

تشخيص مركبات عنقودية لعناصر الروديوم ، والإيريديوم



بعد تفاعلها مع لواقق إضافة مثالية باستخدام أحادي وثنائي الأبعاد للرنين النووي المغناطيسي و مطياف الكتلة

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ملخص البحث :

المركبات العنقودية لعناصر الروديوم والإيريديوم المختلطة $[\text{RhIr}_2(\mu\text{-PPh}_2)_3(\text{CO})_5]$ و $[\text{IrRh}_2(\mu\text{-PPh}_2)_3(\text{CO})_5]$ تم تخليقها ، والتحقق من تفاعلها مع لواقق إضافة مثل (CO) و (DPPM). تم تشخيص هذه المركبات باستخدام (1-D , 2-D) $\text{NMR } \{^1\text{H}\} \text{COSY } ^{31}\text{P}$ (أحادي وثنائي الأبعاد للرنين النووي المغناطيسي و (-FAB MS) مطياف الكتلة. النشاط الكيميائي لهذه المركبات من خلال التفاعل مع لواقق إضافة مثالية وتم مقارنته مع نظائرها من المركبات المتجانسة الفلزات .

$[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_6]$ و $[\text{Ir}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]$ وأظهر اختلافات في التفاعلات ترجع الى تأثير فلز على الآخر في المركب الواحد. هذا التأثير غالباً ما تكون له أهمية بالغة في انظمة المحفزات من حيث تصميمها لأهداف ، و تفاعلات كيميائية محددة. ففي تفاعلات الهدرجة على سبيل المثال تستغل قوة المركز الفلزي لعنصر على الآخر في المركب الواحد ، وتستخدم هذه الخاصية في محفزات من هذا النوع في العديد من التفاعلات العضوية التي تتطلب إضافة ذرة هيدوجين او كربون في حالة الهيدروفورمولة. لذا نرى أهمية لهذه المركبات في دراسة عديد التفاعلات العضوية و الغير عضوية

1-D and 2-D COSY $^{31}\text{P}\{^1\text{H}\}$ NMR Spectra of mixed Rhodium-Iridium clusters $[\text{RhIr}_2(\mu\text{-PPh}_2)_3(\text{CO})_5]$ reaction with PPh_3 and DPPM.

Abstract.

The synthesis of mixed rhodium and iridium clusters $[\text{RhIr}_2(\mu\text{-PPh}_2)_3(\text{CO})_5]$, and $[\text{IrRh}_2(\mu\text{-PPh}_2)_3(\text{CO})_5]$ and their reactions with triphenylphosphine (PPh_3), and Bis(diphenylphosphino)methane

(Dppm) was investigated. These derivatives were characterized by 1-D and 2-D COSY $^{31}\text{P}\{^1\text{H}\}$ NMR, fab-mass spectrometry and x-ray crystallography. The reactivity of these mixed metal clusters with (CO) and $\text{P}(\text{OMe})_3$ was compared to their analogues homonuclear clusters $[\text{Ir}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]$, and $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_6]$ and showed significant differences attributable to the effect of one metal on the other.

Introduction

Heterometallic transition metal clusters are of considerable interest in recent years. This area of research has been reviewed in past few decades to indicate the considerable potential of mixed-metal clusters in homogeneous catalysis⁽¹⁻⁴⁾. Braunstein and co-workers⁽⁵⁾ synthesized the Pd-Mo heterogeneous catalyst derived from the cluster $[\text{Pd}_2\text{Mo}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_6(\text{PPh}_3)_2]$. This catalyst resulted in a total conversion of and higher selectivity for reductive carbonylation of nitrobenzene to phenylisocyanate than did conventional bimetallic catalysts. Clusters such as $\text{Fe}_2\text{Ru}(\text{CO})_{12}$ and $\text{Ru}_2\text{Fe}(\text{CO})_{12}$ played a significant role as heterometallic carbonyl clusters in homogeneous catalysis in the hydrogenation and isomerization of alkynes and dienes⁽⁶⁾. It has been found that in some instances, cluster catalysis occurs and that the activity is related to the electronic effects of substituent⁽⁷⁾.

