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Some Reactions of Compounds of the Type $[(\text{diene})\text{RhX}]_2$ (diene = cycloocta-1,5-diene, bicyclo[2.2.1]hepta-2,5-diene; X = Cl, Br) with Tertiary Phosphines and Phosphites[1]

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The reactions of various monodentate ligands with the dimeric compounds $[(\text{diene})\text{RhX}]_2$ (diene = C_8H_{12}, X = Cl, Br; diene = C_7H_8, X = Cl) are described. Whereas it has been previously established that amines and tertiary phosphines, L, cleave the halogen bridges of $[(\text{diene})\text{RhX}]_2$ to form derivatives of the type (diene)RhLX, it is now found that $P(OC_6H_5)_3$ preferentially displaces the diene groups. Thus stepwise addition of $P(OC_6H_5)_3$ to $[(\text{diene})\text{RhX}]_2$ in dichloromethane leads to the formation of the complexes $[P(OC_6H_5)_3]_2(\text{diene})X_2Rh_2$, $\{Rh[P(OC_6H_5)_3]_2X\}_2$, and $Rh[P(OC_6H_5)_3]_3X$. It is also shown that halogen displacement in (diene)RhLCl by the ligands L can be effected provided that alcohols are used as solvents. Thus the reactions of $[(\text{diene})\text{RhCl}]_2$ with the ligands L in methanol at room temperature and in the presence of $NaB(C_6H_5)_4$ afford derivatives of the type $[(\text{diene})\text{RhL}_2]B(C_6H_5)_4$ [diene = C_8H_{12}, L = $P(C_6H_5)_3$, $P(n\text{-}C_4H_9)_3$, $C_6H_{11}NH_2$; diene = C_7H_8, L = $P(C_6H_5)_3$]. The novel ionic derivative $\{Rh[P(OC_6H_5)_3]_4\}B(C_6H_5)_4$ is similarly obtained by allowing excess $P(OC_6H_5)_3$ to react with $[C_8H_{12}RhCl]_2$ in methanol at room temperature. The preparation of the analog $\{Rh[P(n\text{-}C_4H_9)_3]_4\}B(C_6H_5)_4$ is also described.

Introduction

It is well-established that monodentate ligands, L, containing group V donor atoms readily react with compounds of the type $[(\text{diene})\text{RhX}]_2$ [diene = C_8H_{12} (cycloocta-1,5-diene), C_7H_8 (bicyclo[2.2.1]hepta-2,5-diene); X = Cl, Br, I] with cleavage of the halogen bridges to form the neutral derivatives (diene)RhLX.[2-6] Until very recently[7,8] further reaction of these ligands, L, with the compounds (diene)RhLX involving displacement of the halogen to yield derivatives of the type $[(\text{diene})\text{RhL}_2]X$ had not been observed. For instance the addition of ligand L to the compound $C_8H_{12}RhLCl$ [L = $P(C_6H_5)_3$, $As(C_6H_5)_3$] in a number of solvents had been monitored conductometrically, but no evidence was found for the presence of any ionic species in solution.[5]

A kinetic study on the reaction of mono- and bidentate ligands with the compounds $C_8H_{12}RhLCl$ [L = amine, $P(C_6H_5)_3$] using methanol as solvent gave results that were significantly different from those obtained using other solvents.[9] In view of this anomaly it was decided to reinvestigate the reactions of the compounds $[(\text{diene})\text{RhX}]_2$ with triphenylphosphine and related ligands in alcohols and other solvents. The results of this preparative study are reported here.

Experimental Section

The compounds $[C_8H_{12}RhX]_2$ (X = Cl, Br) and $[C_7H_8RhCl]_2$ were synthesized by established methods.[2,10] All ligands were obtained commercially. The nmr spectra were recorded using a Varian A-60 instrument. Conductivities were determined by conventional methods. The elemental analyses were performed by the Bernhardt Microanalytical Laboratory, Elbach über Engelskirchen, West Germany, and by Mr. K. P. Kunz, National Chemical Research Laboratory, CSIR, Pretoria, Republic of South Africa. All yields were good varying between 60 and 80%.

