

Variable Temperature $^{31}\text{P}\{^1\text{H}\}$ nmr Study of The Dynamic Exchange Processes of Rhodium Trimethylphosphite Cluster.

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Abstract :

The cluster $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_2\{\text{P}(\text{OMe})_3\}_3]$ was synthesized, the crystal structure of the cluster was determined by x-ray crystallography, and the dynamic behavior studied by $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR. The dynamic exchange involves two possible different mechanisms. The first involves fast migration of trimethylphosphite ligands around the Rh_3 core forcing the unique phosphido bridge to bend back in the plane of the Rh_3 triangle. This allows all the bridges to be chemically and magnetically equivalent to

give one line in the $^{31}\text{P}\{^1\text{H}\}$ nmr spectrum. The second possible mechanism is when the CO ligands are in a hopping mode (i.e. CO ligands bridge or semi-bridge one at a time to the unique Rh atom). In this case, this motion might force the three bridges to be in the same plane of Rh₃ triangle, which consequently leads to similar phosphido bridges and similar trimethylphosphite ligands.

Introduction :

Metal clusters containing more than one bridging atom or group, which generally stabilize the clusters and assist in binding metal centers together. It is also hoped that by stabilizing the metal centers, bridges can assist molecular arrangements and reactions involving two or more metal centers. This work will consider only selected systems in which the bridging moieties contain phosphorus. Among the systems in which phosphorus is part of a bridging group is the phosphido ligand $\mu\text{-PR}_2$, which is found in a considerable number of dinuclear and cluster complexes which may contain one, two, or three such bridging ligands. Various synthetic methods have been employed in which a wide range of metal fragments may be found [1-3]. The interest in the chemistry of transition metal clusters with phosphido-bridged ligands ($\mu\text{-PR}_2$) is largely due to their electronic properties as three electron donors, and geometrical flexibilities [4]. This kind of flexibility is observed in a wide range of M-($\mu\text{-PR}_2$)-M angles, from ca 70° to 138°, depending on metal-metal bonds are present or not [5,6]. Bellonet. al. [7] prepared the novel phosphido-bridged diiridium complex $\{[\text{Ir}(\text{CO})(\text{PPh}_3)(\mu\text{-PPh}_2)]_2\}$ from the

two different iridium hydride complexes $\text{IrH}_3(\text{PPh}_3)_3$ and $\text{Ir}(\text{CO})(\text{H})(\text{PPh}_3)_3$ in boiling DMF (Dimethylformamide) under nitrogen for three hours. The two metals of $[\{\text{Ir}(\text{CO})(\text{PPh}_3)(\mu\text{-PPh}_2)\}_2]$ are connected by a formal double bond 2.551 Å long, and bridged by two PPh_2 ligands. In a related study Geoffroy and co-workers [8] reported oxidative addition to phosphido-bridged dirhodium complexes to investigate the stability of the bridges and the changes in metal-metal bonds. Meek and his group [9,10] extensively studied diphenylphosphido-bridged dirhodium complexes.

A large number of phosphido-bridged clusters has been reported in recent years. Hains and co-workers have synthesized and characterized the tetranuclear clusters $[\text{Rh}_4(\mu\text{-PPh}_2)_4(\mu\text{-Cl})_2(\text{PPhH})_2(\text{CO})_4]$ [11], and $[\text{Rh}_4(\mu\text{-PPh}_2)_4(\mu\text{-CO})_2(\text{CO})_4]$ [12] as investigative study of the potential of diphenylphosphido ligands, PPh_2 , for stabilizing homonuclear and heteronuclear clusters of unusual geometry and stereochemistry [13-15]. In principle, phosphido-bridged are able to preserve the integrity of the cluster while permitting the breaking and making metal-metal bonds. A number of these phosphido-bridged clusters have been reported, and examples include $[\text{Co}_3(\mu\text{-PPh}_2)_2(\mu\text{-CO})(\text{CO})_6]$ [16], $[\text{Rh}_3(\mu\text{-PBu}^t_2)_3(\text{CO})_5]$ [17,18], $[\text{Ir}_3(\mu\text{-PBu}^t_2)_3(\text{CO})_6]$ [19], $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]$ [21], and $[\text{Ir}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]$ [20]. 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 [21] have synthesized the 46-electron cluster $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]$ with average Rh-Rh bond 2.77 Å, they also

investigated its reactivity with CO (Carbon monoxide) and PPh_2H (Diphenylphosphine). Saturation of the cluster with CO converts the cluster to $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_9]$ which quickly degrades to the unstable 50-electron cluster $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_7]$ with average Rh-Rh bonds of 3.15\AA . This expansion from bonding to non-bonding metal-metal distances is also present in the cluster $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{PPh}_2\text{H})(\text{CO})_6]$ with average Rh-Rh bond of 3.17\AA . The neutral ligand PPh_3 (triphenylphosphine) substitutes CO ligands instead of adding to $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]$.

