. Molecular structure of $[\text{FeIr}(\mu\text{-CO})(\text{CO})_4(\mu\text{-P}^t\text{Bu}_2)(^t\text{Bu}_2\text{PH})]$ (**2**)

2 crystallizes in the orthorhombic space group *Pbca* with eight molecules in the unit cell. The molecular structure of **2** is shown in Fig. 1, selected bond lengths and angles are listed in Table 1. The molecule consists of a folded $\text{FeIr}(\mu\text{-CO})(\mu\text{-P}^t\text{Bu}_2)$ core in a butterfly configuration with three terminal carbonyl ligands at the electronically saturated iron center and one carbonyl and one $^t\text{Bu}_2\text{PH}$ ligand at the electronically unsaturated iridium center.



3

Scheme 1.

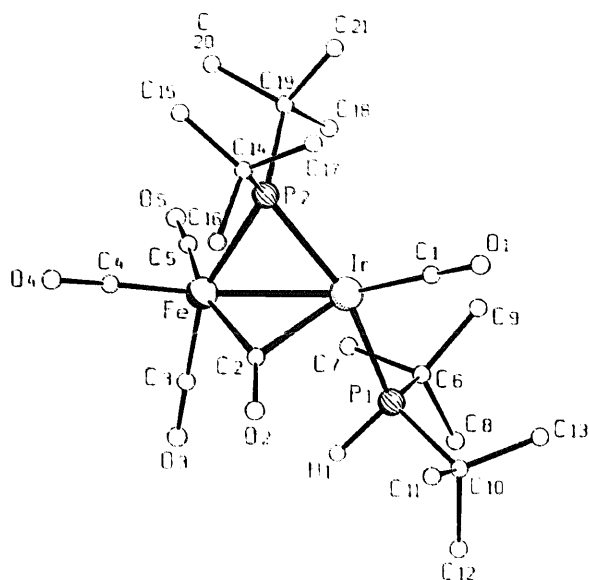


Fig. 1. The molecular structure of **2** in the crystal. The hydrogen at the phosphine ligand is shown but other H are omitted for clarity.

Since the structure of molecule **2** is new, no structural comparisons with other complexes of the type $[L_3Fe(\mu-PR_2)(\mu-CO)IrL_2]$ (L = neutral two electron donor) are possible. The molecular arrangement of **2** is closely related to $[FeRh(CO)_5(\mu-P^tBu_2)(^tBu_2PH)]$ (**6**) [6], but the remarkable difference is that in **2** a *bridging* carbonyl ligand is observed. In **6** a *semi-bridging* coordination mode for one carbonyl bound to the iron was found. Use of the α criterion for semi-bridging carbonyl groups [9] applied to **6** leads to a calculated value $\alpha = 0.233$. In our case of **2** this criterion is not fulfilled ($\alpha = 0.078$), e.g. one carbonyl ligand in **2** is *bridging*.