Cycloocta-1,5-dienebis(triphenylphosphine)rhodium(I) Tetraphenylborate–Dichloromethane Solvate (I).—Triphenylphosphine (0.5 g, 1.9 mmol) was added to a suspension of $[C_8H_{12}RhCl]_2$ (0.5 g, 1 mmol) in methanol (25 ml) and the solution was stirred until complete dissolution. Addition of sodium tetraphenylboron (1.0 g, 2.9 mmol) in methanol (5 ml) resulted in the precipitation of the complex, which was crystallized from dichloromethane–pentane.

Cycloocta-1,5-dienebis(tri-*n*-butylphosphine)rhodium(I) Tetraphenylborate (II).—The precipitate obtained from the reaction of $[C_8H_{12}RhCl]_2$ (0.3 g, 0.6 mmol), tri-*n*-butylphosphine (0.8 ml, 4 mmol), and sodium tetraphenylboron (0.5 g, 1.5 mmol) by the method described for I was crystallized from methanol.

Bis(cyclohexylamine)cycloocta-1,5-dienerhodium(I) Tetraphenylborate (III).—Cyclohexylamine (0.2 g, 1.8 mmol) was added to a suspension of $[C_8H_{12}RhCl]_2$ (0.1 g, 0.2 mmol) in methanol (20 ml) at 50° and the solution was stirred until complete dissolution. Addition of sodium tetraphenylboron (0.5 g, 1.5 mmol) in methanol (5 ml) to this solution led to the formation of yellow crystals of the required complex.

Bicyclo[2.2.1]hepta-2,5-dienebis(triphenylphosphine)rhodium(I) Tetraphenylborate (IV).—The precipitate obtained from the reaction of $[C_7H_8RhCl]_2$ (0.25 g, 0.5 mmol), triphenylphosphine (0.6 g, 2.3 mmol), and sodium tetraphenylboron (0.5 g, 1.5 mmol) by the method described for I was crystallized from dichloromethane–methanol.

Di-μ-chloro-cycloocta-1,5-dienebis(triphenyl phosphite)dirhodium(I) (V).—Triphenyl phosphite (0.37 g, 1.1 mmol) was added to $[C_8H_{12}RhCl]_2$ (0.3 g, 0.6 mmol) in dichloromethane (10 ml) and the solution was stirred for 5 min. The solvent was removed under reduced pressure and the oily residue was crystallized from dichloromethane–pentane.

Di-μ-bromo-cycloocta-1,5-dienebis(triphenyl phosphite)dirhodium(I) (VI).—The product was obtained from the reaction of

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[1] A preliminary communication of this work has been presented: L. M. Haines, *Inorg. Nucl. Chem. Letters*, **5**, 399 (1969).

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[5] K. Vrieze, H. C. Volger, and A. P. Praat, *J. Organometal. Chem.* (Amsterdam), **13**, 185 (1968).

[6] K. Vrieze, H. C. Volger, and A. P. Praat, *ibid.*, **15**, 195 (1968).

[7] At the same time as the preliminary account of this work appeared, Osborn and coworkers reported the preparation of the cation $C_8H_{12}Rh[P(C_6H_5)_3]_2^+$, by the same method.[8]

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[9] W. Robb and L. M. Haines, unpublished results.

[10] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959).

