Journal of Organometallic Chemistry, 102 (1975) 387—396

OLEFIN COMPLEXES OF RHODIUM(I) CONTAINING THE LIGANDS BUT-3-ENYLDIPHENYLPHOSPHINE AND DIPHENYLPENT-4-ENYLPHOSPHINE

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(Received July 28th, 1975)

Summary

But-3-enyldiphenylphosphine (mbp) and diphenylpent-4-enylphosphine (mpp) react with $Rh_2Cl_2(C_2H_4)_4$ (molar ratio 2/1) to form the four coordinate dimeric complexes $Rh_2Cl_2(mbp)_2$ and $Rh_2Cl_2(mpp)_2$ respectively, while but-3-enyldiphenylphosphine reacts with $Rh_2Cl_2(C_2H_4)_4$ (molar ratio 4/1) to form $RhCl(mbp)_2$, a five coordinate complex in the solid state. The dimers further react with sodium tetraphenylborate to give the π-bonded tetraphenylborate complexes $Rh[mbp][(C_6H_5)_4B]$ and $Rh[i\text{-}mpp][(C_6H_5)_4B]$ where i-mpp = $(C_6H_5)_2P(CH_2CH_2CH{=}CHCH_3)$. $RhCl(CO)(mbp)_2$ reacts with sodium tetraphenylborate to form the five coordinate cationic complex $[Rh(CO)(mbp)_2][(C_6H_5)_4B]$. Both $RhCl(CO)(mbp)_2$ and $RhCl(mbp)_2$ react with hydrogen in methanol saturating the olefin to form $RhCl[CO][(C_6H_5)_2P(C_4H_9)]_2$ and $Rh_2Cl_2[(C_6H_5)_2P(C_4H_9)]_2$ respectively.

Introduction

In a previous communication [1], we discussed the hydrogenation and isomerization of potentially bidentate tertiary unsaturated phosphine ligands in the rhodium complexes *trans*-$RhCl[CO][(C_6H_5)_2P(CH_2)_nCH{=}CH_2]$, where n = 0—3. In these complexes in solution, the phosphorus atoms were coordinated while the olefins were not bonded to the metal centre. Since then, we have carried out a more detailed study of the factors involved in the hydrogenation and isomerization of such complexes [2]. In general, unsaturated tertiary phosphine ligands have been found to be very useful in the preparation of stable five coordinate

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rhodium(I)—olefin complexes. The ligands *o*-styryldiphenylphosphine [3], bis(*o*-styryl)phenylphosphine [4], tris(*o*-styryl)phosphine [4,5], bis(but-3-enyl)phenylphosphine [6], tris(but-3-enyl)phosphine [7-9] and tris(pent-4-enyl)phosphine [9] all form five coordinate complexes of rhodium(I). In this present paper, we have studied the preparation and properties of rhodium(I) four and five coordinate complexes containing the bidentate phosphine ligands $(C_6H_5)_2P(CH_2CH_2 \cdot CH{=}CH_2)$ (mbp) and $(C_6H_5)_2P(CH_2CH_2CH_2CH{=}CH_2)$ (mpp), in which both the phosphorus and olefin are bonded to the rhodium atom.

Experimental

The complex $Rh_2Cl_2(C_2H_4)_4$ [10] and the ligands but-3-enyldiphenylphosphine [11] and diphenylpent-4-enylphosphine [11] were prepared by the standard literature methods.

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

Infrared spectra were recorded using Perkin—Elmer 137, 137G and 621 spectrometers. Proton magnetic spectra were recorded on a Varian HA100 spectrometer operated in the field sweep mode. Air sensitive samples were prepared in an inert atmosphere and the NMR tube sealed under a vacuum. The temperature of the probe 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 a A.E.I. MS-9. Melting points were measured on a Fisher—Johns melting point apparatus, and are uncorrected.

