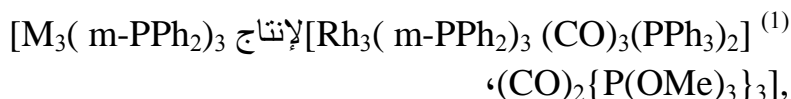


دراسة تأثير مركز فلزي على مركز فلزي مجاور في معقد من خلال تفاعل ثلاثي ميثيل الفوسفات مع معقدات الروديو والاريدوم المختلطة.

د. فتحي محمد الصيد - كلية علوم الزاوية، جامعة الزاوية

الملخص :

لاصقة ثلاثي ميثيل الفوسفات $P(OMe)_3$ بسهولة تحل محل لاصقة ثلاثي
فينيل الفوسفين PPh_3 في المركبات العنقودية المتجانسة تم دراستها مسبقاً $[Ir_3(m-PPh_2)_3(CO)_3(PPh_3)_2]$



$[RhIr_2(m-PPh_2)_3]$ ، بينما في هذه الدراسة المعقدات الغير متجانسة، $M=Ir$ or Rh
 $PPh_2)_3(CO)_5(PPh_3)_2]$

لاصقة ثلاثي ميثيل الفوسفات $P(OMe)_3$ تحل محل لاصقة اول كسيد الكربون
(CO) فقط ولا تحل محل لاصقة ثلاثي فينيل الفوسفين PPh_3 ، الدليل الواضح علي
تأثير مركز فلزي على مركز فلزي مجاور من حيث النشاط الكيميائي. جسدت
هذه الدراسة الاعتماد على الرنين النووي المغناطيسي لذرة الفوسفور من حيث
ازدواجها النشط مع ذرات الفوسفور الاخرى والروديووم في هذا النوع من
المعقدات عملية اربط والضع الهندسي للمراكز الفلزية في هذه المعقدات.

Study of the effect of one metal center on adjacent metal through thereaction of $P(OMe)_3$ with $[RhIr_2(\square\square-PPh_2)_3$ $(CO)_3(PPh_3)_2]$ and $[RhIr_2(\square\square-PPh_2)_3(CO)_5]$ using $^{31}P\{^1H\}$ NMR and FAM-MS

Abstract.

Trimethylphosphite $P(OMe)_3$, easily replaces ligands
such as PPh_3 in the homonuclear clusters $[Ir_3(\square\square-PPh_2)_3$

$(\text{CO})_3(\text{PPh}_3)_2]$ and $[\text{Rh}_3(\square\square\text{-PPh}_2)_3 (\text{CO})_3(\text{PPh}_3)_2]^{(1)}$ to afford $[\text{M}_3(\square\square\text{-PPh}_2)_3 (\text{CO})_2\{\text{P}(\text{OMe})_3\}_3]$, $\text{M}=\text{Ir}$ or Rh , whereas, in $[\text{RhIr}_2(\square\square\text{-PPh}_2)_3 (\text{CO})_5(\text{PPh}_3)_2]$, $\text{P}(\text{OMe})_3$ replaces only the carbonyl ligand on Rh leaving the PPh_3 ligands unaffected. This represents another example which demonstrates the effect of one metal on the reactivity of adjacent metal. $^{31}\text{P}\{^1\text{H}\}$ nmr was a vital technique in probing this phenomenon.