TABLE I

COLOR, CONDUCTIVITY, MOLECULAR WEIGHT, AND ANALYTICAL DATA

No.	Compound	Color	Conductivity,[a] ohm^{-1} cm^2 mol^{-1}	Mol wt[b]		Anal, %							
						Calcd				Found			
				Calcd	Found	C	H	P or N	Cl or Br	C	H	P or N	Cl or Br
I	$\{Rh(C_8H_{12})[P(C_6H_5)_3]_2\}B(C_6H_5)_4 \cdot CH_2Cl_2$	Orange	89	...	...	72.7	5.7	...	6.2	72.6	5.6	...	6.0
II	$\{Rh(C_8H_{12})[P(n\text{-}C_4H_9)_3]_2\}B(C_6H_5)_4$	Brown	85	...	...	71.9	9.3	...	...	71.2	9.2	...	...
III	$\{Rh(C_8H_{12})(C_6H_{11}NH_2)_2\}B(C_6H_5)_4$	Yellow	81	...	...	72.5	8.0	3.8	...	72.3	7.8	3.8	...
IV	$\{Rh(C_7H_8)[P(C_6H_5)_3]_2\}B(C_6H_5)_4$	Red	87	...	...	77.5	5.6	...	...	77.7	5.5	...	...
V	$Rh_2Cl_2(C_8H_{12})[P(OC_6H_5)_3]_2$	Orange	0.3	1006	976	52.6	4.2	6.2	7.1	52.5	4.2	6.1	6.9
VI	$Rh_2Br_2(C_8H_{12})[P(OC_6H_5)_3]_2$	Orange	0.5	1095	1058	48.2	3.9	...	14.6	48.4	3.8	...	14.9
VII	$Rh_2Cl_2(C_7H_8)[P(OC_6H_5)_3]_2$	Yellow	0.3	...	*c*	52.2	3.9	...	...	52.1	3.9	...	...
VIII	$\{RhCl[P(OC_6H_5)_3]_2\}_2$	Yellow	0.2	1518	1368[d]	57.0	4.0	...	4.8	56.9	3.9	...	5.0
IX	$\{RhBr[P(OC_6H_5)_3]_2\}_2$	Yellow	0.4	1607	1367[d]	53.8	3.8	...	10.0	53.8	3.9	...	10.1
X	$RhCl[P(OC_6H_5)_3]_3$	Yellow	0.2	1069	1070	60.7	4.3	...	3.3	60.2	4.1	...	4.6
XI	$RhBr[P(OC_6H_5)_3]_3$	Yellow	0.3	1114	1104	58.2	4.1	...	7.2	58.0	4.2	...	7.3
XII	$Rh[P(OC_6H_5)_3]_2(CH_3COCHCOCH_3)$	Pale yellow	0.4	...	*c*	59.9	4.5	7.5	...	59.8	4.5	7.6	...
XIII	$\{Rh[P(OC_6H_5)_3]_4\}B(C_6H_5)_4$	Yellow	74	...	...	69.3	4.9	...	...	68.8	4.8	...	...
XIV	$\{Rh[P(OC_6H_5)_3]_4\}ClO_4$	Yellow	80	...	...	59.9	4.2	...	2.5	59.7	4.2	...	2.3
XV	$\{Rh[P(n\text{-}C_4H_9)_3]_4\}B(C_6H_5)_4$	Brown	94	...	...	70.2	10.5	10.1	...	70.0	10.4	10.0	...

[a] Solutions are ~10^{-3} *M* in acetone. [b] Solutions are ~2×10^{-2} *M* in benzene. [c] Not measured. [d] Decomposition.

triphenyl phosphite (0.32 g, 1.1 mmol) and $[C_8H_{12}RhBr]_2$ (0.3 g, 0.5 mmol) by the method described for V.

Di-μ-chloro-bicyclo[2.2.1]hepta-2,5-dienebis(triphenyl phosphite)dirhodium(I) (VII).—The product was obtained from the reaction of triphenyl phosphite (0.33 g, 1.1 mmol) and $[C_7H_8RhCl]_2$ (0.25 g, 0.5 mmol) by the method described for V.

Di-μ-chloro-tetrakis(triphenyl phosphite)dirhodium(I) (VIII).—Triphenyl phosphite (0.76 g, 2.5 mmol) was added to $[C_8H_{12}RhCl]_2$ (0.3 g, 0.6 mmol) in dichloromethane (10 ml) and the solution was stirred for 5 min. The solvent was removed under reduced pressure, and the resultant oil was washed with methanol and then crystallized from dichloromethane–methanol.

Di-μ-bromo-tetrakis(triphenyl phosphite)dirhodium(I) (IX).—The complex was obtained from the reaction of triphenyl phosphite (0.64 g, 2.1 mmol) and $[C_8H_{12}RhBr]_2$ (0.3 g, 0.5 mmol) by the method described for VIII.