Hydrogenation experiments with phosphido-bridged clusters as catalysts showed that the activity is dependent neither on the presence of hydrido- or phosphido-bridges nor on their number^(24,25). With respect to analyzing reaction mechanisms in cluster systems, mixed-metal clusters are particularly useful to provide information with regard to (1) the effect of one metal on the reactivity of the adjacent metal centers; (2) details concerning

site(s) of chemical reactions; and (3) the mechanisms of the cluster assembly process⁽⁸⁾. Information relevant to these aforementioned goals has been obtained from the utilization of phosphido-bridged ligands in the development and study of new and chemically heterometallic systems⁽⁹⁻¹⁴⁾.

A few phosphido-bridged trimetallic mixed-metal clusters have been reported. The novel mixed cobalt and iron cluster $\text{Fe}_2\text{Co}(\mu\text{-PMe}_2)_3(\text{CO})_5(\text{NO})_2$ has been prepared by reacting Me_2PH with $\eta^3\text{-C}_3\text{H}_5\text{Co}(\text{CO})_3$ and $(\text{NO})(\text{CO})_3\text{Fe}(\text{PMe}_2\text{H})$ ⁽¹⁵⁾. Dixon and co-workers⁽¹⁶⁾ reported the mixed Palladium and Platinum cluster $[\text{Pd}_2\text{Pt}(\mu\text{-PPh}_2)_2((\mu\text{-Cl})(\text{PPh}_3)_3)]$. Study of this cluster using $^{31}\text{P}\{^1\text{H}\}$ NMR has shown the utility of this technique in work involving previously difficult to characterize cluster systems, and several features of $^{31}\text{P}\{^1\text{H}\}$ NMR spectra are diagnostic of the presence of metal-metal bonds. Braneset. al.,⁽¹⁷⁾ reported a series of 46-electron mixed Co, Rh, and Ir clusters; $[(\text{Cp}^* \text{M})(\text{CpCo})_2(\text{CO})_2]$ (M_2Co series $\text{M}=\text{Ir}, \text{or Rh}$) and $[(\text{Cp}^* \text{M})_2(\text{CpCo})(\text{CO})_2]$ (MCo_2 series $\text{M}=\text{Ir}, \text{or Rh}$). This work focuses on the synthetic approach of the mixed rhodium and iridium clusters $[\text{RhIr}_2(\mu\text{-PPh}_2)_3(\text{CO})_5]$ and $[\text{IrRh}_2(\mu\text{-PPh}_2)_3(\text{CO})_6]$ and their derivatives. With the aid of $^{31}\text{P}\{^1\text{H}\}$ NMR (1D and 2D), line shape analysis, and FAB-MS, identification and characterization of these mixed metal clusters.

Experimental.

All the syntheses described in this work were carried out under an atmosphere of dry nitrogen gas using standard Schlenk preparative techniques at ambient temperature. Microanalysis data were supplied by Canadian Microanalytical Services Ltd. , Vancouver, B.C. Infrared spectra were obtained using a Perkin-

Elmer 283 spectrophotometer, and ultraviolet-visible were measured on a Philips PU 8740 spectrophotometer. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker WM250 and AC360 FT-spectrometer operating at 101.3 MHz, and 145.8 MHz respectively. Protons were decoupled By broad band irradiation at appropriate frequencies. Chemical shifts are reported in ppm relative to 85% H_3PO_4 . Second order $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were analyzed by computer simulation using Vestr and NMRPLOT programs^(18,19). FAB-mass spectra were recorded on a Kratos Concept mass spectrometer using matrix meta-nitrobenzyl alcohol, sample sometimes dissolved in dichloromethane. The data for the crystal structure collected on Enraf-Nonius CAD4 diffractometer. The instrument uses Mo $K\alpha$ radiation.

Most of the commonly used reagents including $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and PPh_3 were purchased from Aldrich Chemicals Ltd. $(\text{NH}_4)_2\text{IrCl}_6$ and K_3RhCl_6 were synthesized from recovered metals using procedures described in references⁽²¹⁾, for Ir and⁽¹⁷⁾, for Rh. $\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2$, [COD = 1,5-cyclooctadiene] and $\text{Ir}_2(\mu\text{-Cl})_2(\text{COE})_4$, [COE = cyclooctene]synthesized according to procedures described in⁽²²⁾.