Preparation of $Rh_2Cl_2(mbp)_2$. To a flask containing a stirred suspension of 0.20 g (0.515 mmol) of $Rh_2Cl_2(C_2H_4)_4$ in 10 ml of ethyl ether under nitrogen, was added dropwise 0.250 ml (1.040 mmol) of but-3-enyldiphenylphosphine in 5 ml of ethyl ether. After stirring the solution for ½ h, the resulting precipitate was separated by filtration, washed with ethyl ether and dried in vacuo. The impure product was recrystallized from methylene chloride/ethanol to yield 0.30 g (77%) of orange crystals. (Found: C, 50.3; H, 4.70; P, 8.27; Cl, 9.55. Mol. wt., 756 (mass spectrum). $C_{32}H_{34}Cl_2P_2Rh_2$ calcd.: C, 50.8; H, 4.49; P, 8.17; Cl, 9.37%. Mol. wt., 756.) M.p. 202-206°C (decomposition point, uncorrected).

Preparation of $Rh[mbp][(C_6H_5)_4B]$. To a stirred suspension of 0.05 g (0.066 mmol) of $Rh_2Cl_2(mbp)_2$ in 5 ml of methanol under nitrogen was added 0.065 g (0.19 mmol) of sodium tetraphenylborate. Within approximately 10 min, the color had changed from orange to yellow. The solution was stirred for 4 h and then filtered. The yellow precipitate was washed with methanol, ethyl ether and then dried in vacuo. The product was recrystallized from methylene chloride/methanol to yield 0.072 g (82%) of yellow crystals.

Preparation of $RhCl(CO)(mbp)_2$. To a stirred solution of 0.322 g (0.855 mmol) of $Rh_2Cl_2(CO)_4$ in 10 ml of methanol under nitrogen was added dropwise 0.83 ml (3.46 mmol) of $(C_6H_5)_2PC_4H_7$ in 5 ml of methanol. This solution was seeded and allowed to evaporate to dryness under a flow of nitrogen. A small quantity of ethanol was added at —78°C, and the solution was filtered. The crystals were washed with cold ethanol and dried in vacuo to yield 0.926 g (86%) of yellow crystals. (Found: C, 60.4; H, 5.69; P, 9.98. Mol. wt., 600 (VPO in chloroform) and 378 (VPO in methanol). $C_{33}H_{34}ClOP_2Rh$ calcd.: C, 61.3; H, 5.30; P, 9.56%. Mol. wt., 647.)

Preparation of [Rh(CO)(mbp)$_2$][(C$_6$H$_5$)$_4$B]. To a stirred solution of 0.20 g (0.31 mmol) of $RhCl(CO)(mbp)_2$ in 10 ml of methanol under nitrogen was added 0.24 g (0.70 mmol) of sodium tetraphenylborate in a minimum amount of methanol. Immediately a very pale yellow precipitate formed. The solution was stirred for another 5 min and then filtered. The precipitate was washed with methanol, then ethyl ether, and then dried in vacuo to yield 0.27 g (93.6%) of product. The product was recrystallized from methylene chloride/methanol. (Found: C, 72.3; H, 5.93; P, 6.64. $C_{57}H_{54}OBP_2Rh$ calcd.: C, 73.6; H, 5.79; P, 6.67%.)

Preparation of RhCl(mbp)$_2$. To a stirred suspension of 0.20 g (0.515 mmol) of $Rh_2Cl_2(C_2H_4)_4$ in 15 ml of ethyl ether under nitrogen was added dropwise 0.5 ml (2.08 mmol) of but-3-enyldiphenylphosphine in 5 ml of ethyl ether. The precipitate was collected, washed with ether and dried in vacuo. The yield of unrecrystallized material was 0.58 g (91.5%). This product could be recrystallized from methylene chloride/methanol. Crystals for an X-ray study were grown in C_6D_6 in an NMR tube. (Found: C, 60.6; H, 5.50; P, 10.06; Cl, 5.82. Mol. wt., 545 (VPO in chloroform). $C_{32}H_{34}ClP_2Rh$ calcd.: C, 62.1; H, 5.50; P, 10.02; Cl, 5.75%. Mol. wt., 618.)

Preparation of RhBr(mbp)$_2$. To a refluxing solution of 0.30 g (0.49 mmol) of $RhCl(mbp)_2$ in 20 ml of refluxing methanol under nitrogen was added 0.25 g (2.9 mmol) of lithium bromide. The solution was refluxed for 2 h, reduced in volume to ca. 5 ml under a flow of nitrogen, then allowed to cool to room temperature. The precipitate was collected by filtration, washed with methanol and then ether. The product was recrystallized from methylene chloride/methanol to yield 0.21 g (65%) of yellow crystals. (Found: C, 57.3; H, 4.86; P, 9.81. $C_{32}H_{34}BrP_2Rh$ calcd.: C, 58.1; H, 5.17; P, 9.34%.)