Chlorotris(triphenyl phosphite)rhodium(I) (X).—Triphenyl phosphite (1.15 g, 3.7 mmol) was added to $[C_8H_{12}RhCl]_2$ (0.3 g, 0.6 mmol) in dichloromethane (10 ml) and the solution was stirred for 5 min. The solvent was removed under reduced pressure, and the oily residue was washed with methanol and then crystallized from dichloromethane–methanol.

Bromotris(triphenyl phosphite)rhodium(I) (XI).—The complex was obtained from the reaction of triphenyl phosphite (0.96 g, 3.1 mmol) and $[C_8H_{12}RhBr]_2$ (0.3 g, 0.5 mmol) by the method described for X.

2,4-Pentanedionatobis(triphenyl phosphite)rhodium(I) (XII).—A mixture of $\{Rh[P(OC_6H_5)_3]_2Cl\}_2$ (0.25 g, 0.2 mmol), anhydrous Na_2CO_3 (0.1 g, 0.9 mmol), and 2,4-pentanedione (0.1 g, 1 mmol) in dry acetone (20 ml) was stirred at room temperature for 2 hr. The acetone was removed under reduced pressure, the residue was extracted with dichloromethane, and the extract was filtered. Addition of pentane to the concentrated filtrate afforded yellow crystals of the complex.

Tetrakis(triphenyl phosphite)rhodium(I) Tetraphenylborate (XIII).—A methanol solution (20 ml) containing triphenyl phosphite (1.5 g, 4.8 mmol) and suspended $[C_8H_{12}RhCl]_2$ (0.3 g, 0.6 mmol) was stirred until complete dissolution. Addition of sodium tetraphenylboron (0.5 g, 1.5 mmol) in methanol (5 ml) to this solution led to the precipitation of the complex, which was crystallized from acetone–water.

Tetrakis(triphenyl phosphite)rhodium(I) Perchlorate (XIV).—The complex was obtained from the reaction of triphenyl phosphite (1.5 g, 4.8 mmol), $[C_8H_{12}RhCl]_2$ (0.3 g, 0.6 mmol), and lithium perchlorate trihydrate (0.4 g, 2.5 mmol) by the method described for XIII.

Tetrakis(tri-*n*-butylphosphine)rhodium(I) Tetraphenylborate (XV).—An ethanol solution (20 ml) containing tri-*n*-butylphosphine (1.3 g, 6.4 mmol) and suspended $[C_8H_{12}RhCl]_2$ (0.2 g, 0.4 mmol) was refluxed for 3 hr. Addition of sodium tetraphenylboron (0.5 g, 0.9 mmol) in ethanol (5 ml) led to the precipitation of the complex, which was crystallized from ethanol.

Results and Discussion

The uv–visible spectra of solutions of the compound $C_8H_{12}RhP(C_6H_5)_3Cl$ alone and in the presence of triphenylphosphine and lithium chloride were investigated as a preliminary to kinetic studies. When methanol was used as solvent, spectral changes were observed which could only be explained in terms of the equilibrium

$$C_8H_{12}RhP(C_6H_5)_3Cl + P(C_6H_5)_3 \rightleftarrows C_8H_{12}Rh[P(C_6H_5)_3]_2{}^+ + Cl^-$$

No such spectral changes were found when other solvents were employed. In view of these observations, an attempt was made to isolate the derivative $\{C_8H_{12}Rh[P(C_6H_5)_3]_2\}Cl$ from a methanol solution of the compound $[C_8H_{12}RhCl]_2$ and excess triphenylphosphine, but this was unsuccessful. However, addition of sodium tetraphenylboron to this methanol solution led to the immediate precipitation of the ionic derivative $\{C_8H_{12}Rh[P(C_6H_5)_3]_2\}B(C_6H_5)_4$. The complexes $[C_8H_{12}RhL_2]B(C_6H_5)_4$ [L = $P(n\text{-}C_4H_9)_3$, $C_6H_{11}NH_2$] were similarly prepared. Replacement of cycloocta-1,5-diene by bicyclo[2.2.1]hepta-2,5-diene had no effect on these reactions, as evidenced by the preparation of the derivative $\{C_7H_8Rh[P(C_6H_5)_3]_2\}B(C_6H_5)_4$. The chemical composition of the complexes $[(diene)RhL_2]B(C_6H_5)_4$ [diene = C_8H_{12}, L = $P(C_6H_5)_3$, $P(n\text{-}C_4H_9)_3$, $C_6H_{11}NH_2$; diene = C_7H_8, L = $P(C_6H_5)_3$] was established by elemental analysis (Table I) and from a comparison of the integrated intensities of the diene and ligand proton resonances in the nmr spectra. All of the compounds are 1:1 electrolytes in acetone and were assumed to be diamagnetic from the sharpness

