

Synthesis of new ruthenium–iridium heterobimetallic complexes via ring-opening reactions of bidentate phosphine ligands and tridentate phosphine ligand: crystal structure of $[(C_5H_5)Ru(\mu-CO)_2\{\mu-Ph_2PN(H)PPh_2\}IrCl_2]$

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Abstract

Treatment of $[Ru(C_5H_5)Cl(dppm)]$ (**1**) [dppm = 1,1-bis(diphenylphosphino)methane], $[Ru(C_5H_5)Cl(dppen)]$ (**2**) [dppen = 1,1-bis(diphenylphosphino)ethene] or $[Ru(C_5H_5)Cl(dppa)]$ (**3**) [dppa = 1,1-bis(diphenylphosphino)amine] with $[IrCl(CO)_2(p\text{-toluidine})]$ leads to the formation of the heterobimetallic complexes $[(C_5H_5)Ru(\mu-CO)_2\{\mu-L\}IrCl_2]$ (L = dppm **4**, dppen **5** or dppa **6**) in high yield. The structure of $[(C_5H_5)Ru(\mu-CO)_2\{\mu-Ph_2PN(H)PPh_2\}IrCl_2]$ (**6**) has been determined by X-ray diffraction. The uncoordinated phosphine group of $[Ru(C_5H_5)Cl\{(PPh_2)_2CHCH_2PPh_2\}]$ (**7**) reacts with $[IrCl(CO)_2(p\text{-toluidine})]$ to give $[(C_5H_5)RuCl\{(PPh_2)_2CHCH_2PPh_2\}Ir(CO)_2Cl]$ (**8**). Treatment of the heterobimetallic complex **8** with $Me_3NO \cdot 2H_2O$ affords $[(C_5H_5)Ru(\mu-CO)\{(PPh_2)_2CHCH_2PPh_2\}IrCl_2]$ (**9**). © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Iridium; Heterometallic complexes; Bidentate phosphines; Tridentate phosphine

1. Introduction

Heterometallic complexes have attracted considerable interest in recent years in relation to possible design of new bifunctional catalysts. Ring-opening (or metal-insertion) reactions of chelated bidentate phosphine ligands provide a useful route to ligand-bridged heterobimetallic complexes [1–12]. In these reactions, the reactant is usually a mononuclear complex containing a chelating phosphine ligand as part of a four-membered ring. On reaction with an appropriate metal complex, this four-membered ring opens to produce a ligand-bridged bimetallic complex in which the bidentate ligand becomes part of a less-strained five-membered ring [5–9]. We and others have previously reported examples of this type of reaction in which the ligands dppm (dppm = $Ph_2PCH_2PPh_2$), dppen (dppen = $Ph_2PC(=CH_2)PPh_2$) or dppa (dppa = $Ph_2PN(H)-$

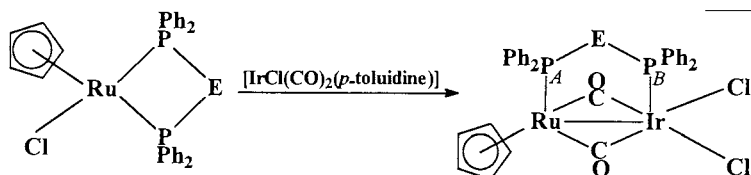
PPh_2) when chelated to iron or ruthenium atoms in the complexes $[(OC)_4Fe(dppm-p)]$, $[Fe(CO)_3(dppen)]$, $[Fe(C_5H_5)(CO)(dppm)]I$ or $[Ru(C_5H_5)Cl(dppa)]$ undergo a ring-opening (or metal-insertion) reaction on treatment with $[\{RhCl(CO)_2\}_2]$ to form the heterobimetallic complexes $[(OC)_4Fe(\mu-dppm)Rh(CO)Cl]$ [3], $[(OC)_4Fe(\mu-dppen)Rh(CO)Cl]$ [4,5], $[(C_5H_5)Fe(\mu-CO)_2(\mu-dppm)RhI_2]$ [13] and $[(C_5H_5)Ru(\mu-CO)_2(\mu-dppa)RhCl_2]$ [14]. In seeking to expand this type of chemistry, we have extended our studies to include three related systems that contain dppm, dppen and dppa ligands. In the course of this work, we have structurally characterized the new Ru–Ir bimetallic complexes by elemental analyses, IR and ^{31}P -NMR spectroscopy and FAB mass spectrometry. The molecular structure $[(C_5H_5)Ru(\mu-CO)_2\{\mu-Ph_2PN(H)PPh_2\}IrCl_2]$ has been determined by single-crystal X-ray diffraction. In addition, we have described the conversion of complex $[(C_5H_5)RuCl\{(PPh_2)_2CHCH_2PPh_2\}Ir(CO)_2Cl]$ into the heterobimetallic complex $[(C_5H_5)Ru(\mu-CO)\{(PPh_2)_2CHCH_2PPh_2\}IrCl_2]$.