Synthesis of $[\text{RhIr}_2(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2]$ (1**) and $[\text{IrRh}_2(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2]$ (**2**)** carbon monoxide was bubbled vigorously through a solution of $[\text{Ir}_2(\mu\text{-Cl})_2(\text{COE})_4]$ (0.20 g ,0.11 mmol) and $[\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2]$ (0.11g mmol), 0.22 in benzene (20 ml) resulting in dark greencolor solution . Diethylamine (0.091 ml, 0.88mmol) was added dropwise to the stirred mixture and after 10 minutes a brow-yellow solution had formed. Addition of diphenylphosphine (0.15 ml, 0.88mmol) caused an immediate change to pink-red solution containing a mixture of $[\text{RhIr}_2(\mu\text{-PPh}_2)_3(\text{CO})_5]$, $[\text{IrRh}_2(\mu\text{-$

$\text{PPh}_2)_3 (\text{CO})_5$, $[\text{Ir}_3(\mu\text{-PPh}_2)_3 (\text{CO})_5]$, and $[\text{Rh}_3(\mu\text{-PPh}_2)_3 (\text{CO})_6]$. Triphenylphosphine (0.15g, 0.59 mmol) was added to the stirred solution and the color changed from pink-red to dark green. After 16 hours solvent was removed in vacuo, and the residue was dissolved in a minimum amount of benzene and transferred to alumina column. A dark purple band was eluted with benzene, solvent was removed in vacuo, and crystallization of the residue from dichloromethane and hexanes gave the product as dark red purple crystals (0.11g). The clusters were isolated as, $[\text{RhIr}_2(\mu\text{-PPh}_2)_3 (\text{CO})_3(\text{PPh}_3)_2]$ (1), $[\text{IrRh}_2(\mu\text{-PPh}_2)_3 (\text{CO})_3(\text{PPh}_3)_2]$ (2), $[\text{Ir}_3(\mu\text{-PPh}_2)_3 (\text{CO})_3(\text{PPh}_3)_2]$ (3), and $[\text{Rh}_3(\mu\text{-PPh}_2)_3 (\text{CO})_3(\text{PPh}_3)_2]$ (4) in the respective ratios 6:4:2:3 (mixture was identified by 2D- and 1D $^{31}\text{P}\{^1\text{H}\}$ NMR, IR, and FAB-MS).

Synthesis of $[\text{RhIr}_2(\mu\text{-PPh}_2)_3 (\text{CO})_3(\text{dppm})]$ (5) and $[\text{IrRh}_2(\mu\text{-PPh}_2)_3 (\text{CO})_3(\text{dppm})]$ (6) carbon monoxide was bubbled vigorously through a solution of $[\text{Ir}_2(\mu\text{-Cl})_2(\text{COE})_4]$ (0.20 g, 0.11 mmol) and $[\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2]$ (0.11g mmol), 0.22 in benzene (20 ml) resulting in dark green color solution. Diethylamine (0.091 ml, 0.88mmol) was added dropwise to the stirred mixture and after 10 minutes a brown-yellow solution had formed. Addition of diphenylphosphine (0.15 ml, 0.88 mmol) caused an immediate change to pink-red solution containing a mixture of $[\text{RhIr}_2(\mu\text{-PPh}_2)_3 (\text{CO})_5]$, $[\text{IrRh}_2(\mu\text{-PPh}_2)_3 (\text{CO})_5]$, $[\text{Ir}_3(\mu\text{-PPh}_2)_3 (\text{CO})_5]$, and $[\text{Rh}_3(\mu\text{-PPh}_2)_3 (\text{CO})_6]$. Bis(diphenylphosphino)methane (Dppm) (0.11g, 0.29 mmol) was added to stirred solution and the color was changed from pink-red to dark purple. After 1.5 hour solvent was removed in vacuo, and the residue dissolved in a 5ml of benzene and transferred to alumina column. A red-purple band was eluted with benzene, solvent was removed in vacuo, followed by crystallization of the residue by dichloromethane and hexanes to afford dark-purple

cubes (0.13). The clusters isolated as, $[\text{RhIr}_2(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{dppm})]$ (**5**), $[\text{IrRh}_2(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{dppm})]$ (**6**), $[\text{Ir}_3(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{dppm})]$ (**7**), and $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{dppm})]$ (**8**) in the respective ratios 5:5:4:3 (mixture was identified by 2D- and 1D $^{31}\text{P}\{^1\text{H}\}$ NMR, IR, and FAB-MS).

