tions are observed.[17] Nonetheless, the predicted increase in absorption intensity in going from the trans to the cis isomer is generally observed. The frequency of the ligand field maxima does vary ($\Delta < 1000$ cm^{-1}) with the amine: $NH_3 \sim NH_2CH_3 > NHC_5H_{10} \geq NH(CH_3)_2 > NH_2C_6H_5 > N(CH_3)_3$. The absorption is generally higher in energy ($\sim$200 cm^{-1}) for the trans as compared to the cis and higher ($\sim$100 cm^{-1}) in methanol than in chloroform. Previous work places the pyridine complex near methylamine in the ligand order.[4] The ligand order does not correspond to the proton basicity of the amine except for the fact that the weakest donor, aniline, appears to the lower end of the list. The order does, however, appear to be related to the bulkiness of the ligand.[18] Steric interactions prevent the formation of a strong bond with the cobalt atom and as a result the ligand field is weakened.

The ultraviolet spectra of the complexes show a relatively weak band at 29.6–32.5 and two strong absorptions at 37.1–39.2 and 43.0–45.0 kK. All the maxima are at higher energy for the methanol solutions than for the chloroform solutions. The low-energy, low-intensity absorption has been assigned to a metal to ligand, $t_{2g} \rightarrow \pi^*$, charge transfer on the basis of MO calculations.[19] The frequency of the maximum is independent of the amine. For example, in methanol solution the band position of the cis isomer is 31.0 ± 0.1 kK and of the *trans* isomer is 29.8 ± 0.1 kK. The only exception to this generalization is seen with aniline when the aromatic absorption shifts the apparent maximum to higher energy. Since the $t_{2g} \rightarrow \pi^*$ transitions only involve the π-bonding d orbitals, changing of the amine σ donor should not affect the energy of the transition. The next highest energy band in the uv spectrum has been variously assigned as a charge-transfer band or ligand band.[19] Recent work[20] indicates that a ligand to metal charge transfer, $\sigma_L \rightarrow e_g$, band should appear in this region for metal β-diketonates. This seems a reasonable assignment for cobalt(III) complexes. The absorption maximum appears to be dependent on the amine ($\Delta < 800$ cm^{-1}) in the same way as the ligand field band. This is to be expected since the energy of the e_g orbital of metal is dependent on the σ-donating ability of the amine. The high-energy band in the spectra has been assigned to $\pi \rightarrow \pi^*$ transition of the acetylacetonate anion.[19] As expected, the absorption maximum is independent of the amine ligand; *e.g.*, the maximum is at 43.4 ± 0.2 kK for the trans isomer and at 44.4 ± 0.4 kK for the cis isomer. There appears to be a substantial blue shift, $\sim$1000 cm^{-1}, of all the ultraviolet bands in going from the trans to the cis isomer. This effect is independent of the nitro ligand since it is observed for the diamine complex.[21]

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Cationic Complexes of Rhodium(I) and Their Reactivity toward Air[1]

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The reaction of $[C_8H_{12}RhCl]_2$ with an excess of the ligands L = $P(O\text{-}i\text{-}C_3H_7)_3$, $P(OCH_3)_2C_6H_5$, $POCH_3(C_6H_5)_2$, $P(CH_3)_2C_6H_5$, and $PCH_3(C_6H_5)_2$ in methanol at room temperature or under refluxing conditions gives the four-coordinate cations RhL_4^+ whereas the corresponding reaction involving the ligands L = $P(OR)_3$ (R = CH_3, C_2H_5, $i\text{-}C_4H_9$, and $n\text{-}C_4H_9$) and $P(OCH_2)_3CCH_3$ yields the five-coordinate species RhL_5^+. However, by employing a rhodium:ligand ratio of 1:4 in those reactions involving the ligands $P(OR)_3$ (R = CH_3 and C_2H_5) the four-coordinate cations $Rh[P(OR)_3]_4^+$ are obtained. Further the reaction of $[C_8H_{12}RhCl]_2$ with excess of the ligands L = $P(CH_3)_2C_6H_5$ and $As(CH_3)_2C_6H_5$ in methanol in the presence of air affords the stable oxygen-containing cations $RhL_4O_2^+$. The cations RhL_4^+, RhL_5^+, and $RhL_4O_2^+$ were characterized as the tetraphenylborates, hexafluorophosphates, or perchlorates. The ionic compounds $\{Rh[P(OR)_3]_4\}B(C_6H_5)_4$ (R = CH_3, C_2H_5, and $i\text{-}C_3H_7$) and $\{Rh[P(OR)_3]_5\}B(C_6H_5)_4$ (R = CH_3, C_2H_5, $i\text{-}C_4H_9$, and $n\text{-}C_4H_9$) decompose in air to form the neutral derivatives $Rh[P(OR)_3]_2B(C_6H_5)_4$ containing one of the phenyl rings of the $B(C_6H_5)_4$ group bonded as an arene to the rhodium atom. The bonded $B(C_6H_5)_4$ group in $Rh[P(OCH_3)_3]_2B(C_6H_5)_4$ is readily displaced by trimethyl phosphite and by the ligand $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ to give the products $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$ and $\{Rh[(C_6H_5)_2PC_2H_4P(C_6H_5)_2]_2\}B(C_6H_5)_4$, respectively. The compound $\{Rh[P(OCH_3)_3]_5\}PF_6$ reacts with the dienes cycloocta-1,5-diene and bicyclo[2.2.1]hepta-2,5-diene in the presence of air to give the ionic derivatives $\{Rh(C_8H_{12})[P(OCH_3)_3]_2\}PF_6$ and $\{Rh(C_7H_8)[P(OCH_3)_3]_3\}PF_6$, respectively. The nmr spectra of the various compounds are discussed.

Introduction

The chemistry of neutral phosphine derivatives of rhodium(I) has received considerable attention of late, particularly since the discovery that $Rh[P(C_6H_5)_3]_3Cl$[2] and $RhH(CO)[P(C_6H_5)_3]_3$[3,4] are effective homogeneous catalysts for the hydrogenation and hydroformylation

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of olefins. In contrast only a few cationic complexes of rhodium(I), *e.g.*, $\{Rh[(C_6H_5)_2PC_2H_4P(C_6H_5)_2]_2\}Cl$,[5] $\{Rh(CO)_3[P(C_6H_5)_3]_2\}ClO_4$,[6] $\{RhP(C_6H_5)_3(2,2'\text{-}C_{10}H_8N_2)[C_2(CN)_4]\}Cl$,[7] and $\{C_8H_{12}Rh[P(C_6H_5)_3]_2\}B(C_6H_5)_4$,[8,9] have been reported and furthermore their oxidative addition reactions and catalytic properties have been even less investigated.

The synthesis of the cationic derivatives $[RhL_4]B(C_6H_5)_4$ [L = $P(n\text{-}C_4H_9)_3$ and $P(OC_6H_5)_3$] was reported in a previous publication.[8] This involved the reaction of $[C_8H_{12}RhCl]_2$ with an excess of the ligand L in alcohol followed by addition of sodium tetraphenylboron to the resultant solution. In view of the unusual nature of the compounds, the reaction was extended to incorporate other ligands. As well as a more complete series of four-coordinate rhodium(I) compounds of the type $[RhL_4]$[anion], five-coordinate derivatives $[RhL_5]$[anion] have been isolated for certain ligands. The characterization of the various four- and five-coordinate rhodium(I) derivatives and their reaction with oxygen from the air are reported here.

Experimental Section

The compound $[C_8H_{12}RhCl]_2$ was synthesized by an established method.[10] All ligands were obtained commercially. All reactions were performed under an atmosphere of nitrogen unless stated otherwise. Yields were good varying between 60 and 80%. The infrared spectra were recorded using a Perkin-Elmer Model 457 grating infrared spectrophotometer. The nmr spectra were obtained with Varian A-60A and Varian HA-100 instruments. Conductivities were determined on *ca.* 10^{-3} *M* solutions in acetone using a Van Waters and Rogers Model 31 conductivity bridge. The molecular weights were measured on *ca.* 2×10^{-2} *M* solutions in benzene using a Mechrolab vapor pressure osmometer. Melting points were obtained with a Kofler hot stage and are corrected. All compounds melted with decomposition. Elemental analyses were performed by the Bernhardt Microanalytical Laboratory, Elbach über Engelskirchen, West Germany, by Pascher and Pascher Microanalytical Laboratory, Bonn, West Germany, and by Mr. G. J. Roberts, National Chemical Research Laboratory, CSIR, Pretoria, Republic of South Africa.