TABLE II

NMR DATA AND ASSIGNMENTS[a]

			Diene			
No.	Compound	Aromatic protons	Olefinic protons	Aliphatic protons	Other protons	Assignment
I	$\{Rh(C_8H_{12})[P(C_6H_5)_3]_2\}B(C_6H_5)_4 \cdot CH_2Cl_2$	2.72 m	5.51 b, s	7.78 b, s	4.77 s	CH_2Cl_2
II	$\{Rh(C_8H_{12})[P(n\text{-}C_4H_9)_3]_2\}B(C_6H_5)_4$	2.83 m	5.24 b, s	7.85 b, s	8.70 m	$P(n\text{-}C_4H_9)_3$
					4.23 m	$-NH_2$
III	$\{Rh(C_8H_{12})(C_6H_{11}NH_2)_2\}B(C_6H_5)_4$	2.70 m	5.89 b, s		8.30 m	All aliphatic protons
IV	$\{Rh(C_7H_8)[P(C_6H_5)_3]_2\}B(C_6H_5)_4$	2.70 m	5.64 b, s	6.23 m, 8,60 m	...	
V	$Rh_2Cl_2(C_8H_{12})[P(OC_6H_5)_3]_2$	2.77	6.26	8.2 m	...	
VI	$Rh_2Br_2(C_8H_{12})[P(OC_6H_5)_3]_2$	2.72 s	6.10	8.2	...	
VII	$Rh_2Cl_2(C_7H_8)[P(OC_6H_5)_3]_2$	2.73 s	6.48	8.94	...	
XII	$Rh[P(OC_6H_5)_3]_2(CH_3COCHCOCH_3)$	2.81 s			4.96 s 8.53 s	H CH_3 } of $CH_3COCHCOCH_3$
XV	$\{Rh[P(n\text{-}C_4H_9)_3]_4\}B(C_6H_5)_4$	2.73 m			8.60 m	$P(n\text{-}C_4H_9)_3$

[a] τ scale; measured in $CDCl_3$ at 38°. Abbreviations: s, singlet; m, multiplet; b, broad.

of the nmr spectral peaks. The assignments of the nmr spectra are given in Table II.

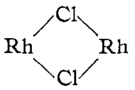
The halogen displacement reactions by the ligands $P(C_6H_5)_3$, $P(n\text{-}C_4H_9)_3$, and $C_6H_{11}NH_2$ only occurred in methanol and ethanol and could not be effected in tetrahydrofuran, acetone, dimethylformamide, chloroform, dichloromethane, and benzene. It has been recently noted that the halogen displacement reactions involved in the preparation of some cationic carbon disulfide derivatives of rhodium and iridium, *e.g.*, $\{M(\pi\text{-}CS_2)[P(C_6H_5)_3]_3\}B(C_6H_5)_4$ (M = Rh, Ir),[11] and in the isomerism of the compound $\{Ir[P(CH_3)_2C_6H_5]_2(CO)Cl_2(\sigma\text{-}C_3H_5)\}$, *via* the cation $Ir[P(CH_3)_2C_6H_5]_2(CO)Cl(\pi\text{-}C_3H_5)^+$,[12] are specific to alcohols.