Introduction

A large number of phosphido-bridged clusters has been reported in recent years. Hains and co-workers have synthesized and characterized the tetranuclear clusters $[\text{Rh}_4(\square\square\text{-PPh}_2)_4(\square\text{-Cl})_2(\text{PPhH})_2(\text{CO})_4]$, and $[\text{Rh}_4(\square\square\text{-PPh}_2)_4(\square\text{-CO})_2(\text{CO})_4]^{(2)}$ as investigative study of the potential of diphenylphosphido ligands, PPh_2 , for stabilizing homonuclear and heteronuclear clusters of unusual geometry and stereochemistry⁽³⁻⁵⁾. In principle, phosphido-bridged are able to preserve the integrity of the cluster while permitting the breaking and making of metal-metal bonds. A number of these phosphido-bridged clusters have been reported, and examples include $[\text{Co}_3(\square\square\text{-PPh}_2)_2(\square\text{-CO})(\text{CO})_6]^{(6)}$, $[\text{Rh}_3(\square\square\text{-P}^t\text{Bu})_3(\text{CO})_5]^{(7,8)}$, $[\text{Ir}_3(\square\square\text{-P}^t\text{Bu})_3(\text{CO})_6]^{(9)}$, and $[\text{Ir}_3(\square\square\text{-PPh}_2)_3(\text{CO})_5]^{(10)}$, $[\text{Rh}_3(\square\square\text{-PPh}_2)_3(\text{CO})_5]^{(11)}$. These types of clusters are known to undergo several types of reactions. Ligand addition, ligand substitution, and oxidative addition are among the reactions that are known to dominate in cluster chemistry. Haines and Steen⁽¹¹⁾ have synthesized the 46-electron cluster $[\text{Rh}_3(\square\square\text{-PPh}_2)_3(\text{CO})_5]$ with average Rh-Rh bond 2.77\AA , they also investigated its reactivity with CO (Carbon monoxide) and PPh_2H (Diphenylphosphine). Saturation of the

cluster with CO converts the cluster to $[\text{Rh}_3(\square\square\text{-PPh}_2)_3(\text{CO})_9]$ which quickly degrades to the unstable 50-electron cluster $[\text{Rh}_3(\square\square\text{-PPh}_2)_3(\text{CO})_7]$ with average Rh-Rh bonds of 3.15Å. This expansion from bonding to non-bonding metal-metal distances is also present in the cluster $[\text{Rh}_3(\square\square\text{-PPh}_2)_3(\text{PPh}_2\text{H})(\text{CO})_6]$ with average Rh-Rh bond of 3.17Å. The neutral ligand PPh_3 (triphenylphosphine) substitutes CO ligands instead of adding to $[\text{Rh}_3(\square\square\text{-PPh}_2)_3(\text{CO})_5]$.

Dixon and co-workers⁽¹⁰⁾ reacted $[\text{Rh}_3(\square\square\text{-PPh}_2)_3(\text{CO})_5]$ with chelating ligand dppm, (bis(diphenylphosphino)methane) to obtain the highly stable derivative, $[\text{Rh}_3(\square\square\text{-PPh}_2)_3(\text{CO})_3(\square\text{-dppm})]$. They also synthesized the iridium analogue of $[\text{Rh}_3(\square\square\text{-PPh}_2)_3(\text{CO})_5]$. In excess CO, the cluster $[\text{Ir}_3(\square\square\text{-PPh}_2)_3(\text{CO})_5]$ is converted to $[\text{Ir}_3(\square\square\text{-PPh}_2)_3(\text{CO})_6]$, whereas reaction with dppm and PPh_3 resulted in replacement of CO to afford $[\text{Rh}_3(\square\square\text{-PPh}_2)_3(\text{CO})_5(\text{L}_2)]$, ($\text{L}=\text{PPh}_3$ or $\text{L}_2=\text{dppm}$). Addition of CO to $[\text{Ir}_3(\square\square\text{-PPh}_2)_3(\text{CO})_3(\square\text{-dppm})]$ resulted in the interesting cluster $[\text{Ir}_3(\square\square\text{-PPh}_2)_3(\text{CO})_4(\square\text{-dppm})]$. Dixon et. al.^(10,12) also investigated the addition of Bu^tNC (*tert*-butylisocyanide) to the cluster $[\text{M}_3(\square\square\text{-PPh}_2)_3(\text{CO})_5]$, $\text{M} = \text{Rh}$ or Ir . The Bu^tNC ligand addition resulted in the product $[\text{M}_3(\square\square\text{-PPh}_2)_3(\text{CO})_5(\text{Bu}^t\text{NC})_3]$, $\text{M} = \text{Rh}$ or Ir , with nonbonding metal-metal distances (3.25Å).