Tetrakis(triisopropyl phosphite)rhodium(I) Tetraphenylborate (I).—Triisopropyl phosphite (1.2 g, 5.8 mmol) was added to a suspension of $[C_8H_{12}RhCl]_2$ (0.2 g, 0.4 mmol) in methanol (*ca.* 10 ml) and the solution was stirred at room temperature until complete dissolution occurred (*ca.* 5 min). Addition of sodium tetraphenylboron (0.4 g, 1.2 mmol) in methanol (*ca.* 3 ml) resulted in the precipitation of the orange complex, which was crystallized from dichloromethane–methanol. *Anal.* Calcd for $\{Rh[P(O\text{-}i\text{-}C_3H_7)_3]_4\}B(C_6H_5)_4$: C, 57.4; H, 8.4; P, 9.9. Found: C, 57.3; H, 8.5; P, 9.6; mp 64–66°; conductivity 89 $ohm^{-1}\ cm^2\ mol^{-1}$.

Tetrakis(dimethyl phenylphosphonite)rhodium(I) Hexafluorophosphate (II).—The yellow precipitate obtained by adding ammonium hexafluorophosphate (0.15 g, 0.9 mmol) to a methanol solution of the product formed by treating $[C_8H_{12}RhCl]_2$ (0.1 g, 0.2 mmol) with dimethyl phenylphosphonite (0.4 g, 2.4 mmol) by the method described for I was crystallized from dichloromethane–methanol. *Anal.* Calcd for $\{Rh[P(OCH_3)_2C_6H_5]_4\}PF_6$: C, 41.4; H, 4.8. Found: C, 41.5; H, 4.7; mp 177°; conductivity 124 $ohm^{-1}\ cm^2\ mol^{-1}$.

Tetrakis(dimethyl phenylphosphonite)rhodium(I) Hexafluoroantimonate (III).—The yellow precipitate obtained by adding potassium hexafluoroantimonate (0.2 g, 0.7 mmol) to a methanol solution of the product formed by treating $[C_8H_{12}RhCl]_2$ (0.1 g, 0.2 mmol) with dimethyl phenylphosphonite (0.4 g, 2.4 mmol) by the method described for I was crystallized from dichloromethane–ethanol. *Anal.* Calcd for $\{Rh[P(OCH_3)_2C_6H_5]_4\}SbF_6$: C, 37.7; H, 4.4. Found: C, 37.5; H, 4.3; mp 177°; conductivity 114 $ohm^{-1}\ cm^2\ mol^{-1}$.

Tetrakis(methyl diphenylphosphinite)rhodium(I) Hexafluorophosphate–Dichloromethane Solvate (IV).—The yellow precipitate obtained by adding ammonium hexafluorophosphate (0.15 g, 0.9 mmol) to a methanol solution of the product formed by treating $[C_8H_{12}RhCl]_2$ (0.1 g, 0.2 mmol) with methyl diphenylphosphinite (0.45 g, 2.1 mmol) by the method described for I was crystallized from dichloromethane–methanol. *Anal.* Calcd for $\{Rh[P(OCH_3)(C_6H_5)_2]_4\}PF_6\cdot CH_2Cl_2$: C, 53.1; H, 4.6; Cl, 5.9. Found: C, 53.3; H, 4.4; Cl, 5.3; mp 175–176°; conductivity 129 $ohm^{-1}\ cm^2\ mol^{-1}$.

Tetrakis(dimethylphenylphosphine)rhodium(I) Hexafluorophosphate (V).—The red-brown precipitate obtained by adding ammonium hexafluorophosphate (0.15 g, 0.9 mmol) to a methanol solution of the product formed by treating $[C_8H_{12}RhCl]_2$ (0.1 g, 0.2 mmol) with dimethylphenylphosphine (0.35 g, 2.5 mmol) by the method described for I was crystallized from dichloromethane–methanol. *Anal.* Calcd for $\{Rh[P(CH_3)_2C_6H_5]_4\}PF_6$: C, 48.0; H, 5.6. Found: C, 47.7; H, 5.5; mp 124–130°; conductivity 121 $ohm^{-1}\ cm^2\ mol^{-1}$.

Tetrakis(dimethylphenylphosphine)rhodium(I) Perchlorate (VI).—Dimethylphenylphosphine (0.35 g, 2.5 mmol) was added to a suspension of $[C_8H_{12}RhCl]_2$ (0.1 g, 0.2 mmol) in methanol (*ca.* 10 ml) and the solution was stirred at room temperature until complete dissolution occurred (*ca.* 10 min). Addition of lithium perchlorate trihydrate (0.13 g, 0.8 mmol) in methanol (*ca.* 5 ml) afforded orange crystals of the complex. *Anal.* Calcd for $\{Rh[P(CH_3)_2C_6H_5]_4\}ClO_4$: C, 50.9; H, 5.9. Found: C, 50.7; H, 5.9; conductivity 109 $ohm^{-1}\ cm^2\ mol^{-1}$.

Tetrakis(methyldiphenylphosphine)rhodium(I) Hexafluorophosphate (VII).—An ethanol solution (*ca.* 10 ml) containing methyldiphenylphosphine (0.4 g, 2.0 mmol) and suspended $[C_8H_{12}RhCl]_2$ (0.1 g, 0.2 mmol) was refluxed for 2 hr. Addition of ammonium hexafluorophosphate (0.15 g, 0.9 mmol) in ethanol (*ca.* 2 ml) to the resultant solution afforded the complex as a red precipitate. This was crystallized from dichloromethane–methanol. *Anal.* Calcd for $\{Rh[P(CH_3)(C_6H_5)_2]_4\}PF_6$: C, 59.5; H, 5.0. Found: C, 59.5; H, 4.9; mp 179–180°; conductivity 130 $ohm^{-1}\ cm^2\ mol^{-1}$.

Tetrakis(methyldiphenylphosphine)rhodium(I) Perchlorate (VIII).—The red-brown precipitate obtained by adding lithium perchlorate trihydrate (0.13 g, 0.8 mmol) to an ethanol solution of the product obtained by treating $[C_8H_{12}RhCl]_2$ (0.1 g, 0.2 mmol) with methyldiphenylphosphine (0.4 g, 2.0 mmol) by the method described for VII was crystallized from dichloromethane–methanol. *Anal.* Calcd for $\{Rh[P(CH_3)(C_6H_5)_2]_4\}ClO_4$: C, 62.3; H, 5.2. Found: C, 62.2; H, 5.1; conductivity 119 $ohm^{-1}\ cm^2\ mol^{-1}$.

Pentakis(trimethyl phosphite)rhodium(I) Tetraphenylborate (IX).—The white precipitate obtained by adding sodium tetraphenylboron (0.5 g, 1.5 mmol) to a methanol solution of the product obtained by treating $[C_8H_{12}RhCl]_2$ (0.3 g, 0.6 mmol) with trimethyl phosphite (1.0 g, 8.1 mmol) by the method described for I was crystallized from dichloromethane–methanol. *Anal.* Calcd for $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$: C, 44.9; H, 6.3; P, 14.9. Found: C, 44.8; H, 6.3; P, 14.9; mp 92°; conductivity 73 $ohm^{-1}\ cm^2\ mol^{-1}$.

Pentakis(trimethyl phosphite)rhodium(I) Hexafluorophosphate (X).—Trimethyl phosphite (0.35 g, 2.8 mmol) was added to a suspension of $[C_8H_{12}RhCl]_2$ (0.1 g, 0.2 mmol) in methanol (*ca.* 5 ml) and the solution was stirred at room temperature until complete dissolution occurred (*ca.* 5 min). Addition of ammonium hexafluorophosphate (0.15 g, 0.9 mmol) in water (*ca.* 10 ml) resulted in the precipitation of the white complex which was crystallized from methanol–water. *Anal.* Calcd for $\{Rh[P(OCH_3)_3]_5\}PF_6$: C, 20.7; H, 5.2. Found: C, 20.6; H, 5.3; mp 94–96°; conductivity 122 $ohm^{-1}\ cm^2\ mol^{-1}$.