Table 1
Selected bond lengths (Å) and bond angles (°) for **2**

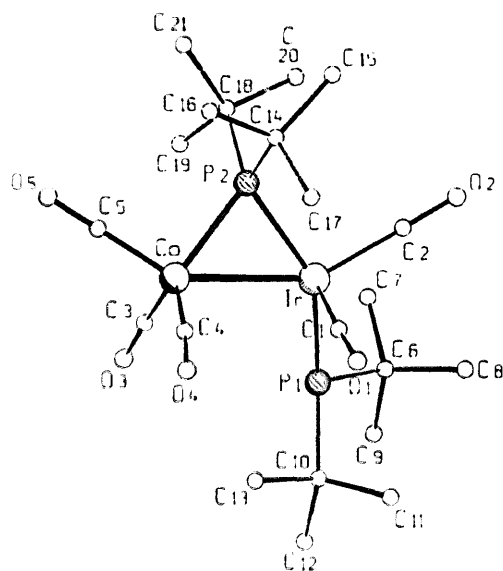
Ir–Fe	2.624(1)	Fe–C(2)	1.918(5)
Ir–P(2)	2.297(1)	Ir–C(1)	1.853(5)
Fe–P(2)	2.287(1)	Fe–C(3)	1.788(5)
Ir–P(1)	2.354(1)	Fe–C(4)	1.799(5)
Ir–C(2)	2.068(5)	Fe–C(5)	1.782(6)
Fe–P(2)–Ir	69.8(1)	P(2)–Fe–Ir	55.3(1)
C(2)–Fe–Ir	51.3(1)	C(2)–Fe–P(2)	85.1(1)
C(1)–Ir–C(2)	122.7(2)	C(4)–Fe–C(2)	102.7(2)
C(1)–Ir–P(2)	105.0(2)	C(5)–Fe–P(2)	94.6(2)
C(2)–Ir–P(2)	81.5(1)	C(3)–Fe–P(2)	159.5(2)
C(1)–Ir–P(1)	98.5(2)	C(4)–Fe–P(2)	100.7(2)
C(2)–Ir–P(1)	89.8(1)	C(5)–Fe–Ir	108.6(2)
P(2)–Ir–P(1)	156.0(1)	C(3)–Fe–Ir	104.6(2)
C(1)–Ir–Fe	154.9(2)	C(4)–Fe–Ir	141.8(2)
C(2)–Ir–Fe	46.4(1)	O(1)–C(1)–Ir	174.7(6)
P(2)–Ir–Fe	54.9(1)	O(2)–C(2)–Fe	147.6(4)
P(1)–Ir–Fe	103.4(1)	O(1)–C(1)–Ir	174.7(6)
C(5)–Fe–C(3)	88.5(2)	O(2)–C(2)–Fe	147.6(4)
C(5)–Fe–C(4)	102.0(3)	O(2)–C(2)–Ir	129.7(4)
C(3)–Fe–C(4)	98.5(2)	Fe–C(2)–Ir	82.2(2)
C(5)–Fe–C(2)	155.0(2)	C(3)–Fe–C(2)	83.7(2)

The coordination sphere around the iron atom, ignoring the Fe–Ir bond, can be described as roughly trigonal bipyramidal. The coordination geometry at the iridium center is nearly square-planar with the phosphido group and the phosphine ligand in *trans* position to each other. This is in good agreement with the ^{31}P NMR results. Compared with other phosphido-bridged Fe–Ir systems the metal–metal distance of 2.624(1) Å is very short. For instance in $[FeIr(CO)_5(\mu-PPH_2)(PPh_3)_2]$ the metal–metal bond is 2.960(1) Å [8], and in the two-fold phosphido-bridged system $[FeIr(CO)_3(\mu-PPH_2)_2Cl(COD)]$ it is 2.703(1) Å [10]. By formal electron counting complex **2** could be considered with respect to the EAN rule as a species containing an iron–iridium double bond. However, some species exist with shorter Ir–Ir bonds than the Fe–Ir bond in **2**, and they are consistent with Ir–Ir double bonds; for instance $[Ir_4(\mu-As^tBu_2)_4(\mu-CO)_2(CO)_2]$ one bond 2.592(6) Å [11], $[Ir_2(CO)_4(\mu-P^tBu_2)_2]$ 2.545(1) Å [12] and $[Ir_2(CO)_2(\mu-PPh_2)_2(PPh_3)_2]$ 2.551(1) Å [13]. This bond length–bond order correlation seems suspect in view of the tendency of $\mu-PR_2$ ligands to favor short metal–metal contacts, therefore we assume a single bond between the metals in **2**. The following aspect of the structure in **2** is still of special interest: in many phosphido-bridged binuclear complexes the iridium center is electronically and coordinatively saturated (18 v.e.). For **2** this is not the case (16 v.e.), and the coordination number 4 is reached at least by the bridging carbonyl ligand. (In the molecule **5** we observed a similar effect by the presence of two weak semi-bridging carbonyl groups.) An electronically saturated composition $[FeIr(CO)_6(\mu-P^tBu_2)(^tBu_2PH)]$ is not possible, probably because of the sterical demands of the phosphido ligand.

2.2. Molecular structure of $[CoIr(CO)_5(\mu-H)(\mu-P^tBu_2)(^tBu_2PH)]$ (**3**)

Compound **3** crystallizes in the monoclinic space group $P2_1/n$ with four molecules per unit cell. A view of the molecule is shown in Fig. 2, selected bond lengths and angles are listed in Table 2.