Recently, we have investigated the reaction of $\text{P}(\text{OMe})_3$ with $[\text{M}_3(\square\square\text{-PPh}_2)_3(\text{CO})_5(\text{PPh}_3)_2]$, $\text{M} = \text{Rh}$ or Ir ⁽¹⁾. This study relates to this work in probing the activity of the metal centers in homogeneous environment versus heterogeneous one, and to examine the effect of one metal on the adjacent one.

Rhodium and iridium metals are mixed in an analogous cluster systems, $[\text{RhIr}_2(\text{PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2]$ and $[\text{RhIr}_2(\text{PPh}_2)_3(\text{CO})_5]$ and allowed to react with $\text{P}(\text{OMe})_3$ for comparison of metal centers activity.

Experimental.

All the syntheses described in this work were carried out under an atmosphere of dry nitrogen gas using standard Schlenck 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 VEA STR and NMRPLOT programs^(13,14). 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 α 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⁽¹⁵⁾, for Ir and ⁽¹⁶⁾, for Rh. $\text{Rh}_2(\square\text{-Cl})_2(\text{COD})_2$ [COD = 1,5-cyclooctadiene] and $\text{Ir}_2(\square\text{-Cl})_2(\text{COE})_4$ [COE = cyclooctene] synthesized according to procedures described in ^(17,18) respectively.

Synthesis of $[\text{RhIr}_2(\square\square\text{-PPh}_2)_3(\text{CO})_2\{\text{P}(\text{OMe})_3\}_3]$

(1). Excess of trimethylphosphite (0.11g, 0.9mmol) added to a stirred solution of the mixture of $[\text{RhIr}_2(\square\square\text{-PPh}_2)_3(\text{CO})_5]$, $[\text{IrRh}_2(\square\square\text{-PPh}_2)_3(\text{CO})_5]$, $[\text{Ir}_3(\square\square\text{-PPh}_2)_3(\text{CO})_5]$, and $[\text{Rh}_3(\square\square\text{-PPh}_2)_3(\text{CO})_5]$ prepared as described in⁽¹⁾. After 30 minutes, the color of solution changed from pink-red to dark red, the solvent was removed in *vacuo*, followed by crystallization of the residue using dichloromethane/hexane to yield $[\text{RhIr}_2(\square\square\text{-PPh}_2)_3(\text{CO})_2\{\text{P}(\text{OMe})_3\}_3]$ (**1**) as red crystals (0.035g).

I.R. (cm^{-1}), (KBr desk), \square (CO), 1979 s, 1936m

Anal. Cal'd, for (**1**). CH_2Cl_2 , $\text{C}_{42}\text{H}_{41}\text{O}_5\text{P}_6\text{Cl}_2\text{RhIr}_2$: C,36.8%, H, 3.02%

Found: C,37.2%, H, 3.76%

Synthesis of $[\text{RhIr}_2(\square\square\text{-PPh}_2)_3(\text{CO})_2(\text{PPh}_3)_2\{\text{P}(\text{OMe})_3\}]$ (**2**).

Excess of trimethylphosphite (0.11g, 0.88mmol) added to a stirred solution of the mixture of $[\text{RhIr}_2(\square\square\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2]$, $[\text{IrRh}_2(\square\square\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2]$, $[\text{Ir}_3(\square\square\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2]$, and $[\text{Rh}_3(\square\square\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2]$ prepared as described in⁽¹⁾. After 30 minutes, the color of solution changed from dark purple to dark red, the solvent was removed in *vacuo*, followed by crystallization of the residue using dichloromethane/hexane to yield $[\text{RhIr}_2(\square\square\text{-PPh}_2)_3(\text{CO})_2(\text{PPh}_3)_2\{\text{P}(\text{OMe})_3\}]$ (**2**) as red crystals (0.045g).

