

TRIS-OLEFIN COMPLEXES OF RHODIUM(I) AND IRIDIUM(I) CONTAINING THE TETRADENTATE LIGANDS TRIS(BUT-3-ENYL)PHOSPHINE AND TRIS(PENT-4-ENYL)PHOSPHINE*

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Summary

The rhodium(I) and iridium(I) complexes, $\text{RhX}(\text{tbp})$, $\text{RhX}(\text{tpp})$, $\text{X} = \text{Cl}$, Br or I , and $\text{IrCl}(\text{tbp})$ and $\text{IrCl}(\text{tpp})$ where $\text{tbp} = \text{P}(\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)_3$ and $\text{tpp} = \text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)_3$ have been prepared. These compounds, except for $\text{RhI}(\text{tbp})$, all exhibit the same "umbrella" type five coordinate structure in the solid state, in which all three olefins are bonded to the metal. At -60° in solution, $\text{RhI}(\text{tbp})$ adopts the same five coordinate stereochemistry. Due to restricted rotation, the methylene protons in $\text{RhCl}(\text{tbp})$ become inequivalent at low temperature. $\text{RhCl}(\text{tbp})$ forms 1/1 adducts with carbon monoxide and triphenylphosphine. Infrared, Raman and PMR studies conclude that the metal-olefin bond is stronger for the iridium complexes compared to the corresponding rhodium complexes.

Introduction

Complexes of catalytically active metals involved in reactions with olefins are usually electron deficient compounds with the metal in a low oxidation state. Such complexes are generally stabilised by electron donating ligands such as phosphines, arsines, etc. Of particular interest has been the rhodium catalyst, $\text{RhCl}(\text{Ph}_3\text{P})_3$ [1]. In our studies of the effects involved in the hydrogenation and isomerization of tertiary unsaturated phosphine ligands complexed to rhodium(I) [2], it became increasingly obvious that such ligands could give rise

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to stereochemically interesting complexes. The potentially four coordinate ligand, tris(but-3-enyl)phosphine, forms the five coordinate complex $\text{RhCl}[\text{P}(\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)_3]$ in which all three olefins are bonded to the metal [3,4]. Similar complexes are formed with the closely related ligand tris(*o*-styryl)phosphine [5-7]. Recent studies with the multi-dentate ligands bis(but-3-enyl)phenylphosphine (*bbp*) and tris(but-3-enyl)phosphine with molybdenum(0), palladium(II) and platinum(II) compounds have shown that the ligands only act as bidentates in these complexes [8,9], and tris(but-3-enyl)arsine only acts as a mono- or bidentate ligand with palladium(II) and platinum(II) complexes [10]. In this paper, the study of rhodium(I) complexes containing tris(but-3-enyl)phosphine (*tbp*) has been extended, and complexes containing tris(pent-4-enyl)phosphine (*tpp*) have been investigated. Studies of the analogous iridium(I) complexes have also been made.

Experimental

Trichlorophosphine was obtained from Matheson, Coleman and Bell; triphenylphosphine from Aldrich Chemical Company; carbon monoxide from the Matheson Company; 5-bromopent-1-ene from Pierce Chemical Company; and the rhodium and iridium trichloride from Englehard. The tris(pent-4-enyl)phosphine was prepared from trichlorophosphine and the Grignard of 5-bromopent-1-ene by the general method previously described [11]. This phosphine was collected at 99-101° and 0.5 mmHg in a yield of 60%. Tris(but-3-enyl)phosphine and $\text{RhCl}(\text{tbp})$ were prepared as before [3]. The rhodium and iridium complexes, $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ [12], $\text{RhCl}(\text{Ph}_3\text{P})_3$ [1] and $\text{Ir}_2\text{Cl}_2(\text{C}_8\text{H}_{12})_2$ [13] (C_8H_{12} = cycloocta-1,5-diene) were prepared by the standard literature methods.

Infrared spectra were recorded using Perkin—Elmer 137, 137G and 621 spectrometers and the Raman spectra on a Cary 81 spectrometer using the He—Ne laser excitation at 6328 Å. Proton magnetic resonance spectra and the decoupled proton magnetic resonance spectra were recorded on the Varian HA100 spectrometer. Air sensitive samples were prepared in an inert atmosphere and the NMR tube sealed under a vacuum. The temperature of the probe of the Varian HA100 spectrometer was calibrated from the chemical shifts of the protons of methanol (low temperature) and glycerol (high temperature). Molecular weights were measured using a Mechrolab Model 301-A vapor pressure osmometer and the mass spectra were recorded on a Varian MAT CH-7 and on an A.E.I. MS-9. Melting points were obtained with a Fisher—Johns melting point apparatus, and are uncorrected.

Microanalyses were performed by the Alfred Bernhardt Microanalytical Laboratory, Elback über Engelskirchen, West Germany, and by Huffman Laboratories, Inc., Wheatridge, Colorado.

Preparation of complexes

(i) $\text{RhBr}(\text{tbp})$. Lithium bromide (0.24 g, 2.75 mmol) in a minimum amount of methanol was added dropwise to a stirred solution of $\text{RhCl}(\text{tbp})$ (0.15 g, 0.45 mmol) under nitrogen in a minimum amount of methanol at room temperature. The resulting very pale yellow precipitate (0.119 g, 70%) was collected, and recrystallized from methylene chloride—methanol to give pale yellow

crystals (0.078 g, 46%) of the desired product. Anal. Found: C, 38.0; H, 5.47; Br, 20.5; m.p. 155-8° (dec.). $C_{12}H_{21}BrPRh$ calcd.: C, 38.0; H, 5.58; Br, 21.0%.