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2. Results and discussion

The complexes $[\text{Ru}(\text{C}_5\text{H}_5)\text{Cl}(\text{dppm})]$ (**1**), $[\text{Ru}(\text{C}_5\text{H}_5)\text{Cl}(\text{dppen})]$ (**2**) or $[\text{Ru}(\text{C}_5\text{H}_5)\text{Cl}(\text{dppa})]$ (**3**) are prepared by a ligand exchange reaction between $[\text{Ru}(\text{C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)_2]$ and dppm [6], dppen [15] or dppa [14], respectively. The interesting features of these molecules are the compression of the P–E–P (E = CH_2 , $\text{C}=\text{CH}_2$ or NH) angle of the free ligands [6,14,15], brought about by chelation of the phosphine ligands to the ruthenium atom. We and others [6,8,14,15] find that the strain induced by chelation, as evidenced by reduced P–E–P bond angles, should make complexes **1**, **2** or **3** susceptible to ring-opening reactions. Indeed, treatment of **1**, **2** or **3** with $[\text{IrCl}(\text{CO})_2(p\text{-toluidine})]$ leads to the formation of the heterobimetallic complexes $[(\text{C}_5\text{H}_5)\text{Ru}(\mu\text{-CO})_2\{\mu\text{-dppm}\}\text{IrCl}_2]$ (**4**), $[(\text{C}_5\text{H}_5)\text{Ru}(\mu\text{-CO})_2\{\mu\text{-dppen}\}\text{IrCl}_2]$ (**5**) and $[(\text{C}_5\text{H}_5)\text{Ru}(\mu\text{-CO})_2\{\mu\text{-dppa}\}\text{IrCl}_2]$ (**6**), respectively, as shown in Eq. (1).



E = CH_2 for **1**, $\text{C}=\text{CH}_2$ for **2** or $\text{N}(\text{H})$ for **3**

The heterobimetallic complexes **4**, **5** and **6** have been confirmed by the presence of two bridging carbonyl groups in the IR spectra ($\nu(\text{CO})$ around 1795 and 1825 cm^{-1}), while the ^{31}P -NMR spectra clearly show the dppm , dppen and dppa ligands are bridging between the Ru and Ir atoms. The ^{31}P -NMR spectra of **4**, **5** or **6** heterobimetallic complexes (Table 1) show two sets of doublets. This pattern arises from two different phosphorus atoms, P_A and P_B . One doublet is due to the phosphorus atom (P_A) coordinated to Ru atom and is centered at δ 57.09 (J_{PP} 62.0 Hz) for complex **4**, at δ 57.8 (J_{PP} 107.422 Hz) for complex **5** or at δ 104.5 (J_{PP}

63.5 Hz) for complex **6**. The second doublet is assigned to phosphorus atom (P_B) coordinated to Ir atom and is centered at δ 9.27 (J_{PP} 62.0 Hz) for complex **4**, at δ 8.4 (J_{PP} 107.422 Hz) for complex **5** or at δ 42.0 (J_{PP} 63.5 Hz) for complex **6**.

Analysis by FAB mass spectroscopy of the heterobimetallic complexes **4**, **5** or **6** did not give a molecular ion peak at the desired position of $m/z = 869$, 881 or 870, respectively. A peak at $m/z = 834$, 846 or 835, however, was observed. There is a difference of 35 amu, indicating the loss of chlorine atom. The spectrum of each complex also shows a peak at $m/z = 778$, 790 or 779, a difference of 56 amu, corresponding to the loss of the two bridging carbonyl groups. Elemental analysis shows good agreement between theoretical and obtained values for **4**, **5** or **6** complexes.