I.R. (cm^{-1}), (KBr desk), $\square\square$ (CO) 1971 s, 1912m

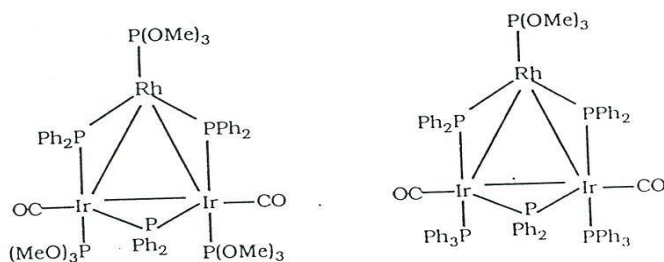
Anal. Cal'd, for (**2**). CH_2Cl_2 , $\text{C}_{76}\text{H}_{66}\text{O}_3\text{P}_6\text{Cl}_2\text{RhIr}_2$: C,51.6%, H, 3.70%

Found: C,51.0%, H, 3.94%

Results and Discussions

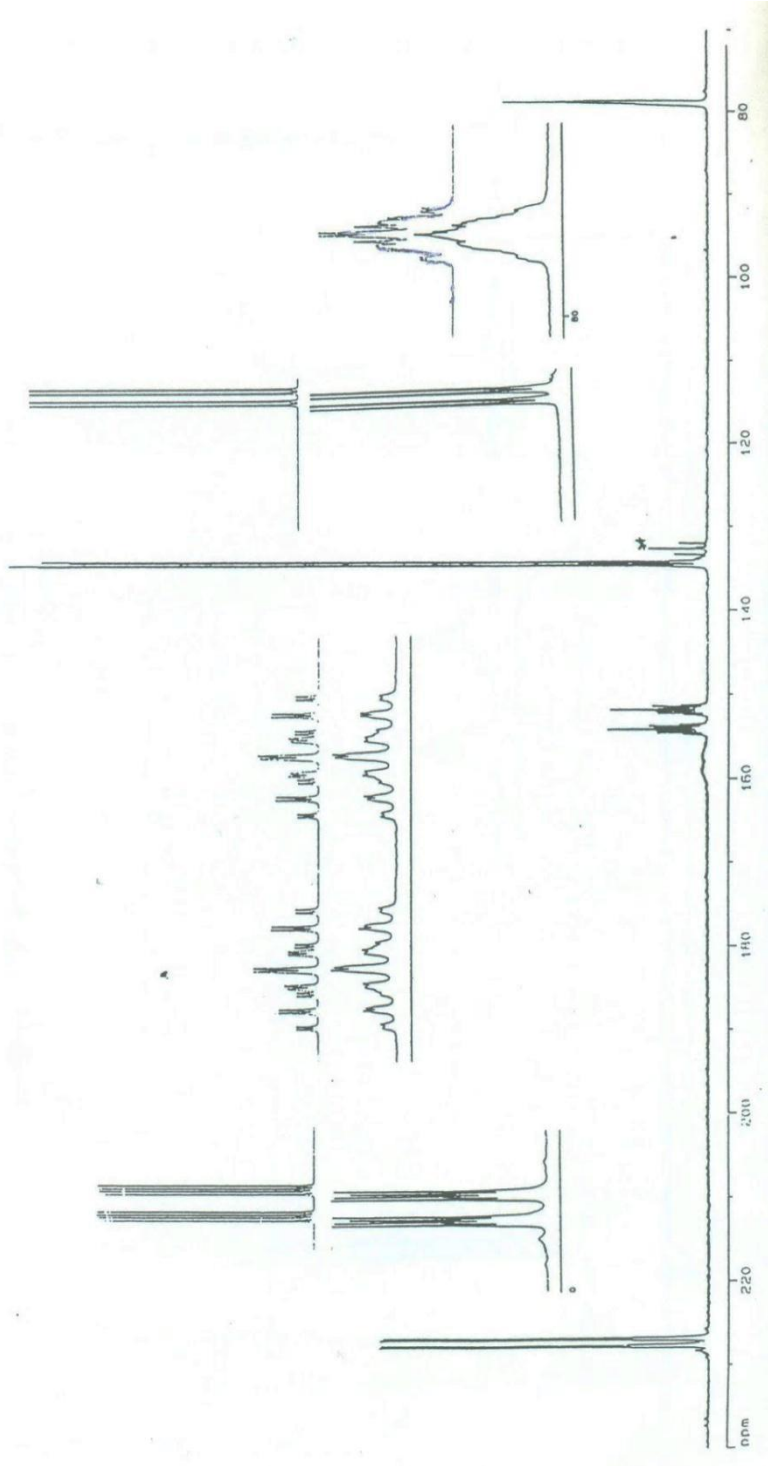
Spectroscopic analysis

$^{31}\text{P}\{^1\text{H}\}$ nmr spectrum of $[\text{RhIr}_2(\text{PPh}_2)_3(\text{CO})_2\{\text{P}(\text{OMe})_3\}_3](\mathbf{1})$ indicate that the cluster is symmetric (Figure.1). The spectrum figure (1) shows a set of four resonances at 227.1, 79.1, 134.4, and 152.9 ppm, due to the respective phosphorus environments, equivalent of phosphorus bridges P(1,2), the unique bridge P(3), the two equivalent $\text{P}(\text{OMe})_3$ ligands, and the unique $\text{P}(\text{OMe})_3$ ligand, P(9) (table 1). The multiplet assigned to P(1,2) exhibits a simple doublet of doublets of doublets (ddd). The large coupling (124 Hz), due to equal coupling of P(1) and P(2) with Rh(6) followed by coupling P(9), resulting in $J(1,9) = J(2,9) = 27\text{Hz}$, that is doubled coupling with P(3) (15Hz). The line due to the unique phosphide-bridge P(3), appearing as a broad multiplet, but computer simulation revealed it to be an overlapping triplet (24Hz) of triplets (15Hz) of doublets (5Hz), assigned to P(3) and viewed as triplet of triplets of doublets (ttd), $J(3,4) = J(3,5) = 24\text{Hz}$, $J(1,3) = J(2,3) = 15\text{Hz}$, and $J(9,3) = 5\text{Hz}$. The multiplet assigned to the unique $\text{P}(\text{OMe})_3$ ligand, P(9), also complicated. It is