Results and discussions

Crystallographic analysis

The crystal structure of $[\text{RhIr}_2(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2]$ (**1**) was determined. The cluster crystallizes in the $\text{Pna}2$ space group. The molecule is shown as an ORTEP diagram in figure 1. The structure is very similar to that of $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2]$ reported by Jamerson and co-workers⁽²⁵⁾. The structure of $[\text{RhIr}_2(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2]$ (**1**) based on triangle of two iridium atoms and one rhodium atom. The relevant selected bond lengths and angles are shown in tables 1. The rhodium atom Rh(1), is two electrons short of the raregas configuration and is thus coordinatively unsaturated. Each edge of the trimetallic triangle of the cluster is bridged by diphenylphosphido ligand. The two PPh_2 groups coordinated to the rhodium atom are coplanar with the metal atoms plan, while the third, coordinated to Ir(1) and Ir(2), is almost perpendicular to the Ir_2Rh plane. The metal-metal distances [Ir(1)-Rh(1), 2.87(4) Å; Ir(2)-Rh(1), 2.837(5) Å; Ir(1)-Ir(2), 2.723(4) Å] correspond with those normally associated with formal metal-metal bonds. Each iridium atom has PPh_3 ligand coordinated to them, and each metal atom has a single CO ligand.

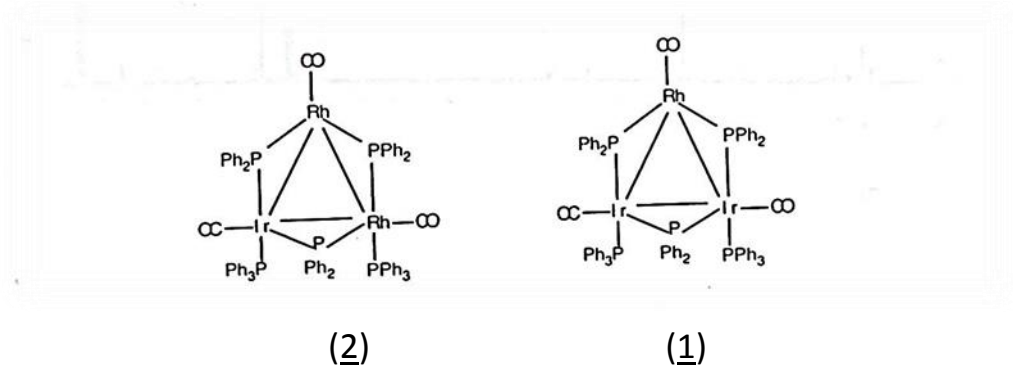
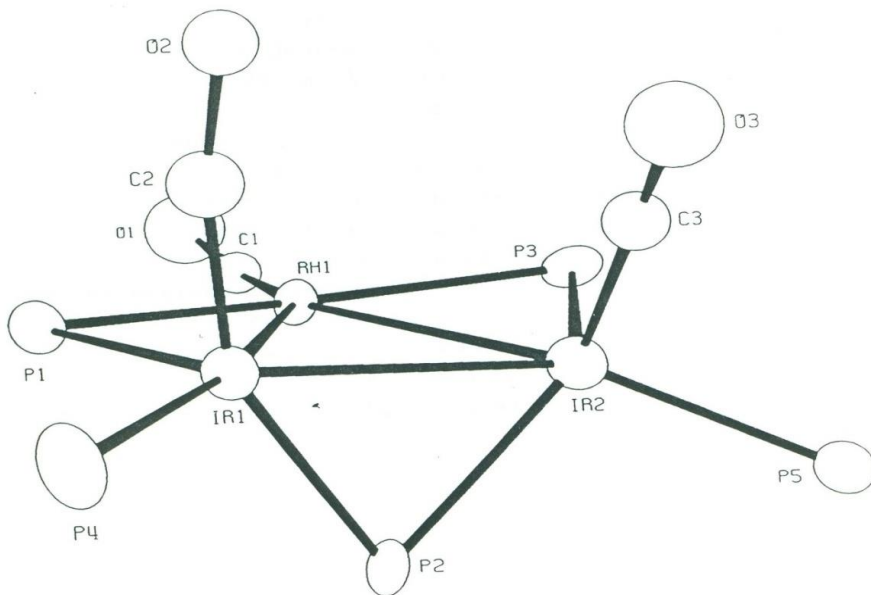