(ii) $RhI(tbp) \cdot 1/6CH_3OH$. Sodium iodide (0.27 g, 1.98 mmol) in a minimum amount of methanol was added to a stirred solution of $RhCl(tbp)$ (0.10 g, 0.30 mmol) in a minimum amount of methanol at room temperature under nitrogen. The yellow-orange precipitate (0.10 g, 78.5%) was recrystallized from methylene chloride—methanol to give orange crystals (0.086 g, 67%). The methanol can be removed by a recrystallization from benzene. Anal. Found: C, 34.3; H, 5.22; I, 28.1; m.p. 127-133° (dec.). $C_{12}H_{21}IPRh \cdot 1/6CH_3OH$ calcd.: C, 33.9; H, 5.04; I, 28.4%.

(iii) $RhCl(CO)(tbp)$. Carbon monoxide was bubbled through a suspension of $RhCl(tbp)$ (0.05 g, 0.15 mmol) in 15 ml of ethyl ether at 0° for 2 h. The color rapidly changed from white to pale yellow. The resulting crystals were filtered, washed with ether and dried in vacuo for 0.5 h. The yield was 0.04 g (74%).

(iv) $RhCl(Ph_3P)(tbp)$. The ligand, tris(but-3-enyl)phosphine (0.27 ml, 1.10 mmol) and $RhCl(Ph_3P)_3$ (1.00 g, 1.08 mmol) were refluxed in 7 ml of benzene under nitrogen for 2 h. The solution rapidly turned yellow and yellow crystals separated upon standing overnight to yield 0.233 g (38%). The same compound was formed from the rapid reaction of triphenylphosphine and $RhCl(tbp)$. The reaction was irreversible under the conditions of refluxing benzene. Anal. Found: mol. wt., 524 (vapour pressure osmometry in chloroform); C, 60.2; H, 6.18; m.p. 126°. $C_{30}H_{36}ClP_2Rh$ calcd.: mol. wt., 597; C, 60.4; H, 6.07%.

(v) $IrCl(tbp)$. Upon the dropwise addition of the ligand tris(but-3-enyl)phosphine (0.18 ml, 0.75 mmol) in 1 ml of benzene to bis(cycloocta-1,5-diene)- $\mu\mu'$ -dichlorodiridium(I) (0.25 g, 0.75 mmol) in 4 ml of benzene at room temperature under nitrogen, the color of the solution rapidly changed from deep orange to pale yellow. Upon stirring, white crystals (0.191 g, 60.8%) of the product formed.

(vi) $RhCl(tpp)$. Tris(pent-4-enyl)phosphine (0.625 ml, 2.10 mmol) in 4 ml of benzene was added dropwise to a warm solution of $Rh_2Cl_2(CO)_4$ (0.40 g, 1.03 mmol) in 16 ml of benzene under nitrogen. The solution became light orange. The solution was then refluxed, and within 2 h white crystals of the compound had precipitated. After an additional ½ h of refluxing, the solution was cooled to room temperature and filtered. The crystals were washed with benzene and dried in a vacuum. The yield of these crystals was 0.404 g. The filtrate was reduced in volume to yield another 0.131 g. Total yield was 0.535 g (69%). This product was quite pure, but could be recrystallized from methylene chloride—benzene to give at least 51% yield. The compound could also be prepared from bis(cycloocta-1,5-diene)- $\mu\mu'$ -dichlorodiridium(I) and the ligand. Anal. Found: mol. wt., 377 (mass spectrum); C, 47.8; H, 7.22; Cl, 9.30; m.p. 170° (dec.). $C_{15}H_{27}ClPRh$ calcd.: mol. wt., 377; C, 47.8; H, 7.22; Cl, 9.41%.

(vii) $RhBr(tpp)$. To 0.2 g (0.53 mmol) of $RhCl(tpp)$ in 5 ml of methanol under nitrogen was added 0.1 g (1.15 mmol) of lithium bromide in 1 ml of methanol. The resulting yellow crystals were collected, washed with methanol and dried in a vacuum to give 0.173 g (77%) of impure bromide. This was recrystallized from methylene chloride—methanol to give 60% yield. The PMR of this product showed that the compound still contained a small quantity of the

chloride. To remove the chloride completely, the product was recrystallized from methylene chloride and methanol containing 0.2 g of lithium bromide. Anal. Found: mol. wt., 421 (mass spectrum); C, 43.2; H, 6.20; m.p. 173° (dec.). $C_{15}H_{27}BrPRh$ calcd.: mol. wt., 421; C, 42.8; H, 6.48%.

(viii) *RhI(tpp)*. To 0.2 g (0.53 mmol) of $RhCl(tpp)$ in 5 ml of methanol under nitrogen was added 0.18 g (1.20 mmol) of sodium iodide in 3 ml of methanol. An immediate canary yellow precipitate formed. The solution was stirred ½ h and then allowed to stand at room temperature for another 2 h. It was filtered, and the crystals were washed with methanol and dried in a vacuum. The yield of $RhI(tpp)$ at this point was 0.237 g (95.5%). The product was then recrystallized from methylene chloride—methanol to give 0.202 g (85%). A PMR of the product indicated no chloride was present. Anal. Found: mol. wt., 468 (mass spectrum); C, 38.6; H, 5.89; I, 27.0; m.p. 167° (dec.). $C_{15}H_{27}IPRh$ calcd.: mol. wt. 468; C, 38.5; H, 5.81; I, 27.1%.