Pentakis(triethyl phosphite)rhodium(I) Tetraphenylborate (XI).—The white precipitate obtained by adding sodium tetraphenylboron (0.2 g, 0.6 mmol) to a methanol solution of the product formed by treating $[C_8H_{12}RhCl]_2$ (0.1 g, 0.2 mmol) with triethyl phosphite (0.5 g, 3.0 mmol) by the method described for I was crystallized from dichloromethane–methanol. *Anal.* Calcd for $\{Rh[P(OC_2H_5)_3]_5\}B(C_6H_5)_4$: C, 51.8; H, 7.7; P, 12.4. Found: C, 52.0; H, 7.6; P, 12.6; mp 89–93°; conductivity 90 $ohm^{-1}\ cm^2\ mol^{-1}$.

Pentakis(triisobutyl phosphite)rhodium(I) Tetraphenylborate (XII).—The white precipitate obtained by adding sodium tetra-

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phenylboron (0.2 g, 0.6 mmol) to a methanol solution of the product formed by treating $[C_8H_{12}RhCl]_2$ (0.1 g, 0.2 mmol) with triisobutyl phosphite (0.7 g, 2.8 mmol) by the method described for I was crystallized from dichloromethane–methanol. *Anal.* Calcd for $\{Rh[P(O\text{-}i\text{-}C_4H_9)_3]_5\}B(C_6H_5)_4$: C, 60.3; H, 9.4. Found: C, 59.9; H, 9.4; mp 114–116°; conductivity 83 $ohm^{-1}\ cm^2\ mol^{-1}$.

Pentakis(tri-*n*-butyl phosphite)rhodium(I) Tetraphenylborate (XIII).—The white complex was obtained as an oily solid by adding sodium tetraphenylboron (0.2 g, 0.6 mmol) to a methanol solution of the product formed by treating $[C_8H_{12}RhCl]_2$ (0.1 g, 0.2 mmol) with tri-*n*-butyl phosphite (0.7 g, 2.8 mmol) by the method described for I. Attempts to crystallize the oily solid were unsuccessful.

Pentakis(4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)rhodium(I) Tetraphenylborate (XIV).—A methanol solution (*ca.* 10 ml) containing the ligand $P(OCH_2)_3CCH_3$ (1.0 g, 6.8 mmol) and suspended $[C_8H_{12}RhCl]_2$ (0.3 g, 0.6 mmol) was refluxed for 30 min. Addition of sodium tetraphenylboron (0.5 g, 1.5 mmol) in methanol (*ca.* 5 ml) to the resultant clear solution afforded the complex as a white precipitate. This was crystallized from dichloromethane–methanol. *Anal.* Calcd for $\{Rh[P(OCH_2)_3CCH_3]_5\}B(C_6H_5)_4$: C, 50.6; H, 5.6; P, 13.3. Found: C, 50.4; H, 5.7; P, 13.2; mp 178°; conductivity 92 $ohm^{-1}\ cm^2\ mol^{-1}$.

Tetrakis(trimethyl phosphite)rhodium(I) Tetraphenylborate (XV).—Trimethyl phosphite (0.4 g, 3.2 mmol) was added to $[C_8H_{12}RhCl]_2$ (0.2 g, 0.4 mmol) in dichloromethane (*ca.* 10 ml) and the solution was stirred for 5 min. The solvent was removed under reduced pressure and the oily residue was dissolved in methanol (*ca.* 10 ml). Addition of sodium tetraphenylboron (0.4 g, 1.2 mmol) in methanol (*ca.* 5 ml) to this solution afforded yellow crystals which were crystallized from dichloromethane–methanol. *Anal.* Calcd for $\{Rh[P(OCH_3)_3]_4\}B(C_6H_5)_4$: C, 47.1; H, 6.2. Found: C, 46.7; H, 6.1; mp 65–155°; conductivity 79 $ohm^{-1}\ cm^2\ mol^{-1}$.

Tetrakis(triethyl phosphite)rhodium(I) Tetraphenylborate (XVI).—The yellow precipitate obtained by adding sodium tetraphenylboron (0.4 g, 1.2 mmol) to a methanol solution of the product formed by treating $[C_8H_{12}RhCl]_2$ (0.2 g, 0.4 mmol) with triethyl phosphite (0.54 g, 3.2 mmol) by the method described for XV was crystallized from dichloromethane–methanol. *Anal.* Calcd for $\{Rh[P(OC_2H_5)_3]_4\}B(C_6H_5)_4$: C, 53.0; H, 7.4; P, 11.4. Found: C, 53.2; H, 7.5; P, 11.3; mp 97–99°; conductivity 84 $ohm^{-1}\ cm^2\ mol^{-1}$.

Dioxygentetrakis(dimethylphenylphosphine)rhodium(I) Hexafluorophosphate (XVII).—A stream of oxygen was passed through a solution of $\{Rh[P(CH_3)_2C_6H_5]_4\}PF_6$ (0.3 g) in dichloromethane (*ca.* 5 ml) for 5 min. The solvent was removed under reduced pressure and the oily residue was crystallized from methanol to give brown crystals. *Anal.* Calcd for $\{Rh[P(CH_3)_2C_6H_5]_4O_2\}PF_6$: C, 46.2; H, 5.4; P, 18.4; F, 13.7; Cl, 0.0. Found: C, 46.2; H, 5.3; P, 18.7; F, 14.3; Cl, 0.2; mp 107–108°; conductivity 129 $ohm^{-1}\ cm^2\ mol^{-1}$.

Dioxygentetrakis(dimethylphenylphosphine)rhodium(I) Perchlorate (XVIII).—The brown complex was obtained from $\{Rh[P(CH_3)_2C_6H_5]_4\}ClO_4$ (0.3 g) by the method described for XVII and crystallized from methanol. *Anal.* Calcd for $\{Rh[P(CH_3)_2C_6H_5]_4O_2\}ClO_4$: C, 48.8; H, 5.7; O, 12.2. Found: C, 48.9; H, 5.6; O, 12.2; conductivity 129 $ohm^{-1}\ cm^2\ mol^{-1}$.

Dioxygentetrakis(dimethylphenylarsine)rhodium(I) Hexafluorophosphate (XIX).—A methanol solution (*ca.* 10 ml) containing dimethylphenylarsine (0.4 g, 2.2 mmol) and suspended $[C_8H_{12}RhCl]_2$ (0.1 g, 0.2 mmol) was refluxed under an atmosphere of air for 2 hr. Addition of ammonium hexafluorophosphate (0.15 g, 0.9 mmol) in methanol (*ca.* 2 ml) to the resultant solution afforded the complex as a brown precipitate. This was crystallized from methanol. *Anal.* Calcd for $\{Rh[As(CH_3)_2C_6H_5]_4O_2\}PF_6$: C, 38.1; H, 4.4; Cl, 0.0. Found: C, 38.2; H, 4.4; Cl, 0.1; mp 162–163°; conductivity 127 $ohm^{-1}\ cm^2\ mol^{-1}$.

Dioxygentetrakis(dimethylphenylarsine)rhodium(I) Perchlorate (XX).—The brown precipitate obtained by adding lithium perchlorate trihydrate (0.13 g, 0.8 mmol) to a methanol solution of the product formed by treating $[C_8H_{12}RhCl]_2$ (0.1 g, 0.2 mmol) with dimethylphenylarsine (0.4 g, 2.2 mmol) by the method described for XIX was crystallized from methanol. *Anal.* Calcd for $\{Rh[As(CH_3)_2C_6H_5]_4O_2\}ClO_4$: C, 39.9; H, 4.6; O, 10.0. Found: C, 40.1; H, 4.6; O, 10.1; conductivity 129 $ohm^{-1}\ cm^2\ mol^{-1}$.

Tetraphenylboronbis(trimethyl phosphite)rhodium(I) (XXI).—A suspension of $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$ (1.0 g) in methanol (*ca.* 25 ml) was stirred under an atmosphere of air at room temperature for 24 hr. The resultant yellow precipitate was isolated and crystallized from dichloromethane–methanol. *Anal.* Calcd for $Rh[P(OCH_3)_3]_2B(C_6H_5)_4$: C, 53.9; H, 5.4; P, 9.3; B, 1.6; mol wt 670. Found: C, 53.9; H, 5.5; P, 9.2; B, 1.7; mol wt 660; mp 163–165°; conductivity 0.3 $ohm^{-1}\ cm^2\ mol^{-1}$.