In order fully to determine the structures of **4**, **5** or **6** complexes, crystallization was set up with complexes **4**, **5** or **6**. It was found that all the crystals grown were too

thin for X-ray purposes of complexes **4** or **5** but in case of complex **6**, a suitable yellow crystal was selected and mounted in a glass fiber. The structure of the heterobimetallic complex $[(\text{C}_5\text{H}_5)\text{Ru}(\mu\text{-CO})_2\{\mu\text{-dppa}\}\text{IrCl}_2]$ (**6**) has been determined by X-ray diffraction. The molecular structure of **6** is shown in Fig. 1 and selected bond lengths and angles are given in Table 2. The molecule consists of a $(\text{C}_5\text{H}_5)\text{Ru}$ unit and an IrCl_2 unit joined together by a bridging dppa ligand, two semi-bridging CO ligands, and a metal–metal bond. The Ru–Ir distance, 2.711(2) Å, is somewhat longer than

Table 1
Spectroscopic data

Complex	$^{31}\text{P}\text{-}\{^1\text{H}\}\text{-NMR}^a$	IR (cm^{-1}) ^b
$[\text{Ru}(\text{C}_5\text{H}_5)\text{Cl}(\text{dppm})]$ (1)	12.4 s	
$[\text{Ru}(\text{C}_5\text{H}_5)\text{Cl}(\text{dppen})]$ (2)	31.8 s	
$[\text{Ru}(\text{C}_5\text{H}_5)\text{Cl}(\text{dppa})]$ (3)	71.94 s	
$[(\text{C}_5\text{H}_5)\text{Ru}(\mu\text{-CO})_2\{\mu\text{-dppm}\}\text{IrCl}_2]$ (4)	57.09 (d), 9.27 (d, J_{PP} 62.0 Hz)	1825w, 1800s
$[(\text{C}_5\text{H}_5)\text{Ru}(\mu\text{-CO})_2\{\mu\text{-dppen}\}\text{IrCl}_2]$ (5)	57.8 (d), 8.4 (d, J_{PP} 107.422 Hz)	1825w, 1790s
$[(\text{C}_5\text{H}_5)\text{Ru}(\mu\text{-CO})_2\{\mu\text{-dppa}\}\text{IrCl}_2]$ (6)	104.5 (d), 42 (d, J_{PP} 63.5 Hz)	1825w, 1795s
$[\text{Ru}(\text{C}_5\text{H}_5)\text{Cl}\{(\text{PPh}_2)_2\text{CHCH}_2\text{PPh}_2\}]$ (7)	36.8 (d), –22.0 (t, J_{PP} 9.8 Hz)	
$[(\text{C}_5\text{H}_5)\text{RuCl}\{(\text{PPh}_2)_2\text{CHCH}_2\text{PPh}_2\}\text{IrCl}(\text{CO})_2]$ (8)	43.5 (d), 17.2 (t, J_{PP} 3.7 Hz)	2015s, 1965s
$[(\text{C}_5\text{H}_5)\text{Ru}(\mu\text{-CO})\{(\text{PPh}_2)_2\text{CHCH}_2\text{PPh}_2\}\text{IrCl}_2]$ (9)	39.1 (d), 26.1 (t, J_{PP} 9.8 Hz)	1799s

^a Recorded in THF/ C_6D_6 solution; chemical shift δ (ppm) relative to H_3PO_4 . Coupling constants in Hz.

^b $\nu(\text{CO})$ in CH_2Cl_2 .