Preparation of RhI(mbp)$_2$. To a refluxing solution of 0.20 g (0.32 mmol) of $RhCl(mbp)_2$ in 15 ml of methanol under nitrogen was added 0.28 g (1.9 mmol) of sodium iodide. The solution was refluxed for ca. 5 min and then slowly cooled to room temperature. Stirring was continued for 2 h. The resulting yellow precipitate was separated by filtration, washed with methanol and then ether. The product was recrystallized twice from methylene chloride/methanol to yield 0.094 g (41%) of orange crystals. (Found: C, 54.0, H, 4.72; P, 8.96. $C_{32}H_{34}IP_2Rh$ calcd.: C, 54.1; H,4.84; P, 8.73%.)

Reaction of RhCl(mbp)$_2$ with carbon monoxide. Carbon monoxide was bubbled into a solution of 0.1 g of $RhCl(mbp)_2$ in 15 ml of methanol. The solution changed color from orange to yellow. It was then concentrated, a small amount of ethyl ether added and then cooled in a dry ice bath. Upon scratching, crystals appeared. These were filtered and washed with petroleum ether to yield $RhCl(CO)(mbp)_2$. The product was identified by its infrared spectrum.

Reaction of RhCl(mbp)$_2$ with hydrogen. $RhCl(mbp)_2$ (0.21 g, 0.34 mmol) was dissolved in 40 ml of methanol and cooled to —5°C in a salt-ice bath. The solution was completely deaerated, then hydrogen was admitted at about two bubbles per second for 70 min. The solution quickly changed from orange to yellow, then to orange and then slowly to a deep cherry red color. At this point, the hydrogen flow was stopped and the excess hydrogen removed under a flow of nitrogen. Upon heating and concentrating the solution under a flow of nitrogen, an orange precipitate formed which was recrystallized from methylene chloride/ethanol to yield 0.76 g (38%) of $Rh_2Cl_2[(C_6H_5)_2P(C_4H_9)]_4$. (Found: C, 60.0; H, 6.01. $C_{64}H_{79}Cl_2P_2Rh_2$ calcd.: C, 61.7; H, 6.11%.)

Preparation of $Rh_2Cl_2(mpp)_2$. To a stirred solution of 0.20 g (0.515 mmol) of $Rh_2Cl_2(C_2H_4)_4$ in 10 ml of methylene chloride under nitrogen was added dropwise 0.26 ml (1.05 mmol) of diphenylpent-4-enylphosphine in 5 ml of methylene chloride. The solution was heated and the complex crystallized with the addition of ethanol to yield 0.313 g (77%) of golden-orange crystals. This was recrystallized from methylene chloride/ethanol to yield 0.206 g (50.8%) of product. (Found: mol. wt., 785 (mass spectrum). $C_{34}H_{38}Cl_2Rh_2$ calcd.: mol. wt., 785.)

Preparation of [Rh(i-mpp)] [Ph_4B]. To a stirred suspension of 0.05 g (0.064 mmol) of $Rh_2Cl_2(mpp)_2$ in 5 ml of methanol under nitrogen at room temperature was added 0.065 g (0.19 mmol) of sodium tetraphenylborate. The color changed from orange to yellow. The solution was stirred vigorously for 3 h and then filtered to yield 0.064 g (75%). The product was recrystallized from methylene chloride/methanol.

Discussion

When but-3-enyldiphenylphosphine is added to $Rh_2Cl_2(C_2H_4)_4$ in the molar ratio of 4/1 in methanol or petroleum ether, the yellow crystalline compound (recrystallized from methylene chloride/methanol) $RhCl(mbp)_2$ can be isolated in a 90% yield. The compound is readily soluble in such solvents as methylene chloride, chloroform and benzene; moderately soluble in methanol and almost insoluble in ether. When the ligand but-3-enyldiphenylphosphine and $Rh_2Cl_2(C_2H_4)_4$ are reacted in the molar ratio of 2/1, however, an orange crystalline product is obtained which is only sightly soluble in chlorinated organic solvents, and insoluble in methanol and diethyl ether. A similar compound is obtained from the reaction of diphenylpent-4-enylphosphine and $Rh_2Cl_2(C_2H_4)_4$ in the molar ratio of 2/1. Physical measurements indicate that these compounds are the dimeric complexes $Rh_2Cl_2(mbp)_2$ and $Rh_2Cl_2(mpp)_2$ respectively.