The X-ray studies were hampered by poor crystal quality, therefore the structure model could be refined to an R -value of only 7.5%. But we have included these X-ray data in this paper since they provide some fundamental information on the framework of compound **3**. The molecule consists of a $CoIr(\mu-H)(\mu-P^tBu_2)$ core probably in a butterfly configuration. Although the position of the hydride could not be localized in the structure, the geometry of the molecule indicates that it occupies a bridging position between the Co and the Ir atom (1H NMR). A structural comparison with the closely related compound $[CoRh(CO)_4(\mu-H)(\mu-P^tBu_2)(^tBu_2PH)]$ (**4**) [3] is not possible because of the lack of suitable single crystals for X-ray diffraction

Fig. 2. The molecular structure of **3** in the crystal (without H atoms).

studies of **4** (despite intensive efforts!). In this context merely a comparison with the substitution product $[\text{CoRh}(\text{CO})_3(\mu\text{-H})(\mu\text{-P}^i\text{Bu}_2)(^i\text{Bu}_2\text{PH})(\text{PPh}_3)]$ (**7**) is possible. However, in **7** (and in **4**) the rhodium center is electronically unsaturated in contrast to the iridium center in **3**. In the molecule **3** three terminal carbonyl groups are bound to the cobalt and two carbonyls

Table 2
Selected bond lengths (Å) and bond angles (°) for **3**

Ir–Co	2.773(2)	Ir–P(1)	2.399(5)
Co–P(2)	2.171(5)	Ir–P(2)	2.332(4)
Ir–C(1)	1.89(2)	C(1)–O(1)	1.17(2)
Ir–C(2)	1.91(2)	C(2)–O(2)	1.13(2)
Co–C(3)	1.72(2)	C(3)–O(3)	1.16(2)
Co–C(4)	1.77(2)	C(4)–O(4)	1.16(2)
Co–C(5)	1.73(2)	C(5)–O(5)	1.12(2)
Co–P(2)–Ir	75.9(2)	P(1)–Ir–Co	104.5(1)
P(2)–Ir–Co	49.4(1)	P(2)–Ir–P(1)	146.7(2)
C(1)–Ir–C(2)	100.5(8)	C(3)–Co–C(4)	116.5(9)
C(1)–Ir–P(2)	100.9(6)	C(5)–Co–P(2)	95.5(8)
C(2)–Ir–P(2)	100.2(6)	C(3)–Co–P(2)	122.7(6)
C(1)–Ir–P(1)	97.3(6)	C(4)–Co–P(2)	114.0(5)
C(2)–Ir–P(1)	103.6(6)	C(5)–Co–Ir	148.0(8)
C(1)–Ir–Co	87.1(6)	C(3)–Co–Ir	91.0(6)
C(2)–Ir–Co	149.6(6)	C(4)–Co–Ir	100.1(5)
C(5)–Co–C(3)	98.0(1)	P(2)–Co–Ir	54.7(1)
C(5)–Co–C(4)	103.2(1)		

together with a phosphine ligand in *trans* position to the phosphido group are coordinated at the iridium. This shows the tendency of iridium to prefer a higher coordination number in contrast to rhodium (see also Refs. [7,8,10]).

Molecule **3** contains a single Co–Ir bond [Co–Ir = 2.773(2) Å], which is in accordance with the EAN rule.

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

Identification code	2	3
Empirical formula	$\text{C}_{21}\text{H}_{17}\text{FeIrO}_3\text{P}_2$	$\text{C}_{21}\text{H}_{16}\text{CoIrO}_3\text{P}_2$
Formula weight	679.50	684.59
Temperature	R.T.	R.T.
Wavelength (Å)	0.71073	0.71073
Crystal system	orthorhombic	monoclinic
Space group	<i>Pbca</i>	<i>P2₁/n</i>
Unit cell dimensions (Å)	<i>a</i> = 15.6123(8) <i>b</i> = 11.850(2) <i>c</i> = 28.881(4) $\alpha = \beta = \gamma = 90^\circ$	<i>a</i> = 10.071(1) <i>b</i> = 17.597(2) <i>c</i> = 16.107(2) $\beta = 100.70(1)^\circ$
Volume (Å ³)	5343.1(10)	2804.9(6)
Z	8	4
Density (calc.) (g cm ⁻³)	1.689	1.621
Absorption coefficient (mm ⁻¹)	5.67	5.47
<i>F</i> (000)	2688	1356
θ range for data collection	1.92 to 24.96°	2.31 to 28.16°
Index ranges	$0 \leq h \leq 18, -1 \leq k \leq 14, -34 \leq l \leq 0$	$-13 \leq h \leq 13, -23 \leq k \leq 23, -21 \leq l \leq 21$
Reflections collected	5340	24227
Independent reflections	4674	6825
Refinement method	all non-hydrogen atoms anisotropic	Full-matrix least-squares on <i>F</i> ² Ir, Co, P, O, C (except ^{<i>i</i>} Bu–C) anisotropic
Data/restraints/parameters	4674/0/408	6824/0/192
Goodness-of-fit on <i>F</i> ²	1.047	0.948
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0265, <i>wR</i> ₂ = 0.0621	<i>R</i> ₁ = 0.0746, <i>wR</i> ₂ = 0.1664
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0436, <i>wR</i> ₂ = 0.0682	<i>R</i> ₁ = 0.2059, <i>wR</i> ₂ = 0.2298
Largest difference peak and hole (e Å ⁻³)	0.501 and –0.776	1.366 and –2.193