(ix) *IrCl(tpp)*. This was prepared in a manner analogous to $IrCl(tbp)$, and 0.2 g of bis(cycloocta-1,5-diene)- $\mu\mu'$ -dichlorodiridium(I) yielded 0.042 g (15.1%) of white product.

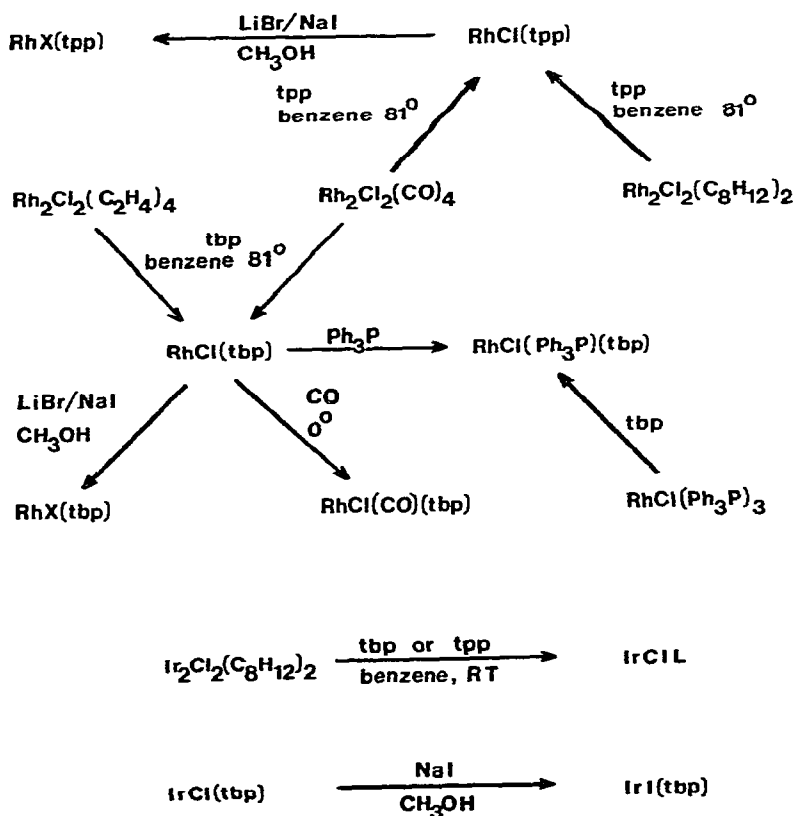


Fig. 1. Preparations and reactions of rhodium(I) and iridium(I) complexes containing the ligands $tbp = P(CH_2CH_2CH=CH_2)_3$ and $tpp = P(CH_2CH_2CH_2CH=CH_2)_3$.

Discussion

The bromide and iodide analogues of $\text{RhCl}(\text{tbp})$ were prepared by metathetical reactions of the chloride complex (see Fig. 1). The pale yellow bromide compound, $\text{RhBr}(\text{tbp})$, exhibits stability and solubility properties similar to the chloride, whereas the iodide (yellow in color) decomposes in solution after several hours in contact with the air. The complex $\text{RhCl}(\text{tbp})$ readily reacts with donor ligands such as carbon monoxide (reversibly) and triphenylphosphine (irreversibly) giving the 1/1 adducts $\text{RhClL}(\text{tbp})$, $\text{L} = \text{CO}$ or Ph_3P , and the triphenylphosphine compound could be prepared from $\text{RhCl}(\text{Ph}_3\text{P})_3$ and tris(but-3-enyl)phosphine. Although the similar phosphine complex $\text{RhBr}(\text{tsp})$, ($\text{tsp} = \text{tris}(o\text{-styryl})\text{phosphine}$, does not react with similar donor ligands [5], the arsine complexes, $\text{RhX}(\text{tsa})$, $\text{X} = \text{Cl}, \text{Br}$ or I and $\text{tsa} = \text{tris}(o\text{-styryl})\text{arsine}$, react with carbon monoxide, pyridine and triphenylarsine [7]. The new ligand tris(pent-4-enyl)phosphine forms the similar complexes $\text{RhX}(\text{tpp})$, $\text{X} = \text{Cl}$ (white), Br (yellow) or I (bright yellow), and all three complexes were quite stable. It has been noticed before that phosphine ligands containing the pent-4-ene moiety complexed to rhodium(I) tend to isomerize to the internal olefin (pent-3-ene)

TABLE 1

INFRARED AND RAMAN DATA ^a OF RHODIUM AND IRIIDIUM COMPLEXES WITH THE LIGANDS $\text{tbp} = \text{P}(\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)_3$ AND $\text{tpp} = \text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)_3$