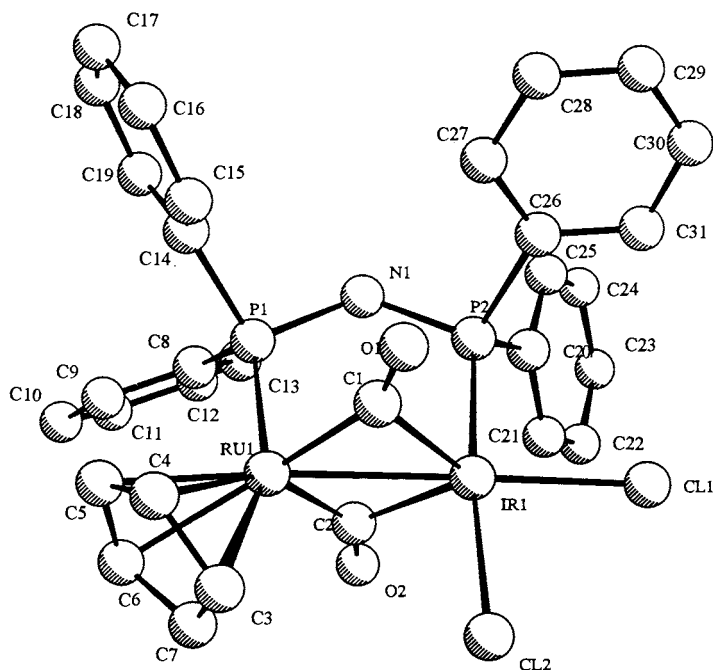


Fig. 1. The molecular structure of $[(C_5H_5)Ru(\mu-CO)_2\{\mu-Ph_2PN(H)PPh_2\}IrCl_2]$ (**6**).

those found, for example, in $[(C_5H_5)Ru(\mu-CO)_2\{\mu-dp-pen\}RhCl_2]$ (2.697(1) Å) [15]. The carbonyl ligands do not bridge symmetrically the Ru–Ir bond, the Ru–C(1) and Ru–C(2) distances being significantly shorter than the Ir–C(1) and Ir–C(2) distances and the Ru–C(1)–O(1) and Ru–C(2)–O(2) angles being significantly greater than the Ir–C(1)–O(1) and Ir–C(2)–O(2) angles. The P(1)–N(1)–P(2) angle of 126.9(6)° in complex **6** is very close to that found in the free ligand dppa 122.8° [16], and reflects the lack of strain at that nitrogen atom when it is involved in a five-membered ring. It is noteworthy that the two Cl ligands on the Ir atom show significantly different Ir–Cl bond lengths. The Ir–Cl bond *trans* to phosphine is longer (2.392 Å) than the Ir–Cl bond *trans* to Ru (2.327 Å).

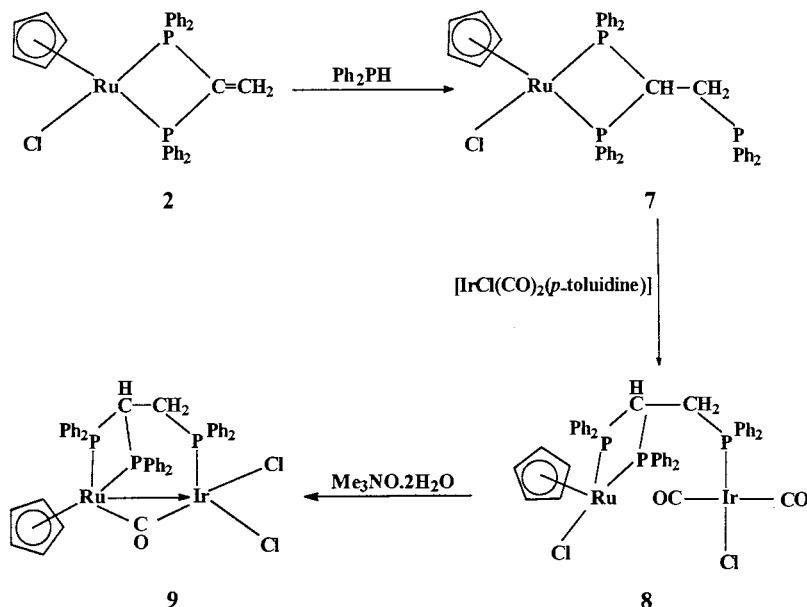
As an extension to our previous work on complex $[Ru(C_5H_5)Cl\{(PPh_2)_2CHCH_2PPh_2\}]$ (**7**), we intend to study the ability to synthesize new organometallic Ru–Ir compounds. The presence of a ‘dangling’ phosphine in complex **7** as shown in Scheme 1 provides an opportunity for further reaction with $[IrCl(CO)_2(p\text{-toluidine})]$ which we formulate as $[(C_5H_5)RuCl\{(PPh_2)_2CHCH_2PPh_2\}Ir(CO)_2Cl]$ (**8**) [17].