Tetraphenylboronbis(triethyl phosphite)rhodium(I) (XXII).—A suspension of $\{Rh[P(OC_2H_5)_3]_5\}B(C_6H_5)_4$ (1.0 g) in methanol (*ca.* 25 ml) was stirred under an atmosphere of air at room temperature for 144 hr. The resultant yellow precipitate was isolated and crystallized from dichloromethane–methanol. *Anal.* Calcd for $Rh[P(OC_2H_5)_3]_2B(C_6H_5)_4$: C, 57.3; H, 6.7; P, 8.2; mol wt 757. Found: C, 57.1; H, 6.8; P, 8.4; mol wt 756; mp 114°; conductivity 0.8 $ohm^{-1}\ cm^2\ mol^{-1}$.

Tetraphenylboronbis(triisopropyl phosphite)rhodium(I)(XXIII).—The orange-yellow precipitate obtained from the reaction of $\{Rh[P(O\text{-}i\text{-}C_3H_7)_3]_4\}B(C_6H_5)_4$ with air by the method described for XXI was crystallized from dichloromethane–methanol. *Anal.* Calcd for $Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2B(C_6H_5)_4$: C, 60.3; H, 7.2; P, 7.4; mol wt 837. Found: C, 59.7; H, 7.3; P, 7.4; mol wt 896 (dec); mp 129–145°; conductivity 3.3 $ohm^{-1}\ cm^2\ mol^{-1}$.

Tetraphenylboronbis(tri-*n*-butyl phosphite)rhodium(I) (XXIV).—The yellow precipitate obtained from the reaction of $\{Rh[P(O\text{-}n\text{-}C_4H_9)_3]_5\}B(C_6H_5)_4$ with air by the method described for XXI was crystallized from methanol–water. *Anal.* Calcd for $Rh[P(O\text{-}n\text{-}C_4H_9)_3]_2B(C_6H_5)_4$: C, 62.5; H, 8.1; P, 6.7; mol wt 923. Found: C, 62.6; H, 8.7; P, 6.9; mol wt 938; mp 97°; conductivity 1.0 $ohm^{-1}\ cm^2\ mol^{-1}$.

Tetraphenylboronbis(triisobutyl phosphite)rhodium(I) (XXV).—The yellow precipitate obtained from the reaction of $\{Rh[P(O\text{-}i\text{-}C_4H_9)_3]_5\}B(C_6H_5)_4$ with air by the method described for XXI was crystallized from methanol–water. *Anal.* Calcd for $Rh[P(O\text{-}i\text{-}C_4H_9)_3]_2B(C_6H_5)_4$: C, 62.5; H, 8.1; P, 6.7; mol wt 923. Found: C, 62.4; H, 8.2; P, 6.9; mol wt 894; mp 122°; conductivity 6.5 $ohm^{-1}\ cm^2\ mol^{-1}$.

Formation of Pentakis(trimethyl phosphite)rhodium(I) Tetraphenylborate from Tetraphenylboronbis(trimethyl phosphite)rhodium(I) (XXVI).—An acetone solution (*ca.* 10 ml) containing $Rh[P(OCH_3)_3]_2B(C_6H_5)_4$ (0.1 g, 0.15 mmol) and trimethyl phosphite (0.1 g, 0.8 mmol) was refluxed for 2 hr. The solvent was removed under reduced pressure and the oily residue was crystallized from dichloromethane–methanol. The complex was identified as $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$ by comparison of its infrared and nmr spectra with those of an authentic sample.

Formation of Bis[1,2-bis(diphenylphosphino)ethane]rhodium(I) Tetraphenylborate from Tetraphenylboronbis(trimethyl phosphite)rhodium(I) (XXVII).—An acetone solution (*ca.* 10 ml) containing 1,2-bis(diphenylphosphino)ethane (0.06 g, 0.15 mmol) and $Rh[P(OCH_3)_3]_2B(C_6H_5)_4$ (0.1 g, 0.15 mmol) was refluxed for 3 hr. Orange crystals separated on cooling and were identified as $\{Rh[(C_6H_5)_2PC_2H_4P(C_6H_5)_2]_2\}B(C_6H_5)_4$ by comparison of their infrared spectrum with that of an authentic sample.

Cycloocta-1,5-dienebis(trimethyl phosphite)rhodium(I) Hexafluorophosphate (XXVIII).—A methanol solution (*ca.* 20 ml) containing $\{Rh[P(OCH_3)_3]_5\}PF_6$ (0.8 g, 0.92 mmol) and cycloocta-1,5-diene (2 ml, 16.4 mmol) was stirred under an atmosphere of air at room temperature for 24 hr. The solvent and excess cycloocta-1,5-diene were removed under reduced pressure and the resultant oily residue was crystallized from methanol–water to give orange crystals. *Anal.* Calcd for $\{RhC_8H_{12}[P(OCH_3)_3]_2\}PF_6$: C, 27.8; H, 5.0; P, 15.4; F, 18.9. Calcd for $\{RhC_8H_{12}[P(OCH_3)_3]_3\}PF_6$: C, 28.0; H, 5.4; P, 17.0; F, 15.7. Found: C, 27.6; H, 4.9; P, 15.6; F, 18.6; mp 138–140°; conductivity 133 $ohm^{-1}\ cm^2\ mol^{-1}$.

Bicyclo[2.2.1]hepta-2,5-dienetris(trimethyl phosphite)rhodium(I) Hexafluorophosphate (XXIX).—The oily residue obtained from the reaction of $\{Rh[P(OCH_3)_3]_5\}PF_6$ (0.8 g, 0.92 mmol) and bicyclo[2.2.1]hepta-2,5-diene (2 ml, 19.8 mmol) by the method described for XXVIII was crystallized from dichloromethane–methanol to give pale yellow crystals. *Anal.* Calcd for $\{RhC_7H_8[P(OCH_3)_3]_2\}PF_6$: C, 26.3; H, 4.5; P, 15.8; F, 19.4. Calcd for $\{RhC_7H_8[P(OCH_3)_3]_3\}PF_6$: C, 27.0; H, 5.0; P, 17.4; F, 16.0. Found: C, 27.3; H, 4.7; P, 17.6; F, 16.2; mp 133–134°; conductivity 131 $ohm^{-1}\ cm^2\ mol^{-1}$.

Results and Discussion

Cations of the Type RhL_4^+ and RhL_5^+.—The dimer $[C_8H_{12}RhCl]_2$, normally slightly soluble in methanol,

TABLE I

NMR DATA AND ASSIGNMENTS FOR IONIC DERIVATIVES[a]