Infrared measurements				
Compound	State	$\nu(\text{CO})$	$\nu(\text{C}=\text{C})$ (free)	Band 1
tbp	oil		1639s	
$\text{RhCl}(\text{tbp})$	KBr			1502s
$\text{RhBr}(\text{tbp})$	KBr			1506s
$\text{RhI}(\text{tbp})$	KBr		1639w	1502w
$\text{RhCl}(\text{CO})(\text{tbp})$	KBr	2012s 1992s	1634w	1504w
	CH_2Cl_2	2024s	1642	b
$\text{RhCl}(\text{Ph}_3\text{P})(\text{tbp})$	KBr		1642w	b
$\text{IrCl}(\text{tbp})$	KBr			1481s
tpp	oil		1639s	
$\text{RhCl}(\text{tpp})$	KBr			1513m
$\text{RhBr}(\text{tpp})$	KBr			1517m
$\text{RhI}(\text{tpp})$	KBr			1515m
$\text{IrCl}(\text{tpp})$	KBr			1488m
Raman measurements ^c				
Compound	M-Olefin (S)	M-olefin (AS)	M-P	
$\text{RhCl}(\text{tbp})$	421	ns	191	
$\text{RhBr}(\text{tbp})$	419	ns	192	
$\text{RhI}(\text{tbp})$	398	492	203 or 220	
$\text{IrCl}(\text{tbp})$	427	493	195	
$\text{RhCl}(\text{tpp})$	375	ns	197	
$\text{RhBr}(\text{tpp})$	376	ns	197	
$\text{RhI}(\text{tpp})$	376	ns	197	
$\text{IrCl}(\text{tpp})$	391	488	192	

^a All measurements in cm^{-1} . ^b Too weak to be observed. ^c All Raman spectra taken of powdered samples. S = symmetric stretching frequency, AS = antisymmetric stretching frequency, s = strong, m = medium, w = weak, ns = not seen.

ligand [2], but a sample of $\text{RhCl}(\text{tpp})$ heated in benzene for ca. 16 h showed no signs of isomerization. The white crystalline iridium complexes $\text{IrCl}(\text{tbp})$ and $\text{IrCl}(\text{tpp})$ were prepared from the reaction of $\text{Ir}_2\text{Cl}_2(\text{C}_8\text{H}_{12})_2$, C_8H_{12} = cycloocta-1,5-diene, and the corresponding ligand and these complexes were quite stable both in the solid state and in solution.

Infrared and Raman spectra

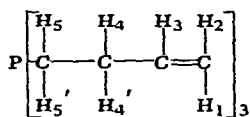
The ligands tris(but-3-enyl)phosphine and tris(pent-4-enyl)phosphine each contain three olefins. The olefinic stretching frequency for each ligand occurs at 1639 cm^{-1} . For all the complexes listed in Table 1 [except for $\text{RhCl}(\text{Ph}_3\text{P})(\text{tbp})$] a new band appears at ca. 1500 cm^{-1} (Band 1 [14]), and this is indicative of a coordinated olefin or olefins in those complexes. The infrared and Raman spectra of $\text{RhCl}(\text{tbp})$, $\text{RhBr}(\text{tbp})$ and $\text{IrCl}(\text{tbp})$ are essentially identical; and those of $\text{RhX}(\text{tpp})$, $\text{X} = \text{Cl}, \text{Br}$ or I and $\text{IrCl}(\text{tpp})$ are essentially identical. From the identical nature of their physical properties in the solid state, it is assumed that each particular series is isostructural. It is immediately obvious from its infrared and Raman spectra that $\text{RhI}(\text{tbp})$ has a different structure in the solid state from $\text{RhX}(\text{tbp})$, $\text{X} = \text{Cl}, \text{Br}$. This compound exhibits free olefin (1639 cm^{-1}), has a markedly lower Rh—olefin symmetrical stretching band and also contains a band at 492 cm^{-1} . The pattern in the Raman is noticeably similar to $\text{Rh}_2\text{I}_2\text{[bbp]}_2$ [15], $\text{bbp} = \text{PhP}(\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2$.

Similar observations have been made with $\text{RhI}(\text{tsa})$, which has been given the proposed dimeric formulation $\text{Rh}_2\text{I}_2(\text{tsa})_2$ [7]. From our evidence, we conclude that $\text{RhI}(\text{tbp})$ most probably has a structure similar to the dimeric complexes $\text{Rh}_2\text{X}_2(\text{bbp})_2$ in the solid state, but has the monomeric "umbrella" type structure in solution (see PMR data and conclusions). The carbonyl compound $\text{RhCl}(\text{CO})(\text{tbp})$, has bands at 1634 cm^{-1} and at 1504 cm^{-1} indicating that it contains both free and bonded olefin. A most likely structure for this compound is one similar to that proposed for $\text{RhX}(\text{CO})(\text{bbp})$ [15]. The difference in basicities from bis(but-3-enyl)phenylphosphine to tris(but-3-enyl)phosphine would increase the electron density on the metal, which would increase the M—C strength and decrease the carbonyl stretching frequency and this is in agreement with the observed CO stretching frequency at 2024 cm^{-1} (CH_2Cl_2).

Proton magnetic spectra (Table 2)

(1) $\text{RhCl}(\text{tbp})$. In the original paper describing this compound [3], it was shown that all three olefins were bonded to the rhodium centre, while the methylene protons on each carbon atom appeared to be equivalent due to a rapid equilibrium (on the PMR time scale) between the different conformers (see Fig. 2). Previously it has been shown that the methylene protons in the complex $\text{RhCl}(\text{CO})(\text{bbp})$ [15] were inequivalent and appeared in the ratio of 1/3/4 in the PMR spectrum at 220 MHz. This same pattern appears in the low temperature spectrum (Fig. 3) of $\text{RhCl}(\text{tbp})$ and it is quite obvious that the inter-conversion of the conformers has been stopped. The upper resonance apparently belongs to the H_5 protons, while the lower two belong to the H_4 protons. The resonances are broad and separated and this is probably due to inequivalent P—H, H_4 — H_5 as well as to possible H—H geminal coupling. This inequivalence in the H_4 protons is indirectly observed in the H_3 proton in which broadening