Dixon and co-workers [20] reacted $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]$ with chelating ligand dppm (bis(diphenylphosphino)methane) to obtain the highly stable derivative, $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_3(\mu\text{-dppm})]$. They also synthesized the iridium analogue of $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]$. In excess CO, the cluster $[\text{Ir}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]$ is converted to $[\text{Ir}_3(\mu\text{-PPh}_2)_3(\text{CO})_6]$, whereas reaction with dppm and PPh_3 resulted in replacement of CO to afford $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_5(\text{L}_2)]$, ($\text{L}=\text{PPh}_3$ or $\text{L}_2=\text{dppm}$). Addition of CO to $[\text{Ir}_3(\mu\text{-PPh}_2)_3(\text{CO})_3(\mu\text{-dppm})]$ resulted in the interesting cluster $[\text{Ir}_3(\mu\text{-PPh}_2)_3(\text{CO})_4(\mu\text{-dppm})]$. Dixon et. al. [20,22] also investigated the addition of Bu^tNC (*tert*-butylisocyanide) to the cluster $[\text{M}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]$, $\text{M} = \text{Rh}$ or Ir . The Bu^tNC ligand addition resulted in the product $[\text{M}_3(\mu\text{-PPh}_2)_3(\text{CO})_5(\text{Bu}^t\text{NC})_3]$, $\text{M} = \text{Rh}$ or Ir , with nonbonding metal-metal distances (3.25\AA).

The dynamic processes of metal clusters was recently investigated to show the structural changes in the core of metallic clusters, Gabriela

et.al. [23] used variable temperature multinuclear NMR to study dynamical behavior of the cluster $[H_4Ru_4(CO)_{11}(L)]$, ($L=P(C_6F_5)_3$, $P(OMe)_3$, and $P(OEt)_3$) and showed both hydride motion and CO exchange. A comparative study by Farrar et. al.[24] on the clusters $[Rh_6(CO)_{15}(L)]$ and $[Os_3(CO)_{11}(L)]$, ($L= P(OMe)_3$) to show changes in the framework of the cluster as result of dynamic exchange.

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. $^{31}P\{^1H\}$ 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 $^{31}P\{^1H\}$ NMR spectra were analyzed by computer simulation using VESTR and NMRPLOT programs [25,26]. 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 [27], for Ir and [28], 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 [29,30] respectively.

Synthesis of $[\text{Ir}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]$ and $[\text{Ir}_3(\mu\text{-PPh}_2)_3(\text{CO})_6]$, carbon monoxide was bubbled vigorously through a solution of $\text{Ir}_2(\mu\text{-Cl})_2(\text{COE})_4$ (0.30g, 0.33mmol) in benzene (20 ml) resulting in a rapid precipitation of a dark green solid which is probably the polymer $[\text{IrCl}(\text{CO})_3]_n$. Diethylamine (0.065 ml, 0.65mmol) was added dropwise to the stirred mixture and after 10 minutes a very pale yellow solution had formed. Addition of diphenylphosphine (0.11 ml, 0.65 mmol) caused an immediate change to red-brown solution containing a mixture of $[\text{Ir}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]$ and $[\text{Ir}_3(\mu\text{-PPh}_2)_3(\text{CO})_6]$.