When tertiary phosphite ligands were used as an extension to these studies, unexpected results were obtained. Thus the reaction sequence

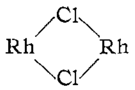
$$[(\text{diene})RhCl]_2 + 2L \xrightarrow{CH_2Cl_2} 2(\text{diene})RhLCl$$

$$(\text{diene})RhLCl + L \xrightarrow{CH_3OH} (\text{diene})RhL_2^+$$

(diene = C_7H_8, C_8H_{12}) was not observed for the ligand L = $P(OC_6H_5)_3$. Instead it was found that the reaction of 2 mol of triphenyl phosphite with 1 mol of the compound $[C_8H_{12}RhCl]_2$ at room temperature in dichloromethane gave a product which was characterized as the complex $[P(OC_6H_5)_3]_2(C_8H_{12})Cl_2Rh_2$. The nmr spectrum of this compound showed the presence of both cycloocta-1,5-diene and triphenyl phosphite ligands, while the dimeric nature was established from molecular weight measurements. Based on this physical and spectral evidence the structure shown in Figure 1 was proposed. This has now been confirmed by an X-ray crystal analysis.[13] The structure determination has also shown that the



moiety in the molecule $[P(OC_6H_5)_3]_2(C_8H_{12})Cl_2Rh_2$ is bent about the Cl–Cl axis. A similar type of bending has been observed for the molecule $[Rh(CO)_2Cl]_2$,[14] but the



group in the dimer $[C_8H_{12}RhCl]_2$[15] is planar.

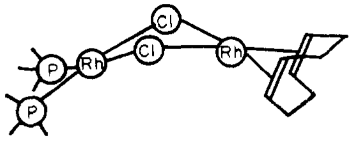


Figure 1.

One mole of the compound $[P(OC_6H_5)_3]_2(C_8H_{12})Cl_2Rh_2$ was found to react with 2 mol of triphenyl phosphite to yield a product in which the sole cycloocta-1,5-diene group has been replaced by the triphenyl phosphite ligands. This product was characterized as the compound $\{Rh[P(OC_6H_5)_3]_2Cl\}_2$. Although molecular weight measurements were unreliable, the dimeric nature of this complex was demonstrated by its reaction with various reagents. Thus with acetylacetone in basic medium the compound $\{Rh[P(OC_6H_5)_3]_2Cl\}_2$ yielded the derivative $Rh[P(OC_6H_5)_3]_2(CH_3COCHCOCH_3)$. It should be noted that the thiocyanato complex $\{Rh[P(OC_6H_5)_3]_2SCN\}_2$ has been synthesized by treating the compound $Rh[P(OC_6H_5)_3]_2(CO)Cl$ with excess potassium thiocyanate.[16,17] The addition of 2 mol of triphenyl phosphite to 1 mol of the complex $\{Rh[P(OC_6H_5)_3]_2Cl\}_2$ resulted in the cleavage of the halogen bridges and the formation of the known compound $Rh[P(OC_6H_5)_3]_3Cl$ previously synthesized from the derivative $Rh[P(OC_6H_5)_3]_2(CO)Cl$.[16,18] Similarly the stepwise addition of triphenyl phosphite to the compound $[C_8H_{12}RhBr]_2$ afforded the derivatives $[P(OC_6H_5)_3]_2(C_8H_{12})Br_2Rh_2$, $\{Rh[P(OC_6H_5)_3]_2Br\}_2$, and $Rh[P(OC_6H_5)_3]_3Br$. The reaction of the compound $[C_7H_8RhCl]_2$ with triphenyl phosphite gave a similar series of derivatives. However, addition of triphenyl

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phosphite to the compound $[C_8H_{12}RhI]_2$ gave unstable products and these were not further studied.

All of the compounds $[P(OC_6H_5)_3]_2(\text{diene})X_2Rh_2$, $\{Rh[P(OC_6H_5)_3]_2X\}_2$, and $Rh[P(OC_6H_5)_3]_3X$ (diene = C_8H_{12}, X = Cl, Br; diene = C_7H_8, X = Cl) were characterized by elemental analysis (Table I) and, where appropriate, from the nmr spectral data. The nature of the species was established from molecular weight measurements. The compounds are nonelectrolytes in acetone and are diamagnetic. The nmr spectral data are given in Table II.