The IR spectrum of complex **8** showed two $\nu(CO)$ bands (2015 and 1965 cm^{-1}), indicating the *cis* arrangement of the CO ligands at the square-planar Ir atom. The ^{31}P -NMR signal of the dangling phosphine moved from $\delta -22.0$ to 17.2 and the phosphorus–phosphorus coupling constant was reduced to 3.7 Hz (Table 1) [17]. Complex **8** transforms slowly in solution over a period of 24 h, or immediately on addition of a methanol solution of $Me_3NO \cdot 2H_2O$ at

room temperature, into complex **9**. The IR spectrum of complex **9** shows a band at 1799 cm^{-1} , which indicating the expected bridging CO ligand. The ^{31}P -NMR spectrum shows a resonance at $\delta 39.8$ (d, J_{PP} 9.8 Hz) due to two phosphorus atoms coordinated to Ru, and a resonance centered at $\delta 26.1$ (t, J_{PP} 9.8 Hz) due to the phosphorus atom coordinated to Ir. The phosphorus–phosphorus coupling constant of 9.8 Hz similar to

Table 2
Selected bond lengths (Å) and angles (°) for $[(C_5H_5)Ru(\mu-CO)_2\{\mu-Ph_2PN(H)PPh_2\}IrCl_2]$ (**6**)

Bond lengths			
Ru–Ir	2.711(2)	Ir–Cl(1)	2.327(3)
Ru–P(1)	2.266(4)	Ir–Cl(2)	2.392(4)
Ru–C(1)	1.98(1)	Ir–C(1)	2.07(1)
Ru–C(2)	1.97(1)	Ir–C(2)	2.04(1)
Ru–C(3)	2.26(1)	C(1)–O(1)	1.16(1)
Ru–C(4)	2.25(1)	C(2)–O(2)	1.18(1)
Ru–C(5)	2.21(1)	P(1)–N(1)	1.70(1)
Ru–C(6)	2.23(1)	P(2)–N(1)	1.673(9)
Ru–C(7)	2.23(1)	N(1)–H(1)	0.7(1)
Ir–P(2)	2.241(4)		
Bond angles			
Ir–Ru–P(1)	93.1(1)	Cl(1)–Ir–Cl(2)	87.3(1)
P(1)–Ru–C(1)	90.8(4)	Ru–C(1)–O(1)	149.0(1)
P(1)–Ru–C(2)	85.2(3)	Ir–C(1)–O(1)	126.6(9)
Ru–Ir–P(2)	94.4(1)	Ru–C(2)–O(2)	147.0(9)
Ru–Ir–Cl(1)	178.3(8)	Ir–C(2)–O(2)	127.7(9)
Ru–Ir–Cl(2)	91.1(1)	P(1)–N(1)–P(2)	126.9(6)
P(2)–Ir–C(1)	87.7(3)	P(1)–N(1)–H(1)	102.0(11)
P(2)–Ir–C(2)	90.5(3)	P(2)–N(1)–H(1)	121.0(11)
Ir–Ru–C(1)	49.3(3)	Ru–P(1)–N(1)	112.5(3)
Ir–Ru–C(2)	48.6(3)	Ir–P(2)–N(1)	112.6(4)



Scheme 1.

that of $\{[(\text{CO})_3\text{Fe}(\text{Ph}_2\text{P})_2\text{CHCH}_2\text{PPh}_2\text{Rh}(\text{CO})\text{Cl}]\}$ [18] and larger than that of $\{[(\text{CO})_3\text{Fe}\{(\text{PPh}_2)_2\text{CHCH}_2\text{PPh}_2\text{Rh}(\text{CO})_3\text{Cl}_2\}]\}$ [19] suggests that a donor Ru–Ir bond is present (Scheme 1).

3. Experimental

All reactions were carried out under nitrogen unless otherwise stated using dry, degassed solvents and standard Schlenk-line techniques. IR spectra were recorded as dichloromethane solutions in 0.5 mm NaCl cells on a Perkin–Elmer 681 spectrophotometer; NMR spectra were recorded on Jeol FX-60 or Bruker WM250 instruments. Chemical shifts are relative to 85% H_3PO_4 for ^{31}P -NMR spectra. Microanalyses were carried out in the Department of Chemistry, University of Liverpool. FAB atom bombardment mass spectroscopy was used to run all the samples in 3-nitrobenzyl alcohol for a duration of 16 min.