$^{31}\text{P}\{^1\text{H}\}$ nmr $[\text{Ir}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]$, $\delta_{1,3}$ (240.5 ppm), δ_2 , (100 ppm), $J_{12} = J_{23} = 15$ Hz

$^{31}\text{P}\{^1\text{H}\}$ nmr $[\text{Ir}_3(\mu\text{-PPh}_2)_3(\text{CO})_6]$, $\delta_{1,2,3}$ (174.8 ppm)

Solvent CD_2Cl_2

Synthesis of $[\text{Ir}_3(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2]$, to a mixture of $[\text{Ir}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]$ and $[\text{Ir}_3(\mu\text{-PPh}_2)_3(\text{CO})_6]$ 0.12 g 0.33 mmol of triphenylphosphine was added, the color was changed from red to dark purple, after 18 hours of stirring the solvent was removed *in vacuo*, and the residue dissolved in a minimum amount of benzene and transferred to

an alumina column. A dark purple band was eluted with benzene, solvent was removed *in vacuo*, and crystallization from dichloromethane and hexane gave the product as dark purple crystals (0.045 g 0.026 mmol), yield 13% based on conversion of of $[\text{Ir}_2(\mu\text{-Cl})_2(\text{COE})_4]$. I.R. (cm^{-1}) (KBr disk) $\nu(\text{CO})$, 1970s, 1910sh, Anal. Calcd. For $\text{C}_{75}\text{H}_{60}\text{Ir}_3\text{O}_3\text{P}_5$: C,51.7; H,3.47. Found: C,51.1 ; H,3.56.

Synthesis of $[\text{Ir}_3(\mu\text{-PPh}_2)_3(\text{CO})_2\{(\text{P}(\text{OMe})_3)_3\}_3]$, 0.05 g (0.029 mmol) of $[\text{Ir}_3(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2]$ dissolved in dichloromethane (20 ml) resulting in a dark purple solution. After stirring for 10 minutes, excess trimethylphosphite (0.014 ml, 0.12mmol) in 10 ml CH_2Cl_2 added slowly. The color of the solution changed rapidly from dark purple to olive green. After 30 minutes the solvent was removed *in vacuo* , and olive green oily residue was removed. $^{31}\text{P}\{^1\text{H}\}$ nmr of $[\text{Ir}_3(\mu\text{-PPh}_2)_3(\text{CO})_2\{(\text{P}(\text{OMe})_3)_3\}_3]$, $\delta_{1,2}$ (110.5 ppm), δ_3 , (114.5 ppm), $\delta_{4,5}$ (84.3 ppm), δ_6 , (154.2 ppm), I.R, (cm^{-1}) (KBr disk) $\nu(\text{CO})$, 1927s , 1955sh.

Synthesis of $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]$, carbon monoxide was bubbled vigorously through a solution of $\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2$ (0.10 g ,0.20 mmol) in benzene (20 ml) , and the color of solution remained unchanged (orange). Diethylamine (0.042 ml, 0.41mmol) was added dropwise to the stirred mixture and after 10 minutes a very pale yellow solution had formed. Addition of diphenylphosphine (0.071 ml, 0.41 mmol) caused an immediate change to red-brown solution containing $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]$. $^{31}\text{P}\{^1\text{H}\}$ nmr $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]$, $\delta_{1,3}$ (264.0 ppm), δ_2 , (257.8ppm). Solvent CD_2Cl_2
I.R, (cm^{-1})(Hexane, solution) $\nu(\text{CO})$, 2050s, 2019s, 2004s, 1991s, 1976s.

Synthesis of $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2]$, a solution of $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]$ in dichloromethane (15 ml) was prepared from $[\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2]$ (0.10 g, 0.20 mmol) as described above. Triphenylphosphine (0.07 g, 0.27 mmol) was added to the stirred solution, the color was changed from intense green to dark olive green, after 30 minutes of stirring the solvent was removed *in vacuo*, and the residue dissolved in a minimum amount of benzene and transferred to an alumina column. A dark olive green band was eluted with dichloromethane, solvent was removed *in vacuo*, and crystallization from dichloromethane and hexane gave the product as dark green crystals (0.013 g, 0.18 mmol), yield 90% based on conversion of $[\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2]$

$^{31}\text{P}\{^1\text{H}\}$ nmr $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2]$, $\delta_{1,2}$ (267.3 ppm), δ_2 , (143.5 ppm), $\delta_{4,5}$ (49.4 ppm).

Solvent CD_2Cl_2

I.R. (cm^{-1}) (KBr disk) $\nu(\text{CO})$, 1990m, 1945s.