viewed as doublet of triplets of triplets of doublets (dtttd). The large doublet (335Hz) is due to coupling of P(9) with Rh(6). Triplets of coupling (66Hz), resulting from coupling of P(9) with terminal $\text{P}(\text{OMe})_3$ P(4) and P(5), followed by coupling with P(1) and P(2), triplet (27Hz), finally doubled by coupling with P(3) (5Hz). The line at 134.4 ppm, attributed to terminal $\text{P}(\text{OMe})_3$, P(4,5) is a doublet



(66Hz) due to coupling with P(9) of doublets (24Hz) due to coupling with P(3).

Figure.2, shows the $^{31}\text{P}\{^1\text{H}\}$ nmr spectrum of $[\text{RhIr}_2(\mu\text{-PPh}_2)_3(\text{CO})_2(\text{PPh}_3)_2\{\text{P}(\text{OMe})_3\}](\underline{2})$, is similar to that interpreted above for cluster(1). The resonance at 223.2 ppm assigned to P(1,2) as doublet of doublets of overlapped doublets. P(1) and P(2) couples strongly with Rh(6), 124Hz, resulting in a doublet followed by coupling with P(9) 26Hz, which is doubled by P(3), 24Hz. The line at 54.9 ppm assigned to the unique phosphido-bridge P(3), appearing as broad multiplet, but computer simulation revealed it to be an overlapping triplet of triplets of doublets, due to coupling with P(1,2), 24Hz, P(4,5), 21Hz, and P(9), 11Hz. P(9) gives rise to multiplet at 149.5 ppm, appearing as doublet of triplets of triplets of doublets (dttd), as a result of coupling to Rh(6), 338 Hz, P(4,5), 40 Hz, P(1,2), 26 Hz, and P(3), 11 Hz. Finally, the resonance at 26.6 ppm, attributable to terminal PPh_3 , P(4,5), viewed as doublet of doublets, as a result of coupling to P(9), 40Hz, and P(3), 21Hz.