No.	Compound	Aromatic protons	P–O–CH$_n$– protons	Other protons	Assignment
I	$\{Rh[P(O\text{-}i\text{-}C_3H_7)_3]_4\}B(C_6H_5)_4$	2.87 m	5.24 m	8.68 d, $J_{H-H} = 6.4$	CH$_3$ of $P(O\text{-}i\text{-}C_3H_7)_3$
II	$\{Rh[P(OCH_3)_2C_6H_5]_4\}PF_6$	2.49 s, b	6.79, $J = 12.5^b$		
IV	$\{Rh[POCH_3(C_6H_5)_2]_4\}PF_6 \cdot CH_2Cl_2$	2.65 s, b	7.38, $J = 11.1^b$	4.69 s	CH_2Cl_2
VIII	$\{Rh[PCH_3(C_6H_5)_2]_4\}ClO_4$	2.55 s, b		9.71^c	CH$_3$ of $PCH_3(C_6H_5)_2$
XVI	$\{Rh[P(OC_2H_5)_3]_4\}B(C_6H_5)_4$	2.90 m	5.98 m	8.69 t, $J_{H-H} = 7.2$	CH$_3$ of $P(OC_2H_5)_3$
IX	$\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$	2.90 m	6.44 s		
XI	$\{Rh[P(OC_2H_5)_3]_5\}B(C_6H_5)_4$	2.94 m	6.00 q, $J_{H-H} = 7.1$	8.75 t, $J_{H-H} = 7.3$	CH$_3$ of $P(OC_2H_5)_3$
XII	$\{Rh[P(O\text{-}i\text{-}C_4H_9)_3]_5\}B(C_6H_5)_4$	2.85 m	6.26 d, b, $J_{H-H} = 7.0$	8.16 m	CH of $P(O\text{-}i\text{-}C_4H_9)_3$
				9.05 d, $J_{H-H} = 6.7$	CH$_3$ of $P(O\text{-}i\text{-}C_4H_9)_3$
XIII	$\{Rh[P(O\text{-}n\text{-}C_4H_9)_3]_5\}B(C_6H_5)_4$	2.94 m	6.09 m	8.44 m	Other CH$_2$ of $P(O\text{-}n\text{-}C_4H_9)_3$
				9.07 t, $J_{H-H} = 6.4$	CH$_3$ of $P(O\text{-}n\text{-}C_4H_9)_3$
XIV	$\{Rh[P(OCH_2)_3CCH_3]_5\}B(C_6H_5)_4$	2.99 m	5.90 s	9.36 s	CH$_3$ of $P(OCH_2)_3CCH_3$
XVII	$\{Rh[P(CH_3)_2C_6H_5]_4O_2\}PF_6{}^d$	2.47 m		8.26 d, $J_{P-H} = 8.4$ 8.44 t, $J_{P-H} = 7.4$	CH$_3$ of $P(CH_3)_2C_6H_5$
XIX	$\{Rh[As(CH_3)_2C_6H_5]_4O_2\}PF_6$	2.36 m, 2.73 s, b		8.52 s, 8.57 s	CH$_3$ of $As(CH_3)_2C_6H_5$
XXVIII	$\{Rh(C_8H_{12})[P(OCH_3)_3]_2\}PF_6$		6.21 t, $J = 11.7^e$	4.35 s, b	Olefinic protons of C_8H_{12}
				7.50 s, b	Aliphatic protons of C_8H_{12}
XXIX	$\{Rh(C_7H_8)[P(OCH_3)_3]_3\}PF_6$		6.28 t, $J = 12.2^e$	6.53 m^f	Olefinic protons of C_7H_8
				8.76 s, b	Aliphatic protons of C_7H_8

[a] τ scale; coupling constants in hertz; measured in $CDCl_3$ at 38°. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad. [b] Resonance pattern as shown in Figure 1; J is the separation of outer peaks. [c] Ill-defined peak. [d] Measured in $(CD_3)_2CO$. [e] Triplet with broad central component and two sharp outer peaks; J is the separation of outer peaks. [f] Partially obscured by $P(OCH_3)_3$ resonances.

rapidly dissolves in this solvent in the presence of a six- to eightfold excess of the ligands L = $P(O\text{-}i\text{-}C_3H_7)_3$, $P(OCH_3)_2C_6H_5$, $POCH_3(C_6H_5)_2$, and $P(CH_3)_2C_6H_5$ at room temperature. The addition of an appropriate large anion, *e.g.*, $B(C_6H_5)_4^-$, to these solutions gave crystalline compounds characterized as $[RhL_4]$[anion]. The complexes $\{Rh[PCH_3(C_6H_5)_2]_4\}$[anion] were obtained similarly, but refluxing conditions were necessary. While the cation $Rh[P(O\text{-}i\text{-}C_3H_7)_3]_4^+$ was characterized as the tetraphenylborate, the species RhL_4^+ [L = $P(OCH_3)_2C_6H_5$, $POCH_3(C_6H_5)_2$, $P(CH_3)_2C_6H_5$, and $PCH_3(C_6H_5)_2$] were isolated and characterized as the hexafluorophosphates or perchlorates in view of the close analytical data for $[RhL_4]B(C_6H_5)_4$ and $[RhL_5]B(C_6H_5)_4$.

In contrast to those discussed above, the reactions of $[C_8H_{12}RhCl]_2$ with a six- to eightfold excess of the tertiary phosphite ligands L = $P(OR)_3$ (R = CH_3, C_2H_5, $i\text{-}C_4H_9$, and $n\text{-}C_4H_9$) and $P(OCH_2)_3CCH_3$ in methanol at room temperature followed by the addition of sodium tetraphenylboron yielded the five-coordinate rhodium(I) derivatives $[RhL_5]B(C_6H_5)_4$. It was possible to isolate the four-coordinate analogs of these latter derivatives by employing a rhodium to ligand ratio of 1:4. Thus $[C_8H_{12}RhCl]_2$ was treated with the ligands $P(OR)_3$ (R = CH_3 and C_2H_5) in dichloromethane in a molar ratio of 1:8 and sodium tetraphenylboron in methanol was added to the resultant solution to give the complexes $\{Rh[P(OR)_3]_4\}B(C_6H_5)_4$.

The ionic compounds described above were characterized by elemental analysis and, where appropriate, from nmr spectral intensity data and were shown to be 1:1 electrolytes in acetone. The derivative $\{Rh[P(O\text{-}n\text{-}C_4H_9)_3]_5\}B(C_6H_5)_4$ was isolated as an oily solid and its composition was inferred from nmr data only.

The proton nmr spectra of these four- and five-coordinate derivatives (Table I) show some interesting features. An unusual methyl resonance pattern of the type shown in Figure 1 is observed in the spectra of the complexes $\{Rh[P(OCH_3)_2C_6H_5]_4\}PF_6$ and $\{Rh[POCH_3(C_6H_5)_2]_4\}PF_6$. It is noteworthy that this pattern is also found in the nmr spectra of derivatives of the cations *trans*-$Rh[P(OCH_3)_3]_4XY^+$ (X = Y = Br; X = H, Y = Br; X = CH_3, Y = I)[11] and $Ir[P(OCH_3)_{3-x}(C_6H_5)_x]_4^+$ (x = 1 and 2).[12] In these complexes the ligands adopt a planar configuration about the metal atom. If it is assumed that, as has been found for numerous rhodium and iridium complexes containing the ligands $P(CH_3)_2C_6H_5$ and $PCH_3(C_6H_5)_2$,[13] coupling between trans phosphorus nuclei is strong but

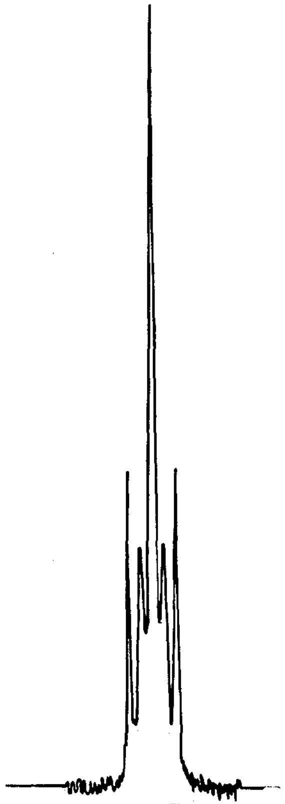


Figure 1.—Methyl resonance pattern observed in the nmr spectra of $\{Rh[P(OCH_3)_2C_6H_5]_4\}PF_6$ and $\{Rh[POCH_3(C_6H_5)_2]_4\}PF_6$.

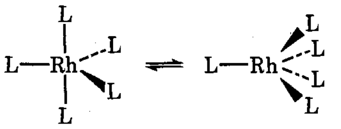
[11] L. M. Haines, *J. Organometal. Chem.*, **25**, C85 (1970); L. M. Haines, *Inorg. Chem.*, **10**, 1693 (1971).

[12] L. M. Haines and E. Singleton, *J. Organometal. Chem.*, **25**, C83 (1970).

[13] P. R. Brookes and B. L. Shaw, *J. Chem. Soc. A*, 1079 (1967).

that between cis nuclei is negligible, the methyl resonances in the spectra of these derivatives will be expected to occur as triplets. It is thus apparent that coupling between cis phosphorus nuclei in these complexes is not negligible but that the simple methyl resonance pattern observed represents a limiting case for a system of the type $AA'A''A'''X_nX'_nX''_nX'''_n$.