Synthesis of $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_2\{\text{P}(\text{OMe})_3\}_3]$, 0.10 g (0.068 mmol) of $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2]$ dissolved in dichloromethane (20 ml) resulting in an olive green solution. After stirring for 10 minutes, excess trimethylphosphite (0.032 ml, 0.27 mmol) in 10 ml CH_2Cl_2 was added slowly. The color of the solution changed rapidly from olive green to dark blue. After 30 minutes the solvent was removed *in vacuo*, and the residue was crystallized from dichloromethane and hexane to give product as dark blue crystals (0.07 g, 0.054 mmol, 79% yield) based on conversion of $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2]$. $^{31}\text{P}\{^1\text{H}\}$ nmr of $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_2\{\text{P}(\text{OMe})_3\}_3]$, I.R. (cm^{-1}) (KBr disk) $\nu(\text{CO})$, 1941s, 1982m. Anal. Calcd. For $\text{C}_{47}\text{H}_{57}\text{Rh}_3\text{O}_3\text{P}_6$: C, 42.7; H, 4.38. Found: C, 42.6; H, 4.39.

Results and Discussions:***Crystallographic analysis:***

The molecular structure of $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_2\{\text{P}(\text{OMe})_3\}_3]$ is shown as an ORTEP diagram in figure(1). The cluster crystallizes in the P1 space group with two molecules in the unit cell. One of the two molecules is shown in the aforementioned figure. The other molecule is similar except for minor conformational changes, presumably induced by crystal packing forces. Table (1) contains a number of selected bond lengths and angles. The two molecules have approximately planar $\text{Rh}_3\text{-P}(1)\text{-P}(2)$ cores similar to that of $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]$ [21]. The third phosphido bridge $\text{Rh}(3)\text{-P}(2)\text{-Rh}(2)$, is almost perpendicular to the metal plane Rh_3 . The three trimethylphosphites ligands are coordinated at the corners of the Rh_3 triangle, roughly co-planar with it. The two carbonyl ligands are coordinated to $\text{Rh}(2)$ and $\text{Rh}(3)$ are almost perpendicular to the metal plane Rh_3 , which places both of the carbonyl ligands in a pseudo trans relationship with phosphido bridge $\text{P}(2)$. The Rh-Rh distances [$\text{Rh}(2)\text{-Rh}(3)$, 2.712(3), $\text{Rh}(1)\text{-Rh}(3)$, 2.811(4), $\text{Rh}(1)\text{-Rh}(2)$, 2.803(4)] correspond with those normally associated formal Rh-Rh bonds which is indicative of the Rh-P-Rh bridging bonding being of a closed type.