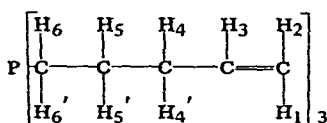
TABLE 2
PMR DATA
COMPOUNDS OF *tbp*



	Chemical shifts ^{a b}				
	H ₁	H ₂	H ₃	H ₄	H ₅
<i>tbp</i>	4.98	5.06	4.15	7.82	8.52
RhCl(<i>tbp</i>)	6.60	6.36	4.71	7.61	8.55
RhBr(<i>tbp</i>)	6.60	6.11	4.67	7.62	8.55
RhI(<i>tbp</i>) (+32°)	6.32	5.64	4.81	7.82	8.55
RhI(<i>tbp</i>) (-60°)	6.74	5.95	4.65	7.0-7.9	8.55
RhCl(CO)(<i>tbp</i>)	6.16	6.00	4.91	7.76	8.30
IrCl(<i>tbp</i>)	6.99	6.95	5.40	~7.76	~8.78
IrI(<i>tbp</i>)	7.10	6.45	5.35	~7.76	~8.80

	Coupling constants ^{c, d}								
	P-H ₅	P-H ₄	H ₁ -H ₃	H ₂ -H ₃	H ₃ -H ₄	H ₄ -H ₅	Rh-H ₁	Rh-H ₂	Rh-H ₃
<i>tbp</i> ^e	0.8	7.8	17.1	10.2	6.0	^c			
RhCl(<i>tbp</i>)	10.0	26.5	12.5	9.0	3.0	7.0	~1.5	~1.5	2.0
RhBr(<i>tbp</i>)	10.0	27.0	12.5	9.0	3.0	7.0	~1.0	~1.5	2.0
RhI(<i>tbp</i>) (+32°)	~9.0	~24.0	<i>f</i>	8.0	<i>f</i>	7.0	<i>f</i>	<i>f</i>	<i>f</i>
RhI (-60°)	<i>g</i>	<i>g</i>	12.5	9.0	~3.0	<i>g</i>	<i>f</i>	<i>f</i>	<i>f</i>
RhCl(CO)(<i>tbp</i>)	~9.0	~20.0	13.0	9.0	~3.0	7.0	<i>f</i>	<i>f</i>	<i>f</i>
IrCl(<i>tbp</i>)	<i>f</i>	<i>f</i>	11.0	7.5	~3.0	<i>f</i>			
IrI(<i>tbp</i>)	<i>f</i>	<i>f</i>	11.0	8.0	~3.0	<i>f</i>			

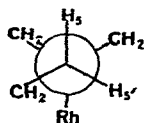
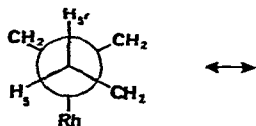
COMPOUNDS OF *tpp* ^h



	Chemical shifts ^{a, b}						Coupling constants ^{c, d}	
	H ₁	H ₂	H ₃	H ₄	H ₅	H ₆	H ₁ -H ₃	H ₂ -H ₃
<i>tpp</i>	5.03	5.07	4.28	7.87	8.7	8.2	17.0	10.0
RhCl(<i>tpp</i>)	6.70	6.16	5.34		[7.0 to 9.2] ⁱ		12.5	9.0
RhBr(<i>tpp</i>)	6.70	5.97	5.13		[7.0 to 9.2] ⁱ		13.0	9.0
RhI(<i>tpp</i>)	6.71	5.59	4.72		[7.0 to 9.2] ⁱ		13.0	9.5
IrCl(<i>tpp</i>)	6.95	6.73	5.92		[6.7 to 9.2] ⁱ		12.0	8.5

^a Relative to TMS = 10 τ . ^b Room temperature except where noted. ^c In Hz. ^d Coupling constants ± 0.5 Hz. ^e See ref. 11, additional coupling constants are: for the ligand, $J(\text{H}_2-\text{H}_4) = 1.3$ Hz, $J(\text{H}_1-\text{H}_4) = 1.8$ Hz, $J(\text{H}_1-\text{H}_2) = 1.8$ Hz; for the complexes, $J(\text{H}_2-\text{H}_4)$, $J(\text{H}_1-\text{H}_4)$, $J(\text{H}_1-\text{H}_2)$ are less than 0.5 Hz. ^f Not measured. ^g Inequivalent. ^h Additional coupling constants are: for the ligand, $J(\text{H}_3-\text{H}_4) = 6.0$ Hz; for the complexes, $J(\text{H}_3-\text{H}_4) = 3.0$ Hz, $J(\text{Rh}-\text{H}_1) = J(\text{Rh}-\text{H}_2) = \sim 1.0$ Hz, $J(\text{Rh}-\text{H}_3) = \sim 2.0$ Hz. ⁱ Overlapping.

a



b

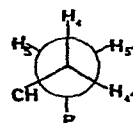
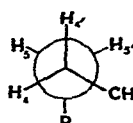


Fig. 2. Conformations of the methylene protons in $\text{RhCl}(\text{tbp})$. (a) Looking down the $\text{CH}_2\text{-P}$ axis. (b) Looking down the $\text{CH}_2\text{-CH}_2$ axis.

occurs due to inequivalent $\text{H}_3\text{-H}_4$ coupling constants. The H_1 and H_2 protons remain sharp and are unaffected as there is little coupling (less than 0.5 Hz) between H_4 , H_1 and H_2 . The fact that the methylene protons become inequivalent at lower temperatures, while the olefinic protons remain unchanged (i.e. $J(\text{H}_2\text{-H}_3)$, $J(\text{H}_1\text{-H}_3)$, $\delta(\text{H}_1)$, $\delta(\text{H}_2)$, $\delta(\text{H}_3)$ are constant) further indicates that the olefins are bonded within the temperature range $+60^\circ$ to -60° .