The spectra of $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$ and $\{Rh[P(OCH_2)_3CCH_3]_5\}B(C_6H_5)_4$ contain singlets at τ 6.44 and 5.90, respectively, which are assigned to the ligand protons P–O–CH_n–. Further the resonance associated with this group in the nmr spectrum of $\{Rh[P(OC_2H_5)_3]_5\}B(C_6H_5)_4$ occurs as a sharp quartet. It is thus apparent that in solution the ligands of these complexes are equivalent on the nmr time scale and that no apparent coupling between the phosphorus and proton nuclei in the P–O–CH_n– group occurs. The ligand equivalence can be readily explained in terms of rapid exchange between different species in solution. For instance it is possible that RhL_5^+ exists in two structural forms, trigonal bipyramid and tetragonal pyramid, in solution and further that the intramolecular rearrangement


(1)

between the two forms is rapid. An analogous equilibrium has been proposed to account for the single resonance observed in the ^{13}C nmr spectrum of $Fe(CO)_5$.[14] Alternatively dissociation of the cation may occur in solution according to the equilibrium

$$RhL_5^+ \rightleftharpoons RhL_4^+ + L \qquad (2)$$

A similar dissociation has been demonstrated for certain neutral five-coordinate rhodium(I) derivatives, *e.g.*, $RhH(CO)[P(C_6H_5)_3]_3$, by molecular weight measurements at different concentrations.[15]

The apparent lack of coupling between the phosphorus and proton nuclei associated with the P–O–CH_n– groups can be explained in terms of two possible mechanisms. For instance it is possible that the nature of either equilibrium 1 or 2 and the signs of the coupling constants $^3J_{P-H}$ for the different ligands in the equilibrium are such that an average $^3J_{P-H}$ coupling constant is observed and is zero.[16] Alternatively phosphorus–hydrogen coupling may be relaxed as a result of an intermediate rate of exchange between bonded and free ligands in equilibrium 2, as has been predicted and observed for other similar systems, *e.g.*, *trans*-$Pd[PCH_3(C_6H_5)_2]_2Cl_2$ and excess ligand $PCH_3(C_6H_5)_2$.[17]

A peak corresponding to the methyl protons was observed in the nmr spectrum of $\{Rh[PCH_3(C_6H_5)_2]_4\}ClO_4$ but unfortunately was extremely broad and ill defined. The spectra of the complexes $\{Rh[P(OR)_3]_4\}B(C_6H_5)_4$ (R = C_2H_5 and *i*-C_3H_7) and $\{Rh[P(OR)_3]_5\}B(C_6H_5)_4$ (R = *n*-C_4H_9 and *i*-C_4H_9) are complex and are not discussed. Furthermore solutions of the complexes $\{Rh[P(OCH_3)_3]_4\}B(C_6H_5)_4$ and $\{Rh[P(CH_3)_2C_6H_5]_4\}PF_6$ react too rapidly with trace amounts of oxygen for satisfactory nmr spectral data to be obtained.

The species RhL_4^+ and RhL_5^+ are novel in that they contain four and five identical monodentate ligands bonded to the metal atom, respectively. It is of interest that the isoelectronic cations CoL_5^+ [L = $P(OCH_3)_3$[18,19] and $P(OCH_2)_3CCH_3$[20]], $Ni[P(OCH_3)_3]_5^{2+}$,[19] and $Pt[P(CH_3)_2C_6H_5]_4^{2+}$ [21] have been reported.

Cations of the Type $RhL_4O_2^+$.—The compounds $\{Rh[P(CH_3)_2C_6H_5]_4\}$[anion] (anion = PF_6 or ClO_4) were observed to react with oxygen from the air slowly in the solid state but rapidly in solution to afford the oxygen adducts $\{Rh[P(CH_3)_2C_6H_5]_4O_2\}$[anion]. These latter complexes, as well as the arsine analogs $\{Rh[As(CH_3)_2C_6H_5]_4O_2\}$[anion] (anion = PF_6 or ClO_4), are also formed from the reaction of $[C_8H_{12}RhCl]_2$ with an excess of the appropriate ligand L in methanol provided oxygen is not excluded from the system. The cation $Rh[As(CH_3)_2C_6H_5]_4O_2^+$ forms so readily that attempts to isolate the parent species $Rh[As(CH_3)_2C_6H_5]_4^+$ from the reaction of $[C_8H_{12}RhCl]_2$ and excess $As(CH_3)_2C_6H_5$ in methanol by careful exclusion of oxygen from the system proved unsuccessful.

The derivatives $[RhL_4O_2]$[anion] [L = $P(CH_3)_2C_6H_5$ and $As(CH_3)_2C_6H_5$; anion = ClO_4 and PF_6] were characterized by elemental analysis including direct oxygen analysis and were shown to be 1:1 electrolytes in solution. The infrared spectrum of a Nujol mull of the perchlorate $\{Rh[P(CH_3)_2C_6H_5]_4O_2\}ClO_4$ contains two bands at 841 and 870 cm^{-1} which are not present in the spectrum of the parent compound $\{Rh[P(CH_3)_2C_6H_5]_4\}ClO_4$. These peaks are associated with the O–O stretching vibrations.[22] Bands at 862 and 867 cm^{-1} in the infrared spectrum of a Nujol mull of $\{Rh[As(CH_3)_2C_6H_5]_4O_2\}ClO_4$ are similarly assigned to these O–O stretching modes.

The structure shown in Figure 2 is proposed for the cations $RhL_4O_2^+$ [L = $P(CH_3)_2C_6H_5$, $As(CH_3)_2C_6H_5$] on the basis of that found by X-ray crystallography for $\{Rh[(C_6H_5)_2PC_2H_4P(C_6H_5)_2]_2O_2\}PF_6$.[23] The nmr spectra of the derivatives $\{Rh[As(CH_3)_2C_6H_5]_4O_2\}$[anion] (anion = PF_6 and ClO_4) are consistent with the structure proposed. The two singlets observed in the region

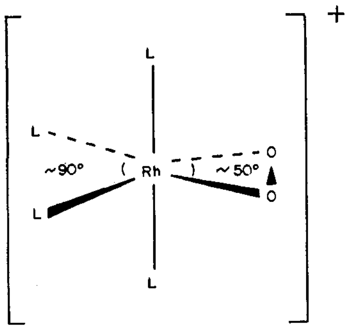


Figure 2.—Proposed structure for the cations $RhL_4O_2^+$.

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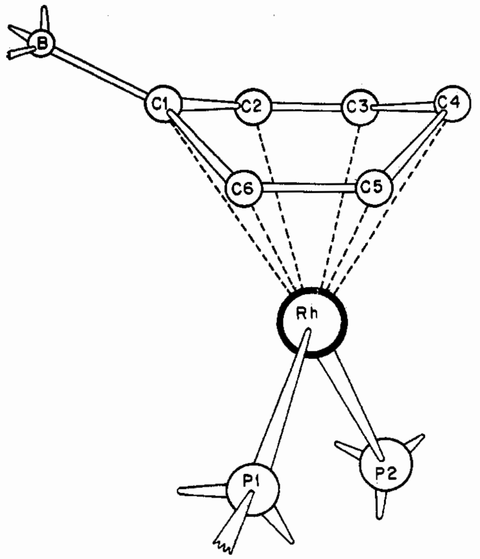

Figure 3.—Molecular geometry of $Rh[P(OCH_3)_3]_2B(C_6H_5)_4$.

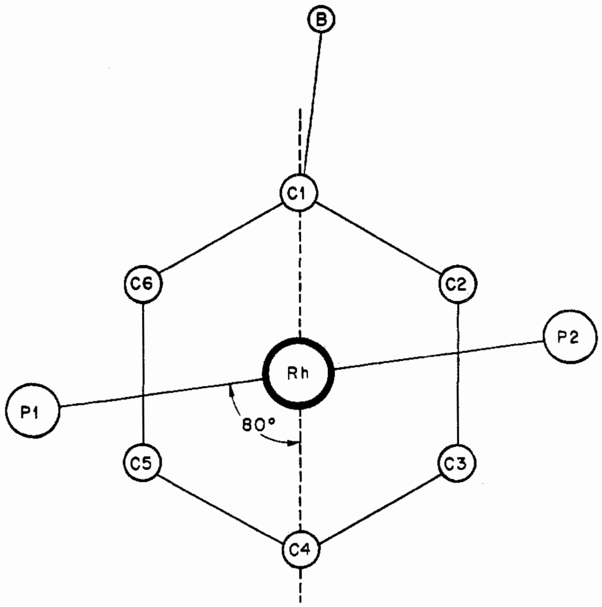

Figure 4.—Structure of $Rh[P(OCH_3)_3]_2B(C_6H_5)_4$ projected onto the plane of phenyl ring A.