The complex $RhCl(mbp)_2$, undergoes a number of reactions (Fig. 1). The complexes $RhBr(mbp)_2$ and $RhI(mbp)_2$ can be prepared by the metathetical reactions of the chloride complex with lithium bromide and sodium iodide respectively, and $RhCl(Ph_2PCH_2CH_2CH{=}CH_2)_2$ readily reacts irreversibly with carbon monoxide to yield $RhCl(CO)(mbp)_2$. This compound was also prepared by the reaction of but-3-enylphosphine and $Rh_2Cl_2(CO)_4$ and such behavior has been observed [12] between $RhCl(Ph_3P)_3$ and $RhCl(CO)(Ph_3P)_2$. $RhCl(CO)(mbp)_2$ ionizes in methanol [2] to form $[Rh(CO)(mbp)_2]^+$, which reacts with hydrogen to give $RhCl[CO][(C_6H_5)_2P(CH_2CH_2CH_2CH_3)]_2$.

In methanol, $RhCl(mbp)_2$ has an orange color, and when hydrogen is admitted, the color quickly changes to yellow. This step is apparently irreversible, as the addition of nitrogen in place of hydrogen at this step does not change the color. Upon continued addition of hydrogen, the color changes from yellow to orange to a cherry-red, but if the reaction is continued, the color eventually be-

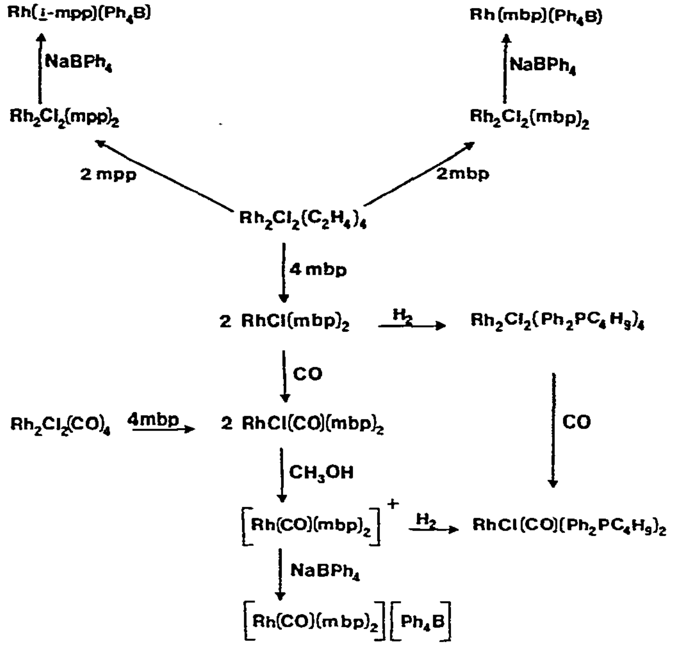

Fig. 1. Preparation and reactions of compounds of rhodium(I) containing the ligands mbp = $(C_6H_5)_2P(CH_2CH_2CH{=}CH_2)$ and mpp = $(C_6H_5)_2P(CH_2CH_2CH_2CH{=}CH_2)$.

comes black. If the solvent is removed at the black stage, a black oil is left behind. By stopping the reaction at the cherry-red stage, the red-orange complex $Rh_2Cl_2[(C_6H_5)_2P(CH_2CH_2CH_2CH_3)]_2$ can be isolated. The complex was characterized by an infrared spectrum, PMR spectrum and elemental analysis. It is assumed to have a dimeric structure similar to $Rh_2Cl_2(Ph_3P)_4$ [12]. Upon reacting the hydrogenated species with carbon monoxide, the complex $RhCl[CO][(C_6H_5)P(CH_2CH_2CH_2CH_3)]_2$ is formed (identified by comparison of its spectrum with and authentic sample).