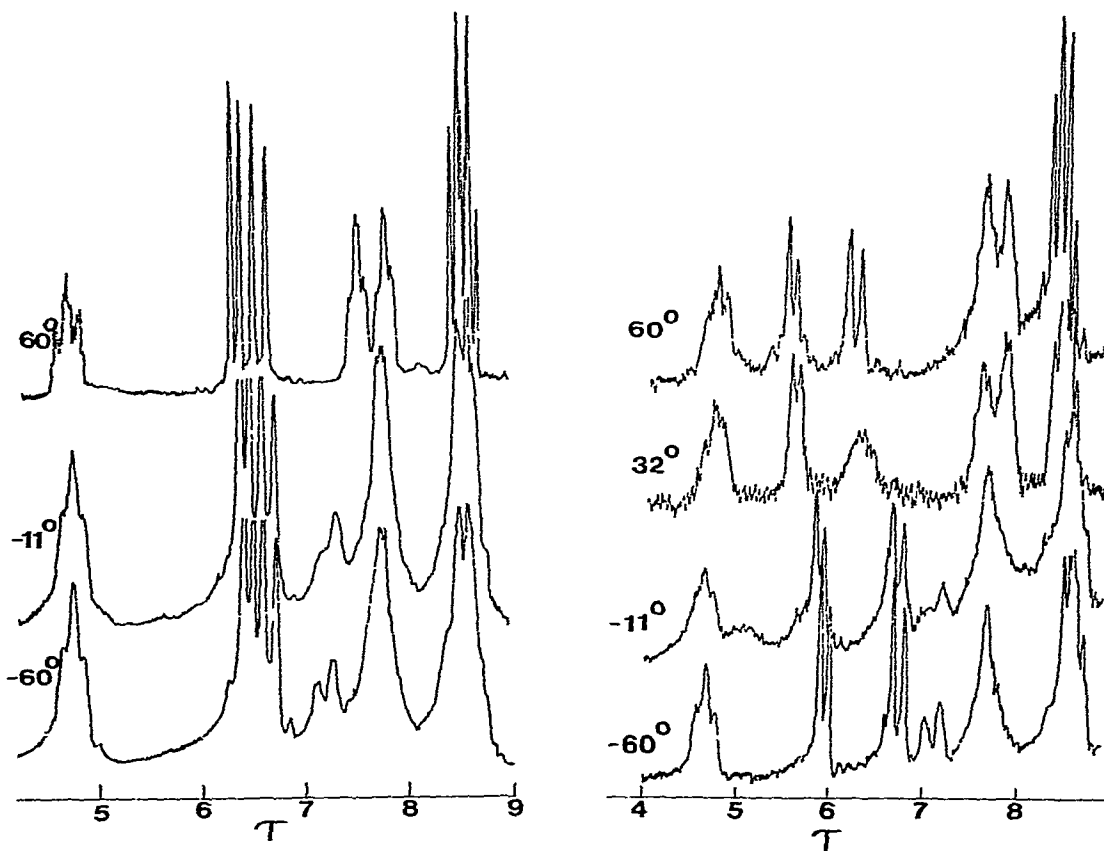


Fig. 3. Variable temperature 100 MHz PMR spectra of $\text{RhCl}(\text{tbp})$ in CDCl_3 , relative to internal TMS = 10 τ .

Fig. 4. Variable temperature 100 MHz PMR spectra of $\text{RhI}(\text{tbp})$ in CDCl_3 , relative to internal TMS = 10 τ .

(II) *RhBr(tbp)*. The spectrum of this compound was quite similar to *RhCl(tbp)* at room temperature.

(III) *RhI(tbp)*. As mentioned previously, there is free olefin present in the compound in the solid state and in solution from infrared studies. In the PMR spectrum at room temperature (Fig. 4), the resonances are much broader than those of the chloride and bromide analogues. At high temperatures (+60°), the resonances are sharp. At low temperatures (-60°), they are again sharp; and the methylene protons are no longer equivalent. Therefore at -60°, the compound has all three olefins bonded, and the structure apparently is the same as for *RhX(tbp)*, X = Cl, Br. At -11°, there is apparently slow exchange between bonded and unbonded olefinic groups. Here (-11°), the inequivalence of the methylene protons is appearing (peaks at ca. 7.2 τ), while both the higher temperature (+60°) and lower temperature (-60°) resonances are present in the olefinic region and if slow exchange was occurring at this temperature, then resonances due to free olefinic protons might be expected to appear. Indeed, there is a broad resonance just above 4 τ and another broad resonance at ca. 5 τ which may be assigned to free olefinic protons.