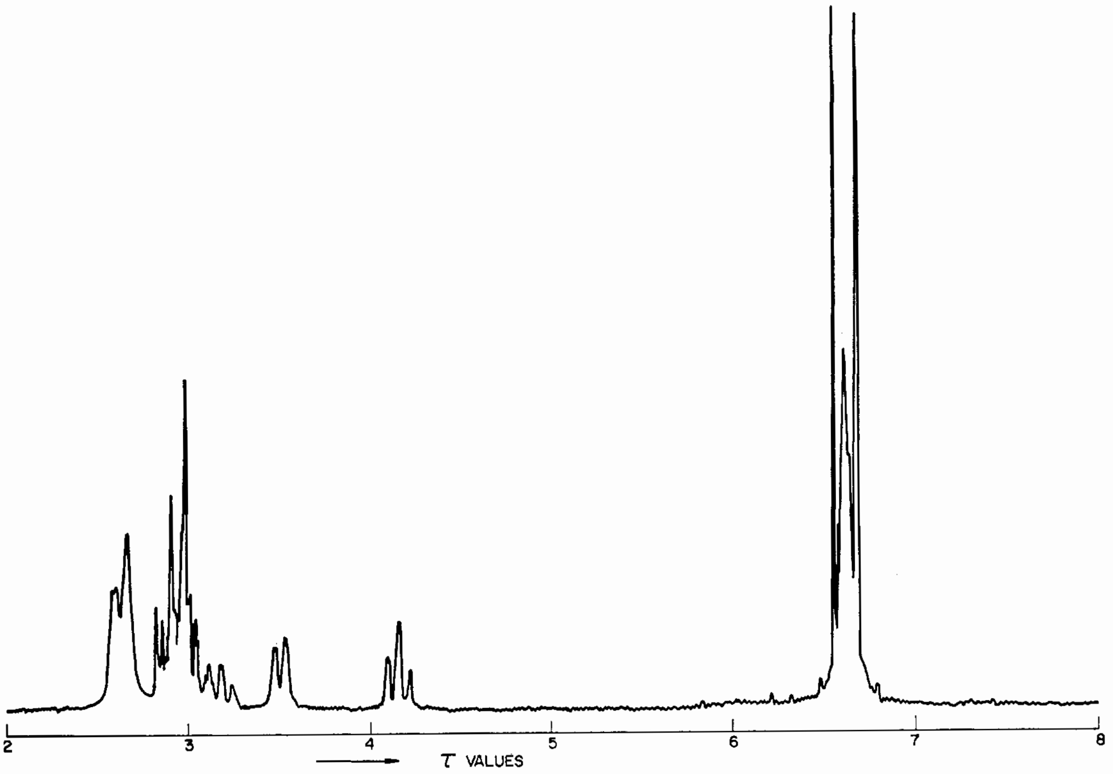

Figure 5.—Nmr spectrum of $Rh[P(OCH_3)_3]_2B(C_6H_5)_4$.

of τ 8.5 can be associated with the methyl groups of two sets of equivalent $As(CH_3)_2C_6H_5$ ligands. The compounds $\{Rh[P(CH_3)_2C_6H_5]_4O_2\}$[anion] (anion = PF_6 and ClO_4) decompose rapidly in solution and it was difficult to obtain reliable nmr data. However the spectrum of a freshly prepared solution of $\{Rh[P(CH_3)_2C_6H_5]_4O_2\}PF_6$ in $(CD_3)_2CO$ was recorded and contains a doublet at τ 8.26 (J = 8.4 Hz) and a triplet at τ 8.44 (J = 7.4 Hz) of equal intensity, which is in accord with the structure proposed.

These oxygen derivatives are of particular interest as only one other rhodium–oxygen complex, *viz.*, $\{Rh[(C_6H_5)_2PC_2H_4P(C_6H_5)_2]_2O_2\}PF_6$, has been fully characterized.[23] It is noteworthy that, whereas the oxygen in this latter complex is readily liberated to regenerate the parent compound $\{Rh[(C_6H_5)_2PC_2H_4P(C_6H_5)_2]_2\}PF_6$, the oxygen in the complexes $[RhL_4O_2]$[anion] [L = $P(CH_3)_2C_6H_5$ and $As(CH_3)_2C_6H_5$] is not so readily evolved.

In contrast $\{Rh[P(n\text{-}C_4H_9)_3]_4\}B(C_6H_5)_4$ and $\{Rh[PCH_3(C_6H_5)_2]_4\}PF_6$ were observed to be stable in air in the solid state over many weeks and to decompose slowly in oxygen-saturated solutions. Furthermore no crystalline products could be isolated from these latter reactions with oxygen.

Complexes of the Type $RhL_2B(C_6H_5)_4$.—The com-

TABLE II

NMR DATA AND ASSIGNMENTS FOR $Rh[P(OR)_3]_2B(C_6H_5)_4$[a]

No.	Compound	Non-bonded phenyl ring protons	Bonded phenyl ring protons attached to			P–O–CH_n- protons	Other protons	Assignments
			C(2), C(6)	C(3), C(5)	C(4)			
XXI	$Rh[P(OCH_3)_3]_2B(C_6H_5)_4$	2.89 m	3.52 d, $J_{H-H} \approx 7.0$	4.16 t, $J_{H-H} \approx 6.5$	3.18 t, $J_{H-H} \approx 6.0$	6.73 t, $J_{P-H} = 10.8$[b]		
XXII	$Rh[P(OC_2H_5)_3]_2B(C_6H_5)_4$	2.90 m	3.55 d, $J_{H-H} \approx 6.2$	4.20 t, $J_{H-H} \approx 6.3$	3.14 t, $J_{H-H} \approx 6.5$	6.28 m	8.88 t, $J_{H-H} = 8.9$	CH_3 of $P(OC_2H_5)_3$
XXIII	$Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2B(C_6H_5)_4$	2.91 m	3.60 d, $J_{H-H} \approx 6.6$	4.22 t, $J_{H-H} \approx 6.5$	[c]	5.56 m	8.87 d, $J_{H-H} = 6.2$	CH_3 of $P(O\text{-}i\text{-}C_3H_7)_3$
XXIV	$Rh[P(O\text{-}i\text{-}C_4H_9)_3]_2B(C_6H_5)_4$	2.96 m	3.53 d, $J_{H-H} \approx 6.4$	4.16 t, $J_{H-H} \approx 5.0$	3.13 t, $J_{H-H} \approx 6.4$	6.53 m	8.24 n, $J_{H-H} = 6.7$ 9.13 d, $J_{H-H} = 6.7$	CH of $P(O\text{-}i\text{-}C_4H_9)_3$ CH_3 of $P(O\text{-}i\text{-}C_4H_9)_3$
XXV	$Rh[P(O\text{-}n\text{-}C_4H_9)_3]_2B(C_6H_5)_4$	2.88 m	3.55 d, $J_{H-H} \approx 5.2$	4.18 t, $J_{H-H} \approx 6.2$	3.15 t, $J_{H-H} \approx 6.0$	6.29 m	8.59 m 9.05 t[d]	Other CH_2 of $P(O\text{-}n\text{-}C_4H_9)_3$ CH_3 of $P(O\text{-}n\text{-}C_4H_9)_3$

[a] τ scale; coupling constants in hertz; measured in $CDCl_3$ at 38°. Abbreviations: d, doublet; t, triplet; n, nonet; m, multiplet. [b] Triplet with broad central component and two sharp outer peaks. [c] Not observed. [d] Ill defined.

plexes $\{Rh[P(OR)_3]_5\}B(C_6H_5)_4$ (R = CH_3, C_2H_5, $i\text{-}C_4H_9$, and $n\text{-}C_4H_9$) and $\{Rh[P(OR)_3]_4\}B(C_6H_5)_4$ (R = CH_3, C_2H_5, and $i\text{-}C_3H_7$) react readily in the solid state with air to afford oily residues from which crystalline compounds of stoichiometry $Rh[P(OR)_3]_2B(C_6H_5)_4$ were obtained. These latter derivatives are most conveniently prepared, however, by stirring a suspension of the appropriate ionic complex in methanol at room temperature under an atmosphere of air. These reactions do not occur under nitrogen and must therefore involve attack of oxygen on the ionic precursors. The mechanism of this reaction has not been further investigated.