Infrared and proton magnetic resonance spectra (Refer to Tables 1 and 2)

The ligands mbp and mpp contain a sharp band at ca. 1635 cm^{-1} in the infrared which is assigned to the C=C stretching frequency.

For the complex, $RhCl(mbp)_2$, no band was observed in the infrared spectrum of a KBr disc of the compound in the 1630-1640 cm^{-1} region. This complex does contain weak bands at 1505 cm^{-1} and at 1252 and 1231 cm^{-1} which can be assigned to the $\nu(C{=}C)$ and $\delta(CH)$ modes. We have assigned the 1505 cm^{-1} band as Band I and either or both the 1252 and 1231 cm^{-1} bands as belonging to Band II consistent with the recent assignments [13]. Since this indicated that both olefins were bonded in the solid state, and molecular weight measurements gave results for a monomeric formulation; it is proposed that the complex is five coordinate. This structure has been confirmed by X-ray methods [14]. The crystals for the structure were grown from a C_6D_6 solution in a NMR tube and this compound contained solvent of crystallization. The structure of the compound is a distorted trigonal bypyramid containing a phosphine and chlorine

TABLE 1

INFRARED DATA[a,b] FOR COMPLEXES CONTAINING THE LIGANDS mbp = $(C_6H_5)_2P(CH_2CH_2CH{=}CH_2)$ AND mpp = $(C_6H_5)_2P(CH_2CH_2CH_2CH{=}CH_2)$

Compound	State	Free $\nu(C{=}C)$	Band I	Band II	$\nu(CO)$
mbp	Oil	1635s			
mpp	Oil	1635s			
$RhCl(mbp)_2$	KBr	None	1505w	1231w or 1252w	
	CH_2Cl_2	1638w	1508w		
$RhBr(mbp)_2$	KBr	None	1524w		
	CH_2Cl_2	1639w	1513w		
$RhI(mbp)_2$	KBr	None	1515w		
	CH_2Cl_2	1642w	1513w		
$RhCl(CO)(mbp)_2$	KBr	1634w	*c*	1250w	1950s
	CH_2Cl_2	1639w			1972s
	CH_3OH				2004s, 1968s
$Rh_2Cl_2(mbp)_2$	KBr	None	*c*	1249w	
	$CHBr_3$	None	*c*		
$Rh_2Cl_2(mpp)_2$	KBr	None	*c*	1249w	
	$CHBr_3$	None	*c*		

Cationic and π-Bonded Tetraphenylborate Complexes

Compound	State	Free $\nu(C{=}C)$	Band I	$\nu(CO)$	1500-1350
$Na[(C_6H_5)_4B]$					1480s, 1452vw 1425s, 1390vw
$[Rh(CO)(mbp)_2][(C_6H_5)_4B$	KBr	None	c	2001s	1481s, 1433s, 1422s, 1389w, (br)
	CH_2Cl_2	None	*c*	2028s	
$[Rh(mbp)_2][(C_6H_5)_4B]$	KBr	None	*c*		1481s, 1437s, 1429a, 1397w(b)
	CH_2Cl_2	1637w	*c*		
$[Rh(mbp)][(C_6H_5)_4B]$	KBr	None	1497w		1479s, 1451m 1445m, 1437s 1427s, 1393m
	CH_2Cl_2	None	1499w		
$[Rh(i\text{-}mpp)][(C_6H_5)_4B]$[d]	KBr	None	1499w		1481s, 1453m, 1437s, 1429s, 1393m

[a] All values measured in cm^{-1}. [b] vw very weak; w weak; m medium; s strong; b broad. [c] Too weak, or obscured under the strong band at 1486 cm^{-1}. [d] *i*-mpp = $(C_6H_5)_2P(CH_2CH_2CH{=}CHCH_3)$.

atom in the apical positions and a phosphorus atom and two olefins in the planar positions. In solution (methylene chloride) in the infrared, a band at 1638 m, due to unbonded olefin, and a band at 1508 w cm^{-1} are both present. In the PMR spectrum at room temperature, the resonances are broadended; there is no sign of free olefin, and the bands (due to olefin) are shifted upfield. When an olefin is bonded to a transition metal, the olefinic resonances are generally shifted upfield [15], and the olefinic resonances of this compound lie between 6.4 to 7.3τ, and it is obvious that there is fluxional character between bonded and non-bonded olefinic groups on the PMR time scale. The temperature dependent PMR was investigated in benzene-d_6 (+8°C to +80°C) and in chloroform-d