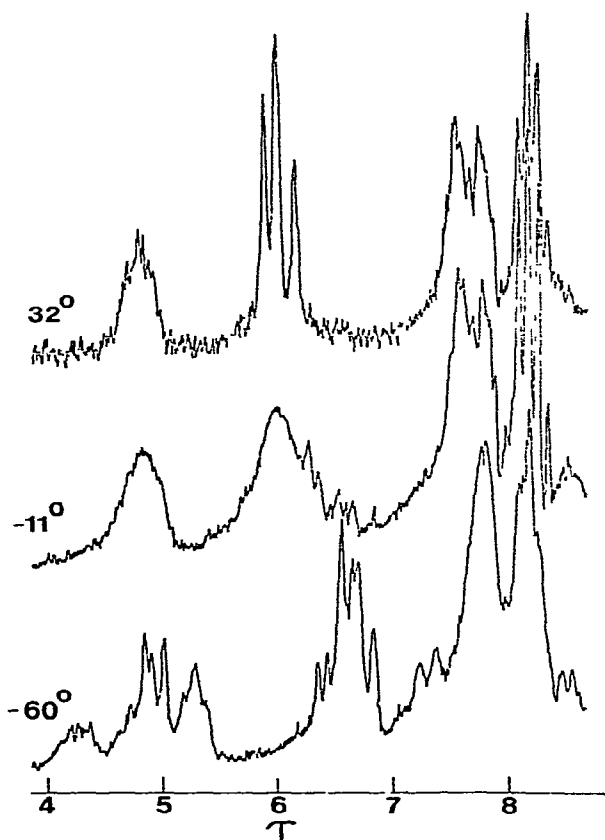


Fig. 5. Variable temperature 100 MHz PMR spectra of *RhCl(CO)(tbp)* in CDCl_3 , relative to internal TMS = 10 τ

(IV) $RhCl(CO)(tbp)$. All the PMR resonances are shifted upfield for the olefinic protons, which are equivalent at room temperature; the resonances are sharp indicating a fast exchange on the PMR time scale at that temperature. Upon lowering the temperature to -11° , the resonances become broad (Fig. 5); and new resonances appear at ca. 6.6τ and at ca. 7.2τ . Upon further cooling (-60°), the resonances again sharpen; and the characteristic doublet at 7.3τ indicates that the equilibrium has stopped. There are resonances at 4.2τ (area 1) and at 4.9τ (area 2) which can be assigned to unbonded olefin. By comparing $RhCl(CO)(tbp)$ (-60°) to $RhCl[CO][PhP(CH_2CH_2CH=CH_2)_2]$ (-60°), the resonances at $5.3, 6.5-6.9 \tau$, and the methylene protons are quite similar (Fig. 6) in their shape and coupling. As mentioned previously [15], the olefinic protons of $RhCl(CO)(bbp)$ are directed the same way (i.e. towards or away from each other) since the olefinic protons are equivalent. In $RhCl(CO)(tbp)$, another isomer (ca. 10%) is apparently present as there are two extra observable resonances for the olefinic (H_1 and H_2) protons at 6.3τ , and an extra broad resonance at ca. 4.7τ which is apparently the H_3 proton. The structure of the compound is proposed to be similar to that of $RhCl(CO)(bbp)$.

(V) $RhX(tpp)$, $X = Cl, Br, I$. Upon complexation at room temperature the

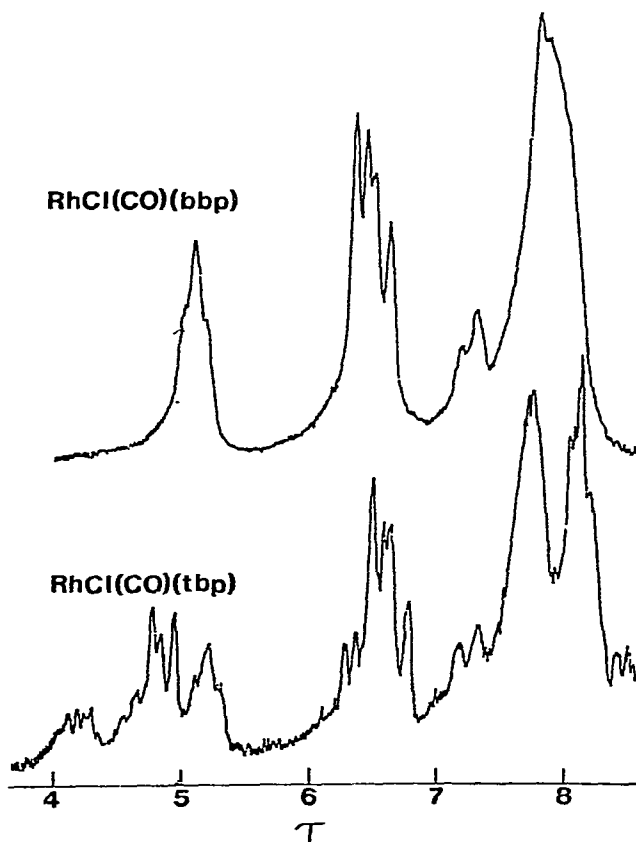


Fig. 6. PMR spectra of $RhCl(CO)(bbp)$ and $RhCl(CO)(tbp)$ at -60° , relative to internal TMS = 10τ .

olefinic protons (H_1 , H_2 and H_3) of the ligand are shifted from 5.03, 5.07 and 4.28 τ to 6.70, 6.16 and 5.34 τ respectively for the complex $RhCl(tpp)$. The methylene protons could become equivalent (Fig. 2) due to the same motion as discussed previously for $RhCl(tbp)$. However, due to the bulkier nature of the pentene ligand compared to the butene ligand, such a rotation might be severely hindered. Indeed, the methylene region of the compound is quite complex. Upon increasing the temperature to $+60^\circ$ there was essentially no change in the chemical shifts or coupling constants of either the methylene or olefinic protons for $RhI(tpp)$.