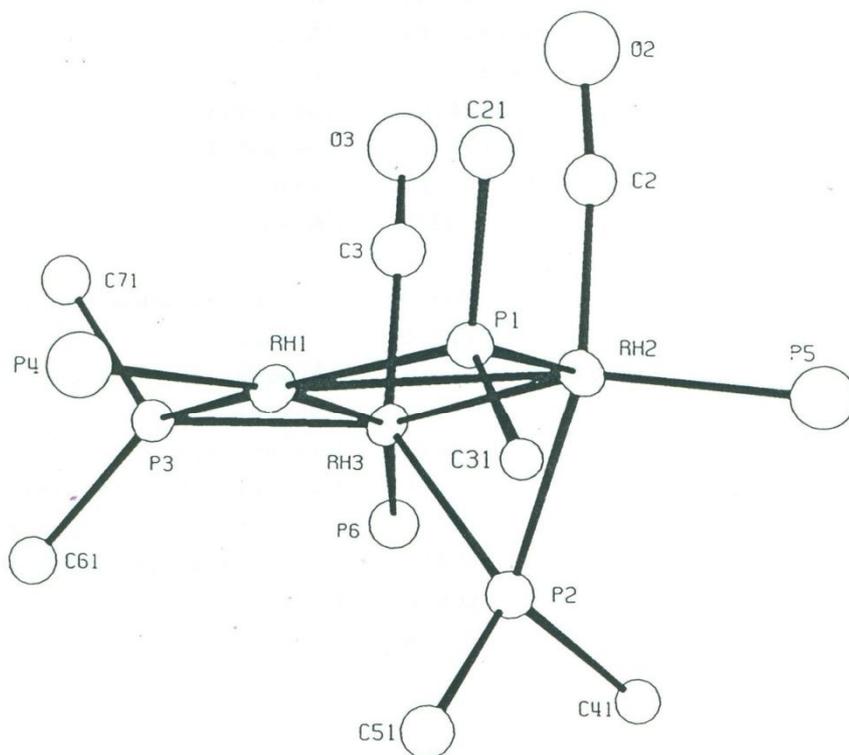


Figure 1. The molecular structure of $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_2\{(\text{P}(\text{OMe})_3)_3\}]$ (Phenyl groups are not shown for clarity). [Crystallographic parameters: formula, $\text{C}_{47}\text{H}_{57}\text{O}_{11}\text{P}_6\text{Rh}_3$; fw, 1294; Space group, P1(No.2); Radiation(\AA), Mo($\lambda=0.71069$); Total reflections collected, 13471; No. of unique reflections in the final database, 8087; $R=0.0.0920$; $R_w=0..0957$]

Table (1). Selected bond distances (Å) and Angles (°) for the cluster $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{P}(\text{OMe})_3)_3]$.

Atoms	Distances	Atoms	Distances
Rh(2)-Rh(1)	2.803(4)	Rh(3)-Rh(1)	2.811(4)
P(3)-Rh(1)	2.271(7)	P(1)-Rh(1)	2.267(6)
Rh(3)-Rh(2)	2.712(3)	P(4)-Rh(1)	2.158(14)
P(1)-Rh(2)	2.293(10)	P(2)-Rh(2)	2.300(7)
P(5)-Rh(2)	2.225(11)	C(2)-Rh(2)	1.830(3)
P(2)-Rh(3)	2.286(8)	P(3)-Rh(3)	2.315(10)
P(6)-Rh(3)	2.208(9)	C(3)-Rh(3)	1.920(3)
C(2)-O(2)	2.220(4)	C(3)-O(3)	1.120(4)

Atoms	Angles	Atoms	Angles
Rh(3)-Rh(1)-Rh(2)	57.8(1)	P(1)-Rh(1)-Rh(2)	52.5(3)
P(1)-Rh(1)-Rh(3)	110.3(3)	P(3)-Rh(1)-Rh(2)	110.6(3)
P(3)-Rh(1)-Rh(3)	52.9(3)	P(3)-Rh(1)-P(1)	163.3(4)
P(4)-Rh(1)-Rh(2)	149.9(2)	P(4)-Rh(1)-Rh(3)	152.1(3)
P(4)-Rh(1)-P(1)	97.5(4)	P(4)-Rh(1)-P(3)	99.2(4)
Rh(3)-Rh(2)-Rh(1)	61.2(1)	P(1)-Rh(2)-Rh(1)	51.6(2)
P(1)-Rh(2)-Rh(3)	112.9(2)	P(2)-Rh(2)-Rh(1)	76.7(3)
P(2)-Rh(2)-Rh(3)	53.5(3)	P(2)-Rh(2)-P(1)	106.1(3)
P(5)-Rh(2)-Rh(1)	154.9(4)	P(5)-Rh(2)-Rh(3)	138.8(3)
P(5)-Rh(2)-P(1)	106.0(4)	P(5)-Rh(2)-P(2)	103.3(4)
Rh(2)-Rh(3)-Rh(1)	61.0(1)	P(2)-Rh(3)-Rh(1)	76.7(3)
P(2)-Rh(3)-Rh(2)	54.0(2)	P(3)-Rh(3)-Rh(1)	51.5(2)
P(3)-Rh(3)-Rh(2)	112.4(11)	P(3)-Rh(2)-P(2)	108.9(3)
P(6)-Rh(3)-Rh(1)	152.9(3)	P(6)-Rh(3)-Rh(2)	136.5(3)
P(6)-Rh(3)-P(2)	98.(3)	P(6)-Rh(3)-P(3)	108.0(3)
C(3)-Rh(3)-Rh(1)	102.4(11)	C(3)-Rh(3)-Rh(2)	92.2(7)
C(3)-Rh(3)-P(2)	142.5(8)	C(3)-Rh(3)-P(3)	98.3(11)
C(3)-Rh(3)-P(6)	97.7(10)		

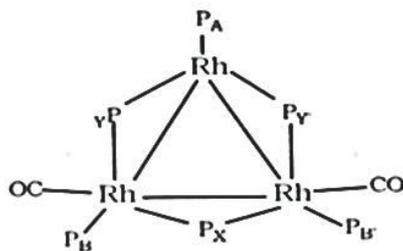
(Estimated standard deviations are given in parentheses)