TABLE 2

PMR DATA[a] FOR COMPLEXES CONTAINING mbp[b] AND *i*-mpp[b]

Compound	Phenyl	Phenyl (bonded)	5, 4	3	2	1
mbp	2.5-2.9		7.9	4.19	5.06	5.11
$RhCl(mbp)_2$	2.1-2.7		≈7.8	5.76	≈6.5	≈6.5
$RhBr(mbp)_2$	2.1-2.7		≈7.8	6.2	[6.6 to 7.2]	
$RhI(mbp)_2$	2.1-2.7		≈7.8	6.4	[6.8 to 7.3]	
$Rh_2Cl_2(mbp)_2$	[d]		7.3-8.4	5.5	[6.7 to 7.1]	
$Rh[mbp][(C_6H_5)_4B]$	2.2-3.0	3.5-4.3 (area 5)	[c]	5.6	[c]	[c]
$[Rh(CO)(mbp)_2][(C_6H_5)_4B]$	2.2-3.2		7.1-7.9[e]	5.96	6.70 (area 1)	
$Rh[i\text{-}mpp][(C_6H_5)_4B]$	2.2-3.1	3.2-4.0 (area 4)	7.3-8.3	5.10	6.00	8.88

[a] Measured at 100 MHz; chemical shifts in ppm relative to internal TMS, τ 10.0; except where noted. [b] mbp = $(C_6H_5)_2P(\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H{=}\overset{2}{C}H\overset{1}{H})$; *i*-mpp = $(C_6H_5)_2P(\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H{=}\overset{2}{C}H\overset{1}{C}H_3)$. [c] Overlapping between τ 7.3-8.5. [d] Benzene lock. [e] Either proton 1 or 2 in this compound occurs in the same region as protons 4 and 5.

(0°C to −60°C). The position of the olefinic resonances shifted upfield (Table 3) in benzene upon a decrease in temperature to +8°C. In chloroform (less than 0°C), the spectrum becomes more complex and it is not possible to make assignments. The resonances remain broad (+80°C to −60°C); but apparently, the equilibrium is shifted towards the more bonded complex.

For the complexes $Rh_2Cl_2(mbp)_2$ and $Rh_2Cl_2(mpp)_2$ no band in the 1630-1640 cm^{-1} range was observed in the infrared either in the solution or solid state. (Table 1). The absorptions around 1500 cm^{-1} assignable to Band I were also absent, but weak absorptions assignable to Band II were observed at ca. 1250 cm^{-1}. It is probable that the absorption assignable to Band I is obscured under the strong band at 1487 cm^{-1}. The PMR spectrum of $Rh_2Cl_2(mbp)_2$ gave supporting evidence that the olefins were bonded to the rhodium metal. The compound was too insoluble for the alkene protons to be observed after one scan. A time-averaged PMR spectrum (428 scans, C_6H_6 lock, sweep time 100 sec, sweep width 500 Hz) contained resonances between τ 6.7-7.1 which can be assigned to the olefinic resonances. The parent ions for $Rh_2Cl_2(mbp)_2$ in the mass spectrum occur at 756, 758 and 760 in the ratio of 3/2/1 due to the isotopic distribution of chlorine. The mass spectrum is interesting in that although parent ions were ob-

TABLE 3[a]

VARIABLE TEMPERATURE PMR OF $RhCl(mbp)_2$[b] in C_6D_6

Temp. (°C)	Proton 3	Protons 2, 1
80	5.42	6.35
69	5.47	6.37
58	5.52	6.38
46	5.50	6.44
35	5.69	6.50
25	5.76	6.53
19	5.79	6.54
8	5.90	6.58

[a] Values in τ relative to TMS, τ 10.0 ppm. [b] mbp = $(C_6H_5)_2P(CH_2CH_2\overset{3}{C}H{=}\overset{2}{C}H\overset{1}{H})$.