(1)

(2)

Figure 1.
 $^{31}\text{P}\{^1\text{H}\}$ nmr spectrum of $[\text{RhIr}_2(\mu\text{-PPH}_2)_3(\text{CO})_2\{(\text{P}(\text{OMe})_3)_3\}]_3(\mathbf{1})$
 Upper trace of expansion is computer simulation
 * Impurities

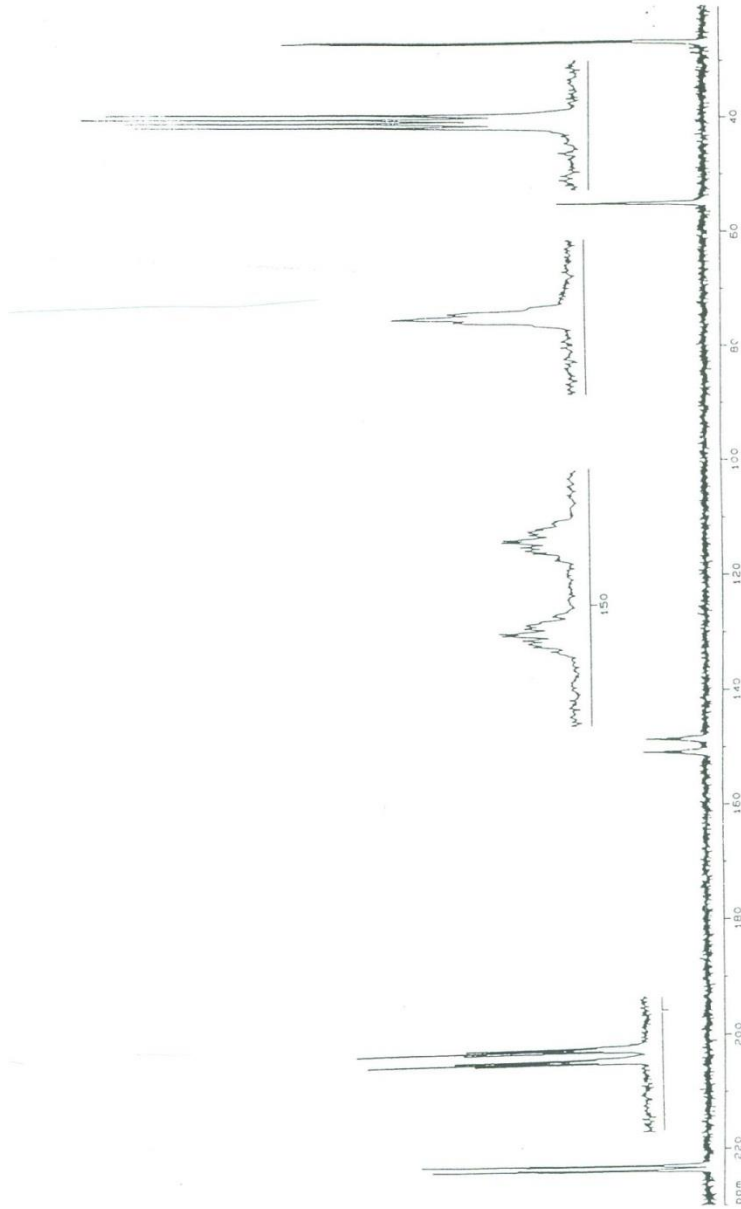


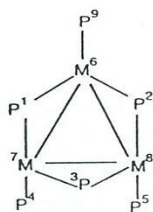
Figure 2.
 $^{31}\text{P}\{^1\text{H}\}$ nmr spectrum of $[\text{RhIr}_2(\mu\text{-PPh}_2)_3(\text{CO})_2(\text{PPh}_3)_2\{(\text{P}(\text{OMe})_3)\}_2]$ (2)

Mass spectra of clusters (1) and (2) complimented spectroscopic data from $^{31}\text{P}\{^1\text{H}\}$ nmr, which confirms both clusters (table.2). The mass spectrum of $[\text{RhIr}_2(\square\square-$