The compounds $(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$ [20], $(\text{Ph}_2\text{PC}(\text{=CH}_2)\text{PPh}_2)$ [21], $(\text{Ph}_2\text{PN}(\text{H})\text{PPh}_2)$ [22], $[\text{Ru}(\text{C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)_2]$ [23], $[\text{Ru}(\text{C}_5\text{H}_5)\text{Cl}(\text{dppm})]$ [6], $[\text{Ru}(\text{C}_5\text{H}_5)\text{Cl}(\text{dppen})]$ [15], $[\text{Ru}(\text{C}_5\text{H}_5)\text{Cl}(\text{dppa})]$ [14], $[\text{Ru}(\text{C}_5\text{H}_5)\text{Cl}\{(\text{PPh}_2)_2\text{CHCH}_2\text{PPh}_2\}]$ [17] $[\text{Ru}(\text{C}_5\text{H}_5)\text{Cl}\{(\text{PPh}_2)_2\text{CHCH}_2\text{PPh}_2\}\text{IrCl}(\text{CO})_2]$ [17] and $[\text{IrCl}(\text{CO})_2(p\text{-toluidine})]$ [24] were prepared by published procedures.

3.1. Preparation of $[(\text{C}_5\text{H}_5)\text{Ru}(\mu\text{-CO})_2\{\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2\}\text{IrCl}_2]$ (**4**)

A solution of $[\text{Ru}(\text{C}_5\text{H}_5)\text{Cl}(\text{dppm})]$ (0.1 g, 0.17 mmol) and $[\text{IrCl}(\text{CO})_2(p\text{-toluidine})]$ (0.064 g, 0.17 mmol) in THF (50 ml) was stirred at 40°C for 1 h. The resulting

yellow solution was evaporated to dryness and the yellow residue was recrystallized from CH_2Cl_2 /heptane to give complex **4** as a yellow solid (0.099 g, 69.2%). Anal. Found: C, 44.44; H, 3.09. Calc. for $\text{C}_{32}\text{H}_{27}\text{Cl}_2\text{IrO}_2\text{P}_2\text{Ru}$: C, 44.19; H, 3.13%.

3.2. Preparation of $[(\text{C}_5\text{H}_5)\text{Ru}(\mu\text{-CO})_2\{\mu\text{-Ph}_2\text{PC}(\text{=CH}_2)\text{PPh}_2\}\text{IrCl}_2]$ (**5**)

A solution of $[\text{Ru}(\text{C}_5\text{H}_5)\text{Cl}(\text{dppen})]$ (0.05 g, 0.084 mmol) and $[\text{IrCl}(\text{CO})_2(p\text{-toluidine})]$ (0.032 g, 0.084 mmol) in toluene (10 ml) was stirred at 40°C for 1 h. The color changed immediately to yellowish–brown. The resulting yellow solution was evaporated to dryness and the yellow residue was recrystallized from CH_2Cl_2 /heptane to give complex **5** as a yellow solid (0.058 g, 80%). Anal. Found: 44.66; H, 3.12. Calc. for $\text{C}_{33}\text{H}_{27}\text{Cl}_2\text{IrO}_2\text{P}_2\text{Ru}$: C, 44.95; H, 3.09%.

3.3. Preparation of $[(\text{C}_5\text{H}_5)\text{Ru}(\mu\text{-CO})_2\{\mu\text{-Ph}_2\text{PN}(\text{H})\text{PPh}_2\}\text{IrCl}_2]$ (**6**)

$[\text{Ru}(\text{C}_5\text{H}_5)\text{Cl}(\text{dppa})]$ (0.058 g, 0.1 mmol) and $[\text{IrCl}(\text{CO})_2(p\text{-toluidine})]$ (0.039 g, 0.1 mmol) were added to degassed THF (20 ml) in the strict absence of air. The color changed immediately to yellowish–brown. The reaction mixture was stirred at 40°C for 1 h. The resulting yellow solution was evaporated to dryness and the yellow residue was recrystallized from CH_2Cl_2 /heptane to give complex **6** as a yellow solid (0.069 g, 79.0%). Anal. Found: 42.81; H, 3.10; N, 1.51. Calc. for $\text{C}_{31}\text{H}_{26}\text{Cl}_2\text{IrNO}_2\text{P}_2\text{Ru}$: C, 42.76; H, 3.01; N, 1.61%.