served for the dimer, no monomeric species occur and similar observations were recorded for $Rh_2Cl_2(mpp)_2$. This behaviour [16] has been observed for the closely related compounds $Rh_2X_2(C_8H_{12})_2$, X = Cl, Br or I and C_8H_{12} = cyclooctadiene. It is not possible (with the present information) to predict whether the phosphorus atoms are *cis* or *trans* with respect to each other. It is proposed that the compound has bridging chlorine atoms and that the olefin is perpendicular to the plane containing the rhodium and chlorine atoms. This would then be analogous to the bridging halide square-planar rhodium(I) complexes $Rh_2Cl_2(C_8H_{12})_2$ and $Rh_2Cl_2(C_2H_4)_4$ whose structures have been determined [10,17]. The square-planes could be bent at the bridging chlorine atoms as is found in $Rh_2Cl_2(C_2H_4)_4$.

Cationic complexes

In methanol $RhCl(CO)(mbp)_2$ ionizes (molec. conductivity 64.0 ohm^{-1} cm^2 mol^{-1}) and contains two carbonyl resonances in the infrared at 2003 and at 1970 cm^{-1}; these can be assigned to the ionized and covalent species respectively. This equilibrium will be discussed in a future paper [2]. When sodium tetraphenylborate is added to a methanolic solution of $RhCl(CO)(mbp)_2$, off white crystals of $[Rh(CO)(mbp)_2][Ph_4B]$ are formed. There are no IR absorptions at 1460 or 1390 cm^{-1} nor any PMR resonances between τ 3.0-4.2 indicative of a π-bonded tetraphenylborate ion [18]. $[Rh(CO)(mbp)_2][Ph_4B]$ has a carbonyl stretching frequency at 2001 in the solid state and 2015 cm^{-1} in solution (methylene chloride). There were no detectable bands at either 1635 or at 1500 cm^{-1} in the solid state. In a concentrated solution in methylene chloride, there was no free olefin detected; but there was a very weak broad band at 1530 cm^{-1} which may belong to Band I. More likely, this mode is obscured by the strong band at 1486 cm^{-1}. The PMR spectrum of the complex in acetone-d_6 shows no observable free olefinic protons. In methylene chloride, in which the compound is more soluble, the spectrum shows resonances assignable to bonded olefinic protons. These resonances are broadened slightly. This could be due to intramolecular rearrangements without dissociation of an olefin as have been recently observed for five-coordinate iridium(I) species [19]. Some of the broadening could also be due to P—H and Rh—H coupling. If there was an equilibrium between bonded and unbonded olefin, the percentage of unbonded olefin would be extremely small and the equilibrium would lie completely towards the bonded complex. We propose that this complex has a five coordinate structure with both olefins bonded as for the complex $[Rh(CO)(SP)_2]Cl$ [3] (SP = *o*-styryldiphenylphosphine).

Attempts were made to form the cation $[Rh(mbp)_2]^+$ with the counterions BF_4^-, PF_6^- and Ph_4B^-. Only the tetraphenylborate complex was readily isolable. The infrared spectrum (Table 1) of this tetraphenylborate complex in the solid state contained bands due to non-bonded tetraphenylborate ion and contained no observable bands due to a π-bonded tetraphenylborate ion [18]. There was no observable band due to free olefin at ca. 1635 cm^{-1}, and the absorbance due to Band I absorption is most probably obscured by the strong band at ca. 1480 cm^{-1}. The infrared spectrum in solution (methylene chloride) does contain a band at 1637 cm^{-1} which is assignable to the free olefinic stretching mode and this is in agreement with the PMR spectrum of the compound. In the PMR spectrum, the olefinic resonances are completely broadened. There are resonances in the τ 3.6-4.2 region which can be assigned to a π-bonded tetraphenylborate ion [18]. The observance of the free olefin in the infrared spectrum in solution, the broadening of the olefinic protons and the observance of a π-bonded tetraphenylborate ion in the PMR spectrum are indications of an equilibrium between bonded and unbonded olefinic groups. The low calculated value of the area (1.5 protons) for the π-bonded tetraphenylborate ion is in agreement with such an equilibrium.