$\text{PPh}_2)_3(\text{CO})_2\{(\text{P}(\text{OMe})_3)_3\}$ (**1**) gives a high mass peak, $[\text{M}]^+$ at m/z 1471 corresponding to the molecular ion $[\text{RhIr}_2(\square\square\text{-PPh}_2)_3(\text{CO})_2\{(\text{P}(\text{OMe})_3)_3\}]^+$ and stepwise loss of two CO groups. No loss of $\text{P}(\text{OMe})_3$ is evident, which indicates that $\text{P}(\text{OMe})_3$ is strongly bound to the metal. The FAB-MS spectrum of $[\text{RhIr}_2(\square\square\text{-PPh}_2)_3(\text{CO})_2(\text{PPh}_3)_2\{(\text{P}(\text{OMe})_3)\}]$ (**2**) also shows a prominent $[\text{M}]^+$, m/z 1748 corresponding to $[\text{RhIr}_2(\square\square\text{-PPh}_2)_3(\text{CO})_2(\text{PPh}_3)_2\{(\text{P}(\text{OMe})_3)\}]^+$. Successive loss of PPh_3 seems to take precedence over loss CO groups, this again shows no loss of $\text{P}(\text{OMe})_3$ groups, to indicate that are more strongly bound to the metal than PPh_3 .

Phosphido-bridged mixed rhodium and iridium clusters are structurally similar to their corresponding homonuclear clusters. Evidence of this similarity can be seen clearly from $^{31}\text{P}\{^1\text{H}\}$ nmr spectroscopy of both homonuclear and heteronuclear cluster systems. The reactivity of both types of clusters with CO and $\text{P}(\text{OMe})_3$ differs to a certain extent. Homonuclear cluster such as $[\text{Rh}_3(\square\square\text{-PPh}_2)_3(\text{CO})_5]^{(11)}$ and $[\text{Ir}_3(\square\square\text{-PPh}_2)_3(\text{CO})_3(\text{dppm})]^{(19)}$, react with CO and result in metal-core expansion. Reaction of $[\text{M}_3(\square\square\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2]$, $\text{M}=\text{Ir}$ or Rh , leads

Table 1. $^{31}\text{P}\{^1\text{H}\}$ nmr chemical shifts (\square , ppm) and coupling constants (Hz) of clusters (**1**) and (**2**)



Parameter	Cluster(1)	Cluster(2)	Parameter	Cluster(1)	Cluster(2)
$\delta (1)$	227.1	223.2			
$\delta (2)$	227.1	223.2			
$\delta (3)$	79.1	54.9			
$\delta (4)$	134.4	26.6			
$\delta (5)$	134.4	26.6			
$\delta (9)$	152.9	149.5			
J(1,2)	0	0	J(3,7)	--	--
J(1,3)	15	24	J(3,8)	--	--
J(1,4)	0	0	J(3,9)	5	11
J(1,5)	0	0	J(4,5)	50	50
J(1,6)	124	124	J(4,6)	0	0
J(1,7)	--	--	J(4,7)	--	--
J(1,8)	--	--	J(4,8)	--	--
J(1,9)	27	26	J(4,9)	66	40
J(2,3)	15	24	J(5,6)	0	0
J(2,4)	0	0	J(5,7)	--	--
J(2,5)	0	0	J(5,8)	--	--
J(2,6)	124	124	J(5,9)	66	40
J(2,7)	--	--	J(6,7)	--	--
J(2,8)	--	--	J(6,8)	--	--
J(2,9)	27	26	J(6,9)	335	338
J(3,4)	24	21	J(7,8)	--	--
J(3,5)	24	21	J(7,9)	--	--
J(3,6)	0	0	J(8,9)	--	--

to replacement of PPh₃ by CO. No reaction is observed when corresponding mixed-metal clusters are treated with CO. The reason for the inertness of mixed-metal clusters toward CO molecules is not clear at present.