Figure 1. The molecular structure of $[\text{RhIr}_2(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2](1)$ (Phenyl groups are not shown for clarity). [Crystallographic parameters: formula, $\text{C}_{75}\text{H}_{60}\text{O}_3\text{P}_5\text{Ir}_2\text{Rh}$; fw, 1652; Space group, $\text{Pna}2_1(\text{No.}33)$; Radiation(\AA), $\text{Mo}(\lambda=0.71069)$;



Total reflections collected, 4406; No. of unique reflections in the final database, 2030; R=0.1003; R_w=0.1293]

Table(1). Selected bond distances (Å) and angles(°) for the cluster [RhIr₂(μ-PPh₂)₃ (CO)₃(PPh₃)₂]

(Estimated standard deviations are given in parentheses)

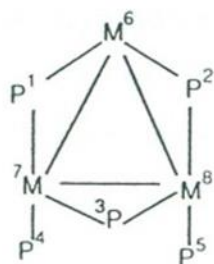
Atoms	Distances	
Ir(1)-Ir(2)	2.723(4)	Rh(1)-
Ir(1)	2.817(4)	
Rh(1)-Ir(2)	2.837(4)	P(1)-Ir(1)
2.310(3)		
P(2)-Ir(1)	2.330(3)	P(4)-Ir(1)
2.340(3)		
C(2)-Ir(1)	1.900(3)	P(2)-Ir(2)
2.350(3)		
P(3)-Ir(2)	2.290(3)	P(5)-Ir(2)
2.310(3)		
C(3)-Ir(2)	1.940(3)	P(1)-
Rh(1)	2.290(3)	
P(3)-Rh(1)	2.250(3)	C(1)-
Rh(1)	1.758(10)	
C(1)-O(1)	1.179(10)	C(2)-O(2)
1.160(3)		
C(3)-O(3)	1.050(3)	

Atoms Angles

Rh(1)-Ir(1)-Ir(2)	61.60(1)
Rh(1)-Ir(2)-Ir(1)	60.80(1)
Ir(2)-Rh(1)-Ir(1)	57.60(1)
P(2)-Ir(1)-P(1)	100.0(6)
P(4)-Ir(1)-P(1)	110.6(6)
P(4)-Ir(1)-P(2)	109.0(7)
C(2)-Ir(1)-P(2)	88.40(3)
P(3)-Ir(2)-P(2)	110.0(6)
P(5)-Ir(2)-P(3)	103.1(6)
P(5)-Ir(2)-P(2)	101.3(6)
C(3)-Ir(2)-P(5)	91.8(3)
P(3)-Rh(1)-P(1)	159.2(6)
Rh(1)-P(1)-Ir(1)	75.60(5)
Ir(2)-P(2)-Ir(1)	71.20(5)
Rh(1)-P(3)-Ir(2)	77.50(6)