A closed M-P-M bridge bond is defined as the bond between two metals, M, which are linked through a bridging phosphorus atom in which the M-M distance corresponds to the range of distances found for formal M-M bonds. The Rh(1) adopts an essentially planar configuration which can be attributed to it being '16-electron center'. A similar explanation will account for the Rh(1)-P(1) and Rh(1)-P(3) distances being shorter than those for Rh(2)-P(1) and Rh(3)-P(3). This effect is also observed for the terminal phosphite-metal bond distances Rh(1)-P(4) being shorter than those of Rh(2)-P(5) and Rh(3)-P(6). The coordinative unsaturation of Rh(1) can be attributed to the presence of phenyl groups on P(2) blocking a coordinating site. A number of attempts were made to obtain crystals of the cluster $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_2\{\text{P}(\text{OMe})_3\}_3]$ for X-ray crystallographic studies but all of these proved unsuccessful.

Spectroscopic analysis:

$^{31}\text{P}\{^1\text{H}\}$ nmr spectra of $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_2\{\text{P}(\text{OMe})_3\}_3]$ indicate that the cluster experiences a dynamic exchange process. Figure (2) shows a set of variable temperature $^{31}\text{P}\{^1\text{H}\}$ nmr spectra of the cluster $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_2\{\text{P}(\text{OMe})_3\}_3]$ over the range of temperature from 21°C to -100°C. The ambient temperature spectrum of the cluster shows two resonances; a broad singlet at 230 ppm attributable to the three phosphido bridges, and a doublet of multiplets centered at 154 ppm due to terminal trimethylphosphite ligands coupled to rhodium ($J(\text{P-Rh})$ 236Hz). This large coupling constant is consistent with rhodium

trimethylphosphite ligand coupling. As the temperature is lowered to (-20°C) the broad singlet disappears completely, and the doublet of multiplets becomes a broad doublet. At the low temperature of (-50°C), the original broad singlet shifts to a new position at 265 ppm, and the broad doublet is now a broad singlet centered at 155 ppm. At -60°C a new spectrum of four different phosphorus environments is starting to emerge, the resonance at 265ppm is becoming sharper and stronger in intensity, whereas the broad singlet at 155 ppm is now surrounded by two distinctive shoulders, that become more resolved as the temperature is lowered to (-75°C). By careful inspection of the high field region of the spectrum obtained at -75°C, one can observe an envelope covering three phosphorus environments, a weak broad doublet at 151 ppm, strong broad doublet at 158 ppm and a possible triplet at 161 ppm.



As temperature is lowered to -90°C, the weak doublet at 151 ppm is almost doublet of triplets, and the resonance at 265 ppm is beginning to split to a doublet. What appears to be happening is that at the ambient temperature all the phosphido bridges $P_Y P_{Y'}$ and P_X are equivalent at the

chemical shift 230 ppm, and the trimethylphosphites P_A , P_B and P_B' also give a single resonance at 154 ppm appearing as symmetric doublet of multiplets. As the temperature is lowered to -90°C , the phosphido bridges $\text{P}_\text{Y}\text{P}_\text{Y}'$ become chemically and magnetically different from P_X , and give two different resonances, one centered at 161 ppm due to P_X and the other centered at 265 ppm attributable to $\text{P}_\text{Y}\text{P}_\text{Y}'$. At -90°C the trimethylphosphites $\text{P}_\text{B}\text{P}_\text{B}'$ also become different from P_A . The coupling constant $J(\text{P}_\text{A}\text{-Rh})$, 332 Hz, almost double that of $J(\text{P}_\text{B}\text{-Rh})$, 186 Hz. This difference in coupling constants can be due to the different coordination around the rhodium metals, P_A is coordinated to an unsaturated rhodium center (formal 16-electron center), whereas P_B and P_B' coordinated to a saturated rhodium (formal 18-electron center). The variable temperature ^1H nmr spectra of the cluster $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_2\{\text{P}(\text{OMe})_3\}_3]$ (figure 3) confirms similar behavior observed from $^{31}\text{P}\{^1\text{H}\}$ nmr spectra. The room temperature of the cluster shows only one resonance at 3.1 ppm indicating only one type of trimethylphosphite in the cluster. As the temperature lowered to -90°C the single resonance at 3.1 ppm splits into two lines with different intensities at 3.1 ppm due to $\text{P}_\text{B}(\text{OMe})_3$ and $\text{P}_\text{B}'(\text{OMe})_3$ and 2.7 ppm due to $\text{P}_\text{A}(\text{OMe})_3$ with respective integration of 2:1.