P(OMe)₃ easily replaces ligands such as PPh₃ in [Rh₃(□□-PPH₂)₃(CO)₃(PPh₃)₂], and [Ir₃(□□-PPH₂)₃(CO)₃(PPh₃)₂], to afford [Rh₃(□□-PPH₂)₃(CO)₃{(P(OMe)₃)₃}], and [Rh₃(□□-PPH₂)₃(CO)₃{(P(OMe)₃)₃}], [Ir₃(□□-PPH₂)₃(CO)₃{(P(OMe)₃)₃}] respectively, Whereas, in [RhIr₂(□□-PPH₂)₃(CO)₃(PPh₃)₂], it replaces only the CO ligand on the rhodium to result in [RhIr₂(□□-PPH₂)₃(CO)₂(PPh₃)₂{(P(OMe)₃)₃}] (**2**), leaving PPh₃ unaffected. This clearly represents another example which demonstrates the effect of one metal on the reactivity of an adjacent metal.

Table 2. Positive ion FAB-MS of clusters (**1**) and (**2**)

Cluster	Matrix	Principal ion (assignments m/z)
(1)	^m NBA/CH ₂ Cl ₂	[M] ⁺ , 1471 [M-CO], 1443 [M-2CO], 1415 [M-2CO-CH ₃ -2OCH ₃], 1338
(2)	^m NBA/CH ₂ Cl ₂	[M] ⁺ , 1748 [M-PPh ₃], 1486 [M-PPh ₃ -CO], 1458 [M-2PPh ₃], 1224

References

1. Asseid, F. M., *University Bulletin – ISSUE No.16, Vol. (2), 2014,p. 49*
2. Haines, R. J., and Steen, N. D. C. T., and English, R. B., *S. Afr. J. Chem.*, 43, (1981),p88.
3. Gabriela Ballinas-Lopez,M., Garcia-Baez, E.V., and Rosales-Hoz, M. J., *Polyhedron*, 22,(2003), p.3404-3411.
4. Haines, R. J., and Steen, N. D. C. T., Laing, M., and Sommerville, P., *J. Organomet. Chem.*, 198,(1980),p.C72.
5. Farrar, D.H., Grachava, E. V., Lough, A., Partirana, C., Poe A. J., and Tunik, S. P., *J. Chem. Soc.Dalton. Trans.*,(2001),p.2015.
6. Burt, J. C., Boese, R., and Schmid, G., *J. Chem. Soc. Dalton. Trans.*,(1978),p.1387
7. Atwood, J. L., Hunter, W. E., Jones, R. A., and Wright, T. C., *Inorg. Chem.*, 22,(1983),p.993.
8. Atwood, J. L., Hunter, W. E., Jones, R. A., and Wright, T. C., *Organometallics.*, 2, (1983),p.470.
9. Atwood, J. L., Arif, A. M., Heaton, D. E., Hunter, W. E., Jones, R. A., Kidd, K. B., Wright, T. C., Whittlesey, R. B., and Zhang, H., *Inorg. Chem.*, 26, (1986)p.4065.
10. Dixon, K. R., and Rattray, A. D., *Inorg. Chem.*, 17,(1978),p.1099.
11. Haines, R. J., and Steen, N. D. C. T., and English, R. B., *J. Chem. Soc. Dalton. Trans.*,(1984),p.515.
12. Dixon, K. R., Derry, D. E., Bushnell, W. W., Moroney, P. M., and Wan, C ., *Inorg. Chem.*, 24,(1985),p.2625.
13. Fenetti, J. A., Harris, R. K., and Johannsen, R. B., *J. Mag. Res.*, 3,(1970),p.84.
14. Swalen, J. D., “ **Computer Programs for Chemistry**” Edited by Detar, D. F.; W. A. Benjamin Inc., New York, (1968)
15. Kauffman, G. B., and Myers, R. D., *Inorg. Synth.*, 18,(1978),p.131.

16. Kauffman, G. B., and Tasi, J. H., *Inorg. Synth*, 8,(1966),p.217.
17. Herde, J. L., Lambert, J.C., and Senoff, C. V., *Inorg. Synth*, 15,(1974),p.17.
18. Sappa, E., and Giordano, R., and Castiglioni, M. J., *Organomet. Chem.*, 362, (1989),p.399.
19. Browning, J.; Dixon, K. R.; Meanwell, N. J. *Inorg. Chim. Acta*1993,213, 171-175.