An inspection of the Ir–P(1) and Ir–P(2) distances of **2** and **3** shows no significant differences (see Tables 1 and 2). Furthermore, these values agree well with the data for **7** [Ir– μ -P 2.297(1) (**3**) vs. Rh– μ -P 2.242(3) (**7**) and Ir–P 2.354(1) (**3**) vs. 2.332(3) (**7**) Å]. The bond lengths concerning the Co(CO)₃ fragment and the Co(CO)₂(PPh₃) in **7** are also 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: [IrCl(^tBu₂PH)₃] [**5**], PPN[PF₆(CO)₄] [**14**], K[Co(CO)₄] [**15**]. IR spectra were obtained using a Mattson 5000 instrument. ¹H NMR spectra were recorded on a Bruker AC 200 spectrometer (at 200.1 MHz), ³¹P NMR spectra on an AC 80 (at 32.4 MHz). The mass spectra were obtained on a Hitachi Perkin–Elmer RMU 6, Nermag R

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}
C(1)	6011(3)	2007(5)	3222(2)	52(1)
C(2)	5337(3)	789(4)	4241(2)	39(1)
C(3)	4162(3)	1423(4)	4755(2)	46(1)
C(4)	3875(4)	–671(5)	4405(2)	55(1)
C(5)	3067(4)	1312(5)	4129(2)	52(1)
C(6)	4833(3)	4617(4)	4044(2)	41(1)
C(7)	3954(4)	4195(5)	4204(3)	58(2)
C(8)	5064(5)	5692(5)	4318(3)	61(2)
C(9)	4800(5)	4872(6)	3523(2)	61(2)
C(10)	6737(3)	3824(4)	4181(2)	47(1)
C(11)	7254(4)	2731(6)	4200(3)	67(2)
C(12)	6929(5)	4499(8)	4622(3)	72(2)
C(13)	7000(5)	4526(8)	3755(3)	73(2)
C(14)	4841(3)	–983(4)	3248(2)	48(1)
C(15)	4175(6)	–1897(5)	3168(3)	74(2)
C(16)	5423(5)	–1390(6)	3633(3)	67(2)
C(17)	5407(5)	–828(6)	2821(2)	77(2)
C(18)	3315(4)	2103(5)	3060(2)	53(1)
C(19)	3466(3)	832(4)	2998(2)	41(1)
C(20)	2624(4)	198(7)	3082(3)	64(2)
C(21)	3766(5)	638(7)	2496(2)	68(2)
O(1)	6545(3)	2027(4)	2953(2)	92(2)
O(2)	5961(2)	553(3)	4450(1)	57(1)
O(3)	4182(3)	1892(3)	5099(1)	70(1)
O(4)	3719(4)	–1545(4)	4543(2)	91(2)
O(5)	2392(3)	1700(4)	4118(2)	79(1)
P(1)	5584(1)	3399(1)	4146(1)	34(1)
P(2)	4325(1)	403(1)	3433(1)	34(1)
Ir	5187(1)	1854(1)	3680(1)	30(1)
Fe	4111(1)	732(1)	4205(1)	37(1)