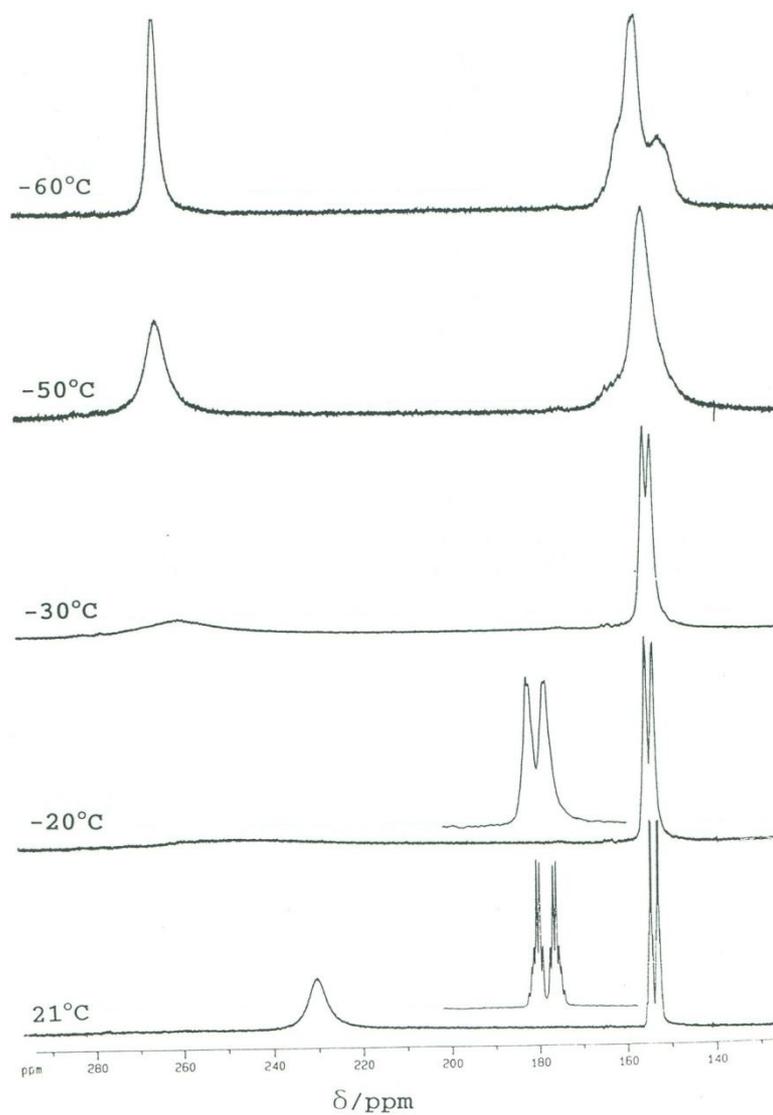


Figure 2. VT $^{31}\text{P}\{^1\text{H}\}$ nmr spectra of the cluster $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_2\{\text{P}(\text{OMe})_3\}_3]$ over the range of temperature from 21°C to -100°C .