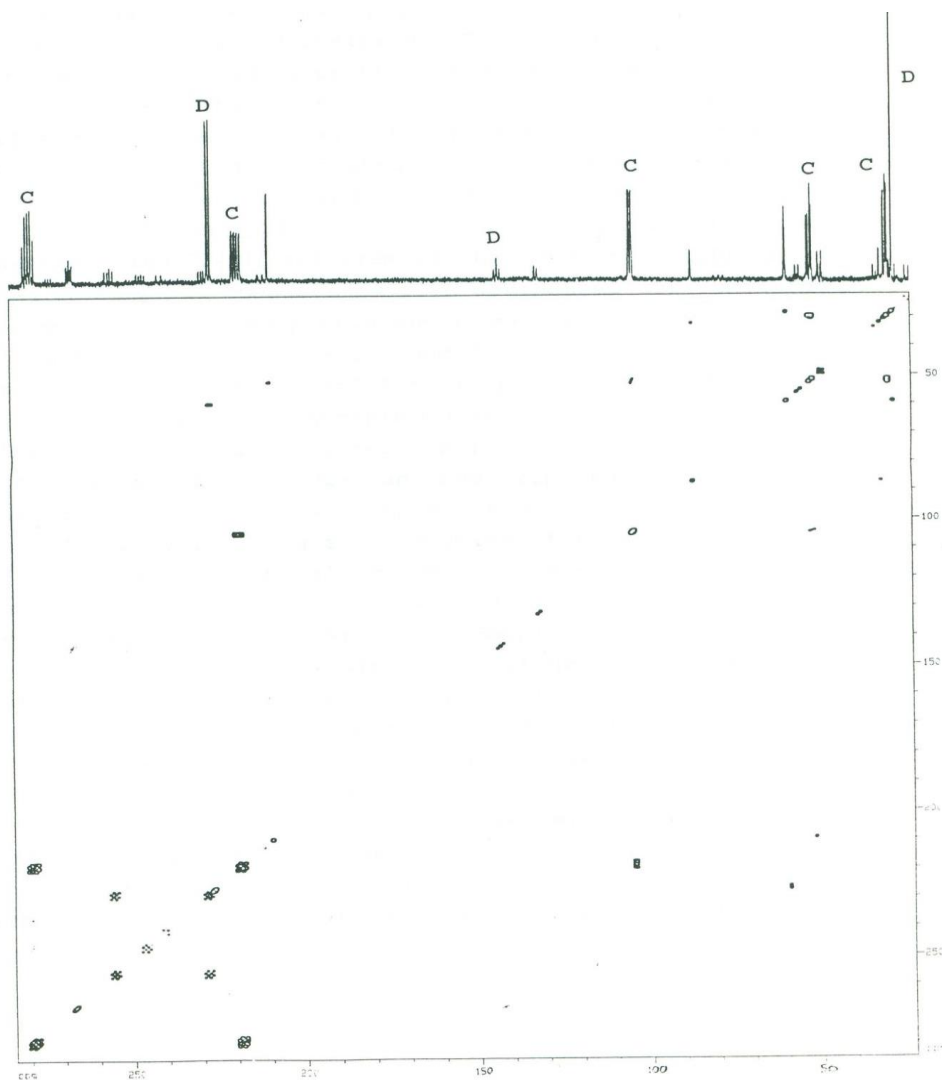
Spectroscopic Analysis

1D- and 2D- $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the mixture (1) – (4) have been obtained and analyzed. The $^{31}\text{P}\{^1\text{H}\}$ COSY NMR spectrum indicates the presence of four different cluster systems (figure 2). Signals due to clusters (3) and (4) are easily matched with their previously reported clustered^(26,27). Correlation of contours resulting from heteronuclear clusters $[\text{RhIr}_2(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2]$ (1) and $[\text{IrRh}_2(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2]$ (2), leads to the identification of both clusters. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the asymmetric $[\text{RhIr}_2(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2]$ (1) consists of five resonances corresponding to five different phosphorus environments. The multiplets at 278.7, 218.3, 104.2, 51.7, and 29.7 ppm are assigned to P(1), P(2), P(3), P(4), and P(5) respectively table(2).



Table(2). ³¹P{¹H} NMR chemical shift (δ ,ppm) and coupling constants (Hz) of the clusters (1) and (2)

	Cluster (2)	Cluster (1)		Cluster(2)	Cluster(1)
$\delta(1)$	278.7	226.3			
$\delta(2)$	218.3	226.3			
$\delta(3)$	104.2	58.9			
$\delta(4)$	51.7	29.8			
$\delta(5)$	29.7	29.8			
J(1,2)	226	0	J(3,5)	0	21
J(1,3)	0	18	J(3,6)	0	0
J(1,4)	0	0	J(3,7)	108	---
J(1,5)	0	0	J(3,8)	---	---
J(1,6)	115	117	J(4,5)	55	0
J(1,7)	115	---	J(4,6)	0	0
J(1,8)	---	---	J(4,7)	159	---
J(2,3)	21	18	J(4,8)	---	---
J(2,4)	0	0	J(5,6)	0	0
J(2,5)	0	0	J(5,7)	0	---
J(2,6)	119	117	J(5,8)	---	---