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

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}
C(1)	–588(22)	913(10)	8964(12)	78(5)
C(2)	2101(18)	1208(11)	9956(14)	81(6)
C(3)	459(20)	2059(12)	6918(11)	78(5)
C(4)	–1214(18)	701(11)	7087(10)	71(5)
C(5)	929(24)	760(15)	6262(14)	108(8)
C(6)	1312(21)	3234(12)	9922(13)	92(6) *
C(7)	2734(22)	3150(13)	9828(13)	96(6) *
C(8)	1094(22)	2891(12)	10785(14)	102(7) *
C(9)	907(28)	4130(16)	9859(17)	137(9) *
C(10)	–1644(21)	2871(12)	8874(13)	92(6) *
C(11)	–2232(23)	2580(14)	9621(15)	112(7) *
C(12)	–2004(32)	3777(18)	8795(20)	157(11) *
C(13)	–2319(20)	2455(12)	8036(13)	88(6) *
C(14)	1812(17)	–523(10)	8261(10)	68(4) *
C(15)	2971(21)	–811(12)	8969(12)	90(6) *
C(16)	1748(23)	–952(13)	7419(14)	105(7) *
C(17)	422(19)	–658(11)	8544(12)	80(5) *
C(18)	3844(22)	775(13)	7985(14)	97(6) *
C(19)	3897(24)	1587(13)	7539(15)	108(7) *
C(20)	4711(25)	821(14)	8875(15)	114(8) *
C(21)	4383(24)	113(14)	7452(15)	112(7) *
O(2)	2705(17)	1057(9)	10598(9)	118(6)
O(1)	–1585(13)	618(8)	9067(9)	97(4)
O(4)	–2317(14)	474(9)	6996(9)	101(4)
O(3)	362(21)	2697(10)	6741(10)	143(7)
O(5)	1300(20)	573(14)	5683(10)	157(8)
P(1)	255(5)	2689(2)	8997(3)	67(1)
P(2)	1978(4)	546(3)	8049(3)	60(1)
Ir	1037(1)	1414(1)	8868(1)	55(1)
Co	408(2)	1107(1)	7152(1)	62(1)

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

30-10 instrument. Elemental analyses: Analytisches Laboratorium des Pharmazeutischen Institutes der Martin-Luther-Universität Halle-Wittenberg.

3.1. Preparation of [FeIr(μ -CO)(CO)₅(μ -P^tBu₂)(^tBu₂PH)] (**2**)

[Fe(CO)₅] (1 ml, 7.6 mmol) was added to a solution of [IrCl(^tBu₂PH)₃] (0.60 g, 0.90 mmol) in 40 ml toluene. The reaction mixture was refluxed for 3 h and the color turned dark red with the formation of some black precipitate. After cooling at room temperature the formed precipitate was filtered off and the solution was passed down an alumina column (6 \times 3 cm) to give a red–orange band which was collected. After removing the toluene in vacuo the residue was dissolved in 10 cm hexane and crystallized in a freezer. After one day orange crystals were obtained and dried in vacuo (yield 75%). Anal. Found: C, 37.03; H, 5.58; $M = 680.11$ (calc.). C₂₁H₃₇FeIrO₅P₂ Calc.: C, 37.05; H, 5.48%. IR: ν (CO) (KBr): 2032s, 1975s, 1938vs, 1813s; ν (PH) 2334w cm^{–1}. ³¹P{¹H} NMR: δ (CDCl₃): 182.9 (d, ²J(PP) = 170.9 Hz, μ -P^tBu₂), 55.8 (d, ²J(PP) =

170.5 Hz, $^1\text{Bu}_2\text{PH}$). ^1H NMR: δ (C_6D_6): 4.94 (d, 1H, $J(\text{PH}) = 336.8$ Hz, $^1\text{Bu}_2\text{PH}$), 1.34 (d, 18H, $^3J(\text{PH}) = 14.7$ Hz, $\mu\text{-P}^1\text{Bu}_2$), 1.15 (d, 18H, $^3J(\text{PH}) = 14.7$ Hz, $^1\text{Bu}_2\text{PH}$). MS: 680, M^+ ; 652 $[\text{M} - \text{CO}]^+$, 624 $[\text{M} - 2\text{CO}]^+$, 596 $[\text{M} - 3\text{CO}]^+$, 568 $[\text{M} - 4\text{CO}]^+$.