As all previous reports have shown that the action of monodentate ligands L on the dimeric compound $[C_8H_{12}RhCl]_2$ results in the formation of derivatives of the type $C_8H_{12}RhLCl$, it is surprising that triphenyl phosphite should, under identical experimental conditions, successively replace the cycloocta-1,5-diene groups in preference to cleaving the halogen bridges. This difference in reaction schemes between triphenyl phosphite and the other donor ligands previously studied can be associated with the softer character of triphenyl phosphite.

In view of the solvent specificity in the synthesis of the derivative $\{C_8H_{12}Rh[P(C_6H_5)_3]_2\}B(C_6H_5)_4$ from the compound $C_8H_{12}RhP(C_6H_5)_3Cl$, the possibility of displacing the halogen in the complex $Rh[P(OC_6H_5)_3]_3Cl$ by triphenyl phosphite in alcohol was investigated. It was found that the compound $Rh[P(OC_6H_5)_3]_3Cl$, normally insoluble in methanol, slowly dissolves in this solvent in the presence of excess triphenyl phosphite. A cationic species $Rh[P(OC_6H_5)_3]_4^+$ precipitated from this solution on addition of sodium tetraphenylboron or lithium perchlorate. An alternative structure for this cation, $[P(OC_6H_5)_3]_3(C_6H_5O)_2\overline{POC_6H_4Rh}H^+$, involving a rhodium–phenyl bond similar to that recently proposed[19] for the derivatives "$M[P(OC_6H_5)_3]_4$" (M = Rh, Ir)[20] was eliminated as there was no nmr or ir evidence for a hydrogen bonded to rhodium. The derivative $\{Rh[P(n\text{-}C_4H_9)_3]_4\}B(C_6H_5)_4$ has also been synthesized by allowing the compound $[C_8H_{12}RhCl]_2$ to react with tri-*n*-butylphosphine in refluxing ethanol and then adding sodium tetraphenylboron. As it has already been established that tri-*n*-butylphosphine reacts at room temperature with the compound $[C_8H_{12}RhCl]_2$ in methanol to form the cation $C_8H_{12}Rh[P(n\text{-}C_4H_9)_3]_2^+$, it is apparent that this ion is an intermediate in the formation of the species $Rh[P(n\text{-}C_4H_9)_3]_4^+$. It has been previously shown that the compound $Rh[P(C_6H_5)_3]_3Cl$ dissociates in solution with loss of triphenylphosphine.[21,22] It is, therefore, not surprising that attempts to isolate the cation $Rh[P(C_6H_5)_3]_4^+$ from the reaction of the compound $Rh[(C_6H_5)_3]_3Cl$ or $[C_8H_{12}RhCl]_2$ with excess triphenylphosphine in refluxing alcohols were unsuccessful.

The compounds $\{RhL_4\}B(C_6H_5)_4$ [L = $P(n\text{-}C_4H_9)_3$, $P(OC_6H_5)_3$] and $\{Rh[P(OC_6H_5)_3]_4\}ClO_4$ were characterized by elemental analysis (Table I) and nmr spectral intensity data where appropriate. The complexes are 1:1 electrolytes in acetone and are diamagnetic. The nmr data are presented in Table II. These complexes are the first examples of four-coordinate rhodium(I) derivatives which contain identical monodentate group V donor ligands. The species $Rh(L_2)_2^+$ [L_2 = $R_2PCH_2CH_2PR_2$ (R = CH_3,[23] C_6H_5[24]), *cis*-$(C_6H_5)_2AsCH{=}CHAs(C_6H_5)_2$[25]], which contain bidentate ligands, have been reported recently. The reactivity of the compound $\{RhL_4\}B(C_6H_5)_4$ toward hydrogen is of interest. The derivative $\{Rh[P(n\text{-}C_4H_9)_3]_4\}B(C_6H_5)_4$ reacts readily with molecular hydrogen to yield a stable complex $\{Rh[P(n\text{-}C_4H_9)_3]_4H_2\}B(C_6H_5)_4$. In contrast, the compound $\{Rh[P(OC_6H_5)_3]_4\}B(C_6H_5)_4$ adds hydrogen reversibly, the resulting hydride being stable only under an atmosphere of hydrogen. The details of these and similar oxidative addition reactions will be the subject of a further publication.

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