π-Bonded tetraphenylborate complexes

These compounds are readily formed by the addition of sodium tetraphenylborate to suspensions of the dimeric compounds $Rh_2Cl_2(mbp)_2$ or $Rh_2Cl_2(mpp)_2$ in methanol and the products can be recrystallized from methylene chloride/methanol. They are slightly soluble in chlorinated solvents, but insoluble in methanol and the complexes are quite stable in the solid state or in solution even when in contact with the air. There is no observable band in ca 1635 cm^{-1} (free olefin); but a weak band at ca. 1500 cm^{-1} for the compounds is present and this is consistent with the olefin being bonded for both of the complexes. The region 1500-1350 cm^{-1} is quite complex and contains five or six major absorbances. Bands at ca. 1481 and at ca. 1433 cm^{-1} are noticed in the complexes $Rh_2Cl_2(mbp)_2$ and $Rh_2Cl_2(mpp)_2$; while strong absorbances are seen at 1480 and at 1425 cm^{-1} for sodium tetraphenylborate. If four similar bands are present in Rh[mbp][$(C_6H_5)_4B$] and Rh[*i*-mpp][$(C_6H_5)_4B$], then there are two new absorbances occurring for these complexes. These occur at ca. 1452 and 1393 cm^{-1}. Such bands have been shown to exist for a π-bonded phenyl group of the tetraphenylborate ion [18].

The olefinic resonances of the ligands (in the PMR) have been shifted upfield for both of the complexes. For Rh[*i*-mpp][$(C_6H_5)_4B$], there is a resonance at τ 8.88 (area = 3, doublet, J 5.5 Hz), and there are two olefinic resonances at τ 5.10 (area = 1, broad triplet) and at τ 6.0 (area = 1, broad doublet). The resonances at τ 5.10 and at 6.0 can be assigned to bonded olefinic protons, while the

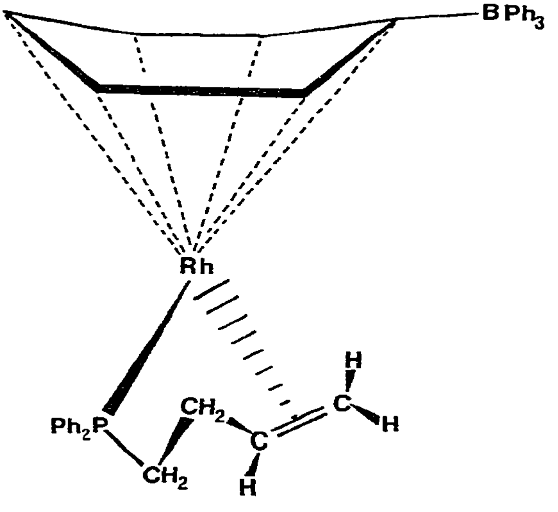

Fig. 2. Proposed structure for the compound Rh[mbp] [$(C_6H_5)_4B$] where mbp = $(C_6H_5)_2P(CH_2CH_2CH{=}CH_2)$

resonance at τ 8.88 is most certainly a methyl group. The isomerization apparently occurred during the reaction of $Rh_2Cl_2(mpp)_2$ with sodium tetraphenylborate, since no methyl resonance was observable in the PMR spectrum of the dimer. At the present time the isomeric nature of the olefin has not been determined, however, the ligand $(C_6H_5)_2P(CH_2CH_2CH_2CH{=}CH_2)$ on the complex $RhCl[CO]$-$[(C_6H_5)_2P(CH_2CH_2CH_2CH{=}CH_2)]_2$ does isomerize upon heating to give the complexed phosphine $(C_6H_5)_2P(CH_2CH_2CH{=}CHCH_3)$ in which the olefin has the *cis* configuration [1]. For $Rh[mbp][(C_6H_5)_4B]$ there are resonances in the τ 3.5-4.3 region (area 5), which can be assigned to a π-bonded phenyl group of the tetraphenylborate ion.

For $Rh[i\text{-}mpp][(C_6H_5)_4B]$, the area of these protons (τ 3.2-4.0) is equivalent to only 4 protons and the other proton is probable obscured by the non-bonded phenyl resonances. The infrared and PMR spectra of the complexes indicate that the phosphine is chelated, and a phenyl group of the tetraphenylborate ion is π-bonded. Thus a structure similar to that found for $Rh[P(OCH_3)_3]_2[(C_6H_5)_4B]$ [20] is proposed. (Figure 2).

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