The stoichiometry $Rh[P(OR)_3]_2B(C_6H_5)_4$ (R = CH_3, C_2H_5, $i\text{-}C_3H_7$, $n\text{-}C_4H_9$, and $i\text{-}C_4H_9$) was established by elemental analysis (Table I) and from nmr spectral intensity data. The compounds were shown to be nonelectrolytes in acetone, although their conductivities were observed to increase slowly with time. The monomeric nature of the complexes in benzene was established from molecular weight measurements.

The molecular structure of the compound $Rh[P(OCH_3)_3]_2B(C_6H_5)_4$ has been determined by an X-ray crystallographic study and is shown in Figure 3.[1] The rhodium atom is situated symmetrically with respect to one of the phenyl rings of the $B(C_6H_5)_4$ group and at a distance of 1.86 Å from the mean plane of that ring (A). This distance is comparable with that of 1.72 Å found for the compound $(C_6H_6)Cr(CO)_3$,[24] and it is therefore clear that the rhodium atom is bonded directly to phenyl ring A. The plane defined by the atoms RhP(1)P(2) makes an angle of 91° with the mean plane of the bonded phenyl ring with the two phosphorus atoms equidistant from the latter. The plane through Rh, P(1), and P(2) intersects the phenyl ring (A) in an asymmetric manner (Figure 4). The RhP(1)P(2) valency angle is 90 ± 1°.

The average estimated standard deviations of the bond lengths Rh–P, Rh–C, and C–C are 0.01, 0.02, and 0.03 Å, respectively. The C–C bond distances in the phenyl ring (A) range from 1.39 to 1.44 Å, but their deviations from the mean are not significant. The nonbonded rings are planar, having rms deviations of 0.01–0.02 Å. By contrast the atoms of the bonded ring (A) show an rms deviation of 0.04 Å with individual displacements consistent with a boat configuration. The dihedral angles between the best plane through C(2)C(3)C(5)C(6) and the C(1)C(2)C(6) and C(3)C(4)C(5) planes are 6°. The four distances Rh–C(2), Rh–C(3), Rh–C(5), and Rh–C(6) are similar to within their esd's and average 2.31 Å, while the other two, Rh–C(1) (2.41 Å) and Rh–C(4) (2.40 Å), are significantly longer. The slight distortion of the phenyl ring (A) to a boat configuration may reflect a small localization of the bonding MO's of this ring (A) on the carbon atoms 2, 3, 5, and 6, although it may also be a consequence of packing forces.

The nmr spectrum of the derivative $Rh[P(OCH_3)_3]_2B(C_6H_5)_4$ in $CDCl_3$ is represented in Figure 5 and is consistent with the structure established for the compound in the crystalline state. The pattern of the methyl resonances is typical of a "virtually coupled" $AA'X_3X'_3$ system, with appreciable but not strong

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phosphorus–phosphorus coupling.[25,26] It is well established that the proton resonances of an arene ring bonded to a metal atom occur at τ 1–2 to high field of those of the free ligand.[27] Thus the multiplet at τ 2.89 is assigned to the protons of the nonbonded phenyl rings, while the two triplets and the doublet to high field of this multiplet are clearly associated with the protons of the bonded phenyl ring (A). On the basis of the relative intensities and on the assumption that coupling only occurs between adjacent protons in the bonded ring, the triplet at τ 4.16, the doublet at τ 3.52, and the ill-defined triplet at τ 3.18 are assigned to the protons attached to C(3), C(5), to C(2),C(6), and to C(4), respectively. The nmr spectra of $Rh[P(OR)_3]_2B(C_6H_5)_4$ (R = C_2H_5, *i*-C_3H_7, *n*-C_4H_9, and *i*-C_4H_9) showed an analogous pattern of aromatic resonances (Table II). It is noteworthy that the pattern of aromatic resonances observed for the bonded phenyl ring in the complexes $Rh[P(OR)_3]_2B(C_6H_5)_4$ is similar to that of the arene derivatives of the type $M(C_6H_5R)(CO)_3$ (M = Cr, Mo, W; R = alkyl).[28]

Subsequent to the preliminary communication[1] dealing with the preparation of the complexes $Rh[P(OR)_3]_2B(C_6H_5)_4$ (R = CH_3, *i*-C_3H_7, *n*-C_4H_9, and *i*-C_4H_9) and the structural determination for the compound $Rh[P(OCH_3)_3]_2B(C_6H_5)_4$, Schrock and Osborn[29] reported the preparation of a series of similar derivatives of the type $Rh(diene)B(C_6H_5)_4$ and $Ir(diene)B(C_6H_5)_4$ (*e.g.*, diene = cycloocta-1,5-diene and hexa-1,5-diene). Apart from those mentioned above only two other arene complexes of rhodium have been reported, *viz.*, $\{Rh[C_6(CH_3)_6]_2\}PF_6$ and $\{Rh[C_6(CH_3)_6]_2\}(PF_6)_2$.[30]

The ionic derivatives $\{Rh[P(OCH_2)_3CCH_3]_5\}B(C_6H_5)_4$ and $[RhL_4]B(C_6H_5)_4$ [L = $P(OC_6H_5)_3$, $P(OCH_3)_2C_6H_5$, and $POCH_3(C_6H_5)_2$], as well as the oxygen adducts $[RhL_4O_2]$[anion] [L = $P(CH_3)_2C_6H_5$ and $As(CH_3)_2C_6H_5$; anion = ClO_4, PF_6, and $B(C_6H_5)_4$], decompose very slowly in solution in the presence of oxygen, but crystalline products and, in particular, arene complexes of the type $RhL_2B(C_6H_5)_4$ could not be isolated.

The neutral complexes $Rh[P(OR)_3]_2B(C_6H_5)_4$ have been observed to show a gradual increase in conductivity in acetone with time, which can be attributed to an equilibrium of the type

$$Rh[P(OR)_3]_2B(C_6H_5)_4 + \text{acetone} \rightleftharpoons Rh[P(OR)_3]_2(\text{acetone})_2^+ + B(C_6H_5)_4^-$$

Accordingly it was found that the $B(C_6H_5)_4$ group may be displaced from $Rh[P(OCH_3)_3]_2B(C_6H_5)_4$ by certain ligands in acetone. For instance the reaction of $Rh[P(OCH_3)_3]_2B(C_6H_5)_4$ with an excess of the ligand $P(OCH_3)_3$ in acetone under reflux regenerates the ionic derivative $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$. Furthermore treatment of $Rh[P(OCH_3)_3]_2B(C_6H_5)_4$ with an equimolar amount of the chelating ligand $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ under similar conditions effects displacement of both the $P(OCH_3)_3$ and the $B(C_6H_5)_4$ groups to give $\{Rh[(C_6H_5)_2PC_2H_4P(C_6H_5)_2]_2\}B(C_6H_5)_4$ together with unreacted starting complex.

Related Complexes.—The displacement of the tertiary phosphite ligands from the cation $Rh[P(OCH_3)_3]_5^+$ by treatment with arenes and olefins other than tetraphenylboron in the presence of air has been investigated. Thus the complex $\{Rh[P(OCH_3)_3]_5\}PF_6$ was observed to react with an excess of the diolefins cycloocta-1,5-diene and bicyclo[2.2.1]hepta-2,5-diene in methanol in the presence of air to give the derivatives $\{C_8H_{12}Rh[P(OCH_3)_3]_2\}PF_6$ and $\{C_7H_8Rh[P(OCH_3)_3]_3\}PF_6$, respectively. Attempts to isolate similar products from the corresponding reactions with hexamethylbenzene and cyclooctene were unsucessful however.

The compounds $\{C_7H_8Rh[P(OCH_3)_3]_3\}PF_6$ and $\{C_8H_{12}Rh[P(OCH_3)_3]_2\}PF_6$ were characterized by elemental analysis and from nmr spectral intensity data and were shown to be 1:1 electrolytes in acetone. The resonances in the nmr spectra of these complexes corresponding to the ligand protons occur as triplets, consisting of a broad central component and two sharp outer peaks, suggesting appreciable phosphorus–phosphorus coupling (Table I).

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