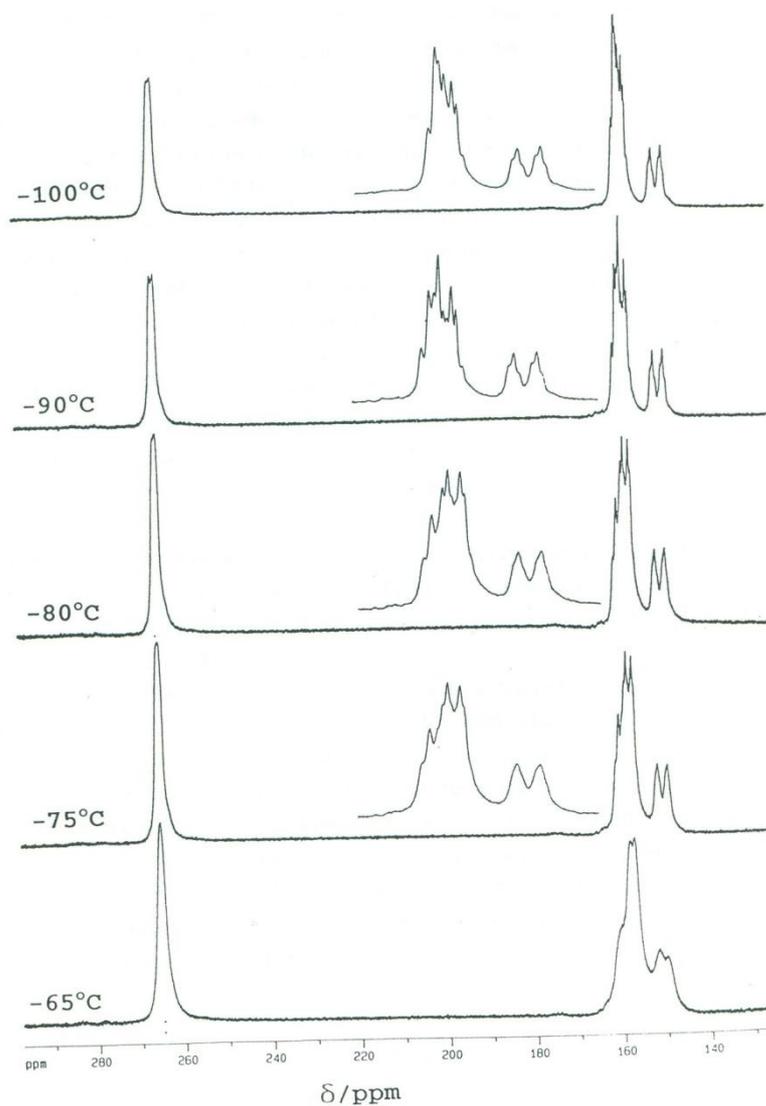


Figure 2. (Continued) VT $^{31}\text{P}\{^1\text{H}\}$ nmr spectra of the cluster $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_2\{\text{P}(\text{OMe})_3\}_3]$ over the range of temperature from 21°C to -100°C .

Both spectra of $^{31}\text{P}\{^1\text{H}\}$ nmr and ^1H nmr could be accounted for two different mechanisms. The first involves fast migration of trimethylphospite ligands around the Rh_3 core forcing the unique phosphido bridge to bend back in the plane of the Rh_3 triangle. This allows all the bridges to be chemically and magnetically equivalent to give one line in the $^{31}\text{P}\{^1\text{H}\}$ nmr spectrum. At low temperature, the $\text{P}(\text{OMe})_3$ migration slows down resulting in the relaxation of the unique phosphido bridge back to its original position (i.e. perpendicular to the Rh_3 plane). The second possible mechanism is when the CO ligands are in a hoping mode (i.e. CO ligands bridge or semi-bridge one at a time to the unique Rh atom). In this case, this motion might force the three bridges to be in the same plane of Rh_3 triangle, which consequently leads to similar phosphido bridges and similar trimethylphosphite ligands. I believe the second situation is more plausible and more likely to take place. The first situation is likely to lead to a transition state to be seen in the $^{31}\text{P}\{^1\text{H}\}$ nmr spectrum i.e. when the phosphate ligands are in bridging mode. Or a significant change in the $J(\text{Rh}-\text{P}(\text{OMe})_3)$ should be observed if the mechanism is a dissociative one.

The iridium analogue $[\text{Ir}_3(\mu\text{-PPh}_2)_3(\text{CO})_2\{\text{P}(\text{OMe})_3\}_3]$ does not appear to experience a dynamic exchange process. The $^{31}\text{P}\{^1\text{H}\}$ nmr spectrum of the cluster $[\text{Ir}_3(\mu\text{-PPh}_2)_3(\text{CO})_2\{\text{P}(\text{OMe})_3\}_3]$ is shown in figure 4. The spectrum recorded at the ambient temperature appears comparatively much simpler. It shows a doublet (88Hz) at 153 ppm due to the two phosphido bridges in the plane of Ir_3 triangle, a triplet (88Hz) at 83

ppm due to the unique phosphido bridge coupling with the other two bridges, unresolved triplet at 113 ppm due to the unique trimethylphosphite ligand coupled with two phosphido bridges, and a doublet (32 Hz) at 109 ppm attributable to the two equivalent trimethylphosphites ligands coupling with the unique phosphido bridge.

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