J(2,7)	0	---	J(6,7)	0	---
J(2,8)	---	---	J(6,8)	---	---
J(3,4)	5	21	J(7,8)	---	---

Figure 2. $^{31}\text{P}\{^1\text{H}\}$ COSY NMR spectrum of the cluster (D): $[\text{RhIr}_2(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2]$ (1) and (C): $[\text{IrRh}_2(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2]$ (2)

The resonance P(1) is interpreted as overlapping doublet of triplets. The doublet results strong coupling of P(1) with P(2) (226 Hz) and the triplets are due to equal coupling of P(1) with Rh(6), and Rh(7) (115Hz). The large J(1,2) value suggests planarity of these two bridging phosphides with metal triangle. The multiplet P(2) is viewed as doublet of doublets of doublets. P(2) couples strongly with P(1) (226Hz), then couples with Rh(6) (119Hz), and finally couples with P(3) (21Hz). The small coupling constant J(2,3) results from the P(3) bridge being perpendicular to the trimetallic core, whereas P(1) and P(2) are in the plane of the metal core. The third resonance P(3) is also viewed as doublet of doublets of doublets. P(3) couple with Rh(7) giving the large doublet (108Hz), then couples with P(2) (21Hz), and finally with P(4) (5Hz). The resonance assigned to terminal PPh_3 P(4) and P(5) are easily analyzed. P(4) couples strongly with Rh(7) (159Hz), to give large doublet, then couples with P(5) (55Hz). The resonance P(5) is observed as doublet (55Hz). The large J(4,5) suggests linearity between $\text{PPh}_3\text{-Rh-Ir-PPh}_3$, which correlates with the small J(3,4) value.

The symmetric cluster $[\text{RhIr}_2(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2]$ (1) gives much simpler $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The resonances at 226.3, 58.9, and 29.8 ppm are assigned to P(1,2), P(3), and P(4,5) respectively (table 3). The first multiplet due to P(1,2) is doublet of doublets, in which P(1) and P(2) are equally coupled with Rh(6) so that $J(1,6)=J(2,6)=117\text{Hz}$, the similarly P(1) and P(2) couple equally with P(3), so that $J(1,3)=J(2,3)=18\text{Hz}$. The resonance due to P(3) is simple triplet (18Hz), due to coupling to both P(1) and P(2). Finally, the terminal P(4) and P(5) couple equally with P(3) to give strong

doublet (21Hz). Structurally the small coupling value of J(3,4) suggests a small angle between the terminal triphenylphosphine and the unique diphenylphosphido bridge P(3). Since the latter is above the metal plane, it is likely that the carbonyl ligands are below the plane.

FAB-MS analysis of the mixture of clusters (1)-(4) is particularly diagnostic of the mixed metal clusters $[\text{RhIr}_2(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2](\underline{1})$ and $[\text{IrRh}_2(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2](\underline{2})$. The mass spectrum of both clusters shows a molecular ion peak at m/z 1652 $[\text{MH}]^+$ corresponds to $[\text{RhIr}_2(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2](\underline{1})$ and a fragment ion peak at m/z 1535, $[\text{M-CO}]$. A sequential loss of CO ligands as well as PPh_3 is observed for both spectra.

Phosphido-bridged mixed iridium and rhodium clusters are structurally similar to their corresponding homonuclear systems. This is evident from $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy of both heteronuclear and homonuclear systems. The reactivity of both systems with CO and $\text{P}(\text{OMe})_3$ on the other hand differs slightly. Homonuclear clusters such as $[\text{Ir}_3(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{dppe})]^{(27)}$, and $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]^{(28)}$ react with CO and result in metal-atom core expansion. No reactions observed when corresponding heteronuclear cluster mixtures treated with excess CO. The reason for this inertness of mixed-metal clusters towards CO molecules is not clear at present. $\text{P}(\text{OMe})_3$ easily replaces ligands such as PPh_3 in $[\text{M}_3(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2]$, $\text{M} = \text{Ir}$ or Rh to result in $[\text{M}_3(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2\{\text{P}(\text{OMe})_3\}]$ leaving PPh_3 ligands unaffected. This represents another example which demonstrates the effect of one metal on the reactivity of an adjacent metal.

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