3.2. Preparation of $[\text{CoIr}(\text{CO})_5(\mu\text{-H})(\mu\text{-P}^1\text{Bu}_2)(^1\text{Bu}_2\text{PH})]$ (**3**)

A solution of $[\text{IrCl}(^1\text{Bu}_2\text{PH})_3]$ (1.0 g, 1.5 mmol) in 20 ml acetone was added to a solution of AgPF_6 (0.36 g, 1.5 mmol) in 20 ml acetone. Precipitation of dark AgCl was observed immediately. After stirring for a few minutes the solution was filtered over silica gel. The filtrate was stirred with $\text{K}[\text{Co}(\text{CO})_4]$ (0.32 g, 1.5 mmol) for a few minutes. After removing the acetone in vacuo the residue was dissolved in THF and stirred for 12 h at room temperature. The solvent was evaporated to dryness and the brown residue was extracted into 50 ml hexane. The solution was passed down an alumina column (6×3 cm). The first orange band was collected and reduced to 5 ml in vacuo. After standing at -40°C for some days, orange crystals were collected (yield 10%). Anal. Found: C, 36.79; H, 5.69; $M = 684.12$ (calc.). $\text{C}_{21}\text{H}_{38}\text{CoIrO}_5\text{P}_2$ Calc.: C, 36.84; H, 5.60%. IR: $\nu(\text{CO})$ (KBr): 2035m, 2005s, 1984s, 1921vs; $\nu(\text{PH})$ 2358w cm^{-1} . $^31\text{P}\{^1\text{H}\}$ NMR: δ (CDCl_3): 265.8 (d, $^2J(\text{PP}) = 117$ Hz, $\mu\text{-P}^1\text{Bu}_2$), 30.6 (d, $^2J(\text{PP}) = 117$ Hz, $^1\text{Bu}_2\text{PH}$). MS: 684, M^+ ; 656 $[\text{M} - \text{CO}]^+$, 628 $[\text{M} - 2\text{CO}]^+$, 600 $[\text{M} - 3\text{CO}]^+$. ^1H NMR: δ (C_6D_6): 5.23 (d, 1H, $J(\text{PH}) = 357.8$ Hz, $\text{P}^1\text{Bu}_2\text{H}$), 1.39 (d, 18H, $^3J(\text{PH}) = 14.4$ Hz, $\mu\text{-P}^1\text{Bu}_2$), 1.06 (d, 18H, $^3J(\text{PH}) = 14.9$ Hz, $^1\text{Bu}_2\text{PH}$), -12.67 (ddd, 1H, $^1J(\text{HH}) = 2.7$, $^2J(\text{PH}) = 14.7$, $^3J(\text{PH}) = 18.4$ Hz, $\mu\text{-H}$).

3.3. Reaction of $[\text{IrCl}(^1\text{Bu}_2\text{PH})_3]$ with $\text{PPN}[\text{HFe}(\text{CO})_4]$

$[\text{IrCl}(^1\text{Bu}_2\text{PH})_3]$ (0.67 g, 1 mmol) and $\text{PPN}[\text{HFe}(\text{CO})_4]$ (0.71 g, 1 mmol) were dissolved in 30 ml THF and stirred for 24 h at room temperature. The solvent was removed in vacuo and the residue was extracted three times with 20 ml pentane. The filtered extract was reduced to 10 ml and cooled at -40°C for some hours. A slight yellow precipitate of $[\text{IrCl}(\text{CO})(^1\text{Bu}_2\text{PH})_2]$ [**16**] resulted (0.08 g, 15%). The residue of the extraction was identified as unreacted $\text{PPN}[\text{HFe}(\text{CO})_4]$.

3.4. Reaction of $[\text{IrCl}(^1\text{Bu}_2\text{PH})_3]$ with $[\text{Co}_2(\text{CO})_8]$

$[\text{IrCl}(^1\text{Bu}_2\text{PH})_3]$ (0.67 g, 1 mmol) and $[\text{Co}_2(\text{CO})_8]$ (0.34 g, 1 mmol) were dissolved in 40 ml toluene and refluxed for 3 h. After cooling to room temperature the solvent was removed in vacuo to dryness. The remaining residue was extracted five times with 20 ml pentane. The filtered extract was reduced to 20 ml and cooled at

-40°C overnight. A slight yellow precipitate of $[\text{IrCl}(\text{CO})(^1\text{Bu}_2\text{PH})_2]$ resulted in nearly quantitative yield.

3.5. X-ray structure determination of **2** and **3**

Crystals of **2** and **3** suitable for X-ray diffraction were grown by cooling a hexane solution (-40°C). For the data collection Stoe STADI-4 (for **2**) and Stoe-IPDS (for **3**) diffractometers were 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 determination are given in Table 3; atomic coordinates and equivalent isotropic displacement parameters for **2** and **3** are given in Tables 4 and 5 respectively. 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 depository numbers CSD-59294 (2,3) and the full literature citation.

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