(VI) $IrClL$, $L = (tbp)$ or (tpp) , $IrI(tbp)$. These complexes have similar PMR spectra to their rhodium analogues. In all three cases (Table 2) there is an upfield shift of the respective olefinic protons and a decrease in the respective olefinic coupling constants. The complex $IrI(tbp)$ was prepared from $IrCl(tbp)$ and sodium iodide and was shown to have no unbonded olefin in solution in the infrared.)

Conclusions from PMR spectra

It is readily observable that in each of the series $RhX(tbp)$, $RhX(tpp)$ and $RhX(CO)(bbp)$ [15], $X = Cl, Br$ or I , there is a significant downfield shift of the H_2 and H_3 olefinic protons, while there is no shift or a negligible shift of the H_1 proton in going from Cl to Br to I . Taking the $P-Rh-X$ line as the Z axis in these compounds (see Fig. 7), the olefins in the plane would back bond through the d_{xy} and $d_{x^2-y^2}$ orbitals; and atoms capable of back bonding in the apical positions would utilize the d_{xz} and d_{yz} orbitals. Thus, the inductive effect due to change in the halide atom should have little influence on the chemical shifts and coupling constants of the olefinic protons; whereas through-space effects such as steric hindrance should be manifested by a chemical shift in the protons nearest the halide atom (i.e. H_2 and H_3). It has been observed that when an olefin is *trans* to a halide, as in the series $PdX_2(mbp)$ [9], $mbp = Ph_2P(CH_2-CH_2CH=CH_2)$, and in *cis*- $PtX_2(R_3P)(C_2H_4)$ [14]; there is a downfield shift of the olefinic protons accompanied by an increase in the coupling constants in changing the halide from Cl to a larger halide. However, when an olefin is *cis* to the halide atom there is a relatively large downfield shift of the protons adjacent to the

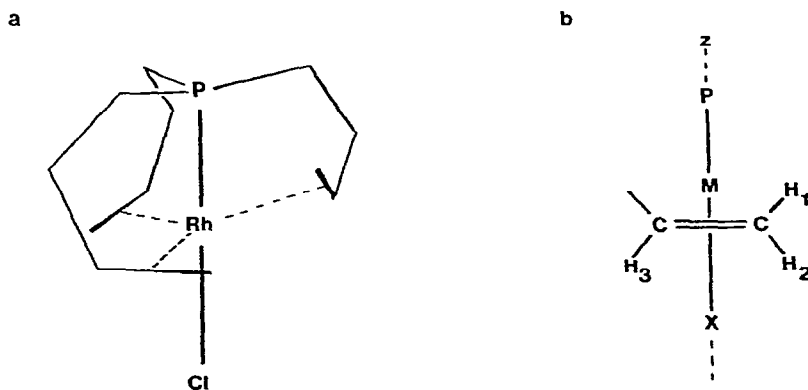
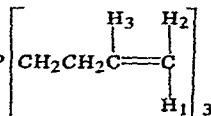
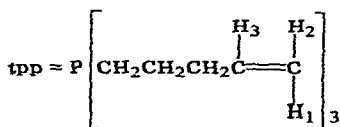


Fig. 7. (a) Skeletal structure of $RhCl(tbp)$. (b) Orientation of the olefinic protons with respect to the halide atom in the compounds $RhX(tbp)$, $RhX(tpp)$, $RhX(CO)(bbp)$, $IrCl(tbp)$ and $IrCl(tpp)$.

TABLE 3
CHEMICAL SHIFT AND COUPLING CONSTANT DIFFERENCES

	Chemical shift difference ^a			Coupling constant difference ^b	
	H ₁	H ₂	H ₃	H ₁ -H ₃	H ₂ -H ₃
RhCl(tbp) ^c to IrCl(tbp)	+0.39	+0.59	+0.69	-1.5	-1.5
RhI(tbp) (-60°) to IrI(tbp)	+0.36	+0.50	+0.70	-1.5	ca. -1.0
RhCl(tpp) to IrCl(tpp)	+0.25	+0.25	+0.57	-0.5	-0.5

^a Difference measured in ppm. ^b Difference measured in Hz. ^c tbp = P 



halide in going from Cl to Br to I, accompanied by very small changes both in the coupling constants, $J(H_1-H_3)$ and $J(H_2-H_3)$, and in the chemical shift of the non-adjacent protons. This is consistent with the results that we have observed.

Comparison of rhodium-olefin bonding and iridium-olefin bonding

Previously, several authors [16] have used the lowering of the olefinic stretching frequency (ca. 1640 cm⁻¹) to ca. 1500 cm⁻¹ (Band 1) [14] as an indirect measure of the comparative strength of the metal-olefin interaction. It appears that such arguments are still valid, although they should be used with caution. The Band 1 frequencies (Table 1) of the iridium complexes IrCl(tbp) and IrCl(tpp) have been lowered an extra 21 cm⁻¹ and 25 cm⁻¹ respectively over their corresponding rhodium compounds. There is also an increase in the symmetric metal-olefin stretching frequency from 421 to 427 cm⁻¹ in going from RhCl(tbp) to IrCl(tbp); and there is an increase (375 to 391 cm⁻¹) for the same mode in going from RhCl(tpp) to IrCl(tpp). These shifts are in agreement with the increased metal-olefin interaction with iridium. The PMR data amply support this contention. The upfield shift coupled with a decrease in the coupling constants (Table 3) is indicative of a stronger metal-olefin bond and a more saturated C-C bond in the iridium complexes.

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