3.4. Preparation of $[(C_5H_5)RuCl\{(PPh_2)_2CH-CH_2PPh_2\}Ir(CO)_2Cl]$ (**8**)

A freshly prepared solution of $[Ru(C_5H_5)Cl\{(PPh_2)_2CHCH_2PPh_2\}]$ [17] (0.058 g, 0.074 mmol) in THF (10 ml) was added to a solution of $[IrCl(CO)_2(p\text{-toluidine})]$ (0.028 g, 0.074 mmol) in THF (10 ml). The mixture was stirred at 50°C and after 10 min, the solution was evaporated to dryness. The remaining solid was recrystallized from THF/benzene to give complex **8** as a yellow solid (0.059 g, 73.6%). Anal. Found: C, 50.15; H, 3.25. Calc. for $C_{45}H_{38}Cl_2IrO_2P_3Ru$: C, 50.6; H, 3.6%.

3.5. Preparation of $[(C_5H_5)Ru(\mu-CO)\{(PPh_2)_2CHCH_2PPh_2\}IrCl_2]$ (**9**)

Complex **8** (0.03 g, 0.028 mmol) was dissolved in THF (20 ml) and stirred at 40°C for 48 h. ^{31}P -NMR spectroscopy showed the reaction had occurred. Alternatively, complex **9** was prepared by the dropwise addition of $Me_3NO \cdot 2H_2O$ (0.003 g, 0.028 mmol) in methanol (2 ml) to a solution of complex **8** in THF (20 ml) with constant stirring. Spectroscopic analyses showed that complete conversion to complex **9** had occurred. The yellowish–brown solution was evaporated to dryness, and was recrystallized from THF/benzene to give complex **9** as a yellow solid (0.016 g, 51.3%). Anal. Found: C, 50.85; H, 3.45. Calc. for $C_{44}H_{38}Cl_2IrOP_3Ru$: C, 50.82; H, 3.68%.

3.6. X-ray crystallography

3.6.1. General information

Yellow crystals of the heterobimetallic complex $[(C_5H_5)Ru(\mu-CO)_2(\mu-Ph_2PN(H)PPh_2)IrCl_2]$ (**6**), suitable for X-ray diffraction studies, were obtained. All measurements were made on a Rigaku AFC6S diffractometer equipped with graphite monochromated $Mo-K_{\alpha}$ radiation. The basic crystallographic procedures used have been fully described elsewhere [25,26]. An empirical absorption correction based on azimuthal scans was applied. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods. The non-hydrogen atoms were refined either anisotropically or isotropically. Hydrogen atoms were included in the structure factor calculation in idealized position, and were assigned isotropic thermal parameters, which were 20% greater than the B_{eq} value of the atom to which they were bonded. All calculations were performed using the TEXSAN crystallographic software package supplied by the Molecular Structure Corporation [27].

3.6.2. Crystal structure analysis of $[(C_5H_5)Ru(\mu-CO)_2(\mu-Ph_2PN(H)PPh_2)IrCl_2]$ (**6**)

Crystals of complex **6** were grown from a dichloromethane/heptane solution. A suitable yellow prism crystal of dimensions $0.35 \times 0.15 \times 0.30$ mm was mounted on a glass fiber. The data were collected at temperature of $-120 \pm 1^\circ C$. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinements using the setting angles of 20 carefully centered reflections in the range $34.9 < 2\theta < 41.33^\circ$. A total of 12 404 reflections recorded, of which 11 924 unique ($\theta = 25^\circ$, $R_{int} = 0.069$) using the ω scan technique. The intensities of three representative reflections, which were measured after every 150 reflections, remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied). The final cycle of full-matrix least-squares refinement was based on 5684 observed reflections ($I > 3\sigma(I)$) and 527 variable parameters. The weighting scheme was $w = 4F_o^2/\sigma^2(F_o)^2$. The final R and R' values were 0.042 and 0.045, respectively.

3.6.3. Crystal data

$C_{31}H_{26}Cl_2IrNO_2P_2Ru$, $M = 870.7$, monoclinic, space group $P2_1/n$ (no. 14), $a = 20.91(2)$, $b = 14.29(1)$, $c = 24.13(1)$ Å, $\beta = 106.52(7)^\circ$, $V = 6912(8)$ Å³ (by least-squares refinement of angles from 20 reflections), $Mo-K_{\alpha}$ ($\lambda = 0.71069$ Å) radiation, $Z = 8$, $D_{calc} = 1.80$ g cm^{-3} , $F(000) = 3648$, $\mu = 45.42$ cm^{-1} , $T = -120^\circ C$, $R = 0.042$ (for 5684 reflections with $I > 3\sigma(I)$).

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