CONTRIBUTION FROM THE NATIONAL CHEMICAL RESEARCH LABORATORY,
SOUTH AFRICAN COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH, PRETORIA, REPUBLIC OF SOUTH AFRICA

Addition and Oxidative Addition Reactions of Some Cationic Complexes of Rhodium(I)[1]

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Received November 13, 1970

The four-coordinate cationic complex $\{Rh[P(OCH_3)_3]_4\}B(C_6H_5)_4$ reversibly adds carbon monoxide to form $\{Rh(CO)[P(OCH_3)_3]_4\}B(C_6H_5)_4$ and also reacts with the acetylenes C_2R_2 ($R = CF_3$ and CO_2CH_3) to give $\{Rh[P(OCH_3)_3]_4C_2R_2\}B(C_6H_5)_4$. $\{Rh[P(n\text{-}C_4H_9)_3]_4\}B(C_6H_5)_4$ adds hydrogen irreversibly to form *cis*-$\{Rh[P(n\text{-}C_4H_9)_3]_4H_2\}B(C_6H_5)_4$ whereas the corresponding reactions involving $\{Rh[P(OR)_3]_4\}B(C_6H_5)_4$ ($R = CH_3$ and C_6H_5) to give *cis*-$\{Rh[P(OR)_3]_4H_2\}B(C_6H_5)_4$ are reversible. Treatment of the five-coordinate complex $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$ with hydrobromic and hydriodic acids in ethanol gives *trans*-$\{Rh[P(OCH_3)_3]_4HBr\}B(C_6H_5)_4$ and *trans*-$\{Rh[P(OCH_3)_3]_4HI\}B(C_6H_5)_4$, respectively. However prolonged reaction of $\{Rh[P(OCH_3)_3]_5\{B(C_6H_5)_4$ with hydrobromic acid yields *cis*-$\{Rh[P(OCH_3)_3]_4Br_2\}B(C_6H_5)_4$. The addition of an equimolar amount of bromine to $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$ gives *trans*-$\{Rh[P(OCH_3)_3]_4Br_2\}B(C_6H_5)_4$ together with a small amount of the cis form. In contrast the corresponding reaction involving iodine affords *cis*-$\{Rh[P(OCH_3)_3]_4I_2\}B(C_6H_5)_4$ as the sole product. $\{Rh[P(OCH_3)_3]_4\}B(C_6H_5)_4$ reacts with methyl iodide to form *trans*-$\{Rh[P(OCH_3)_3]_4(CH_3)I\}B(C_6H_5)_4$. The cations RhL_4^+ $\{L = P(OR)_3$ [$R = CH_3$, C_2H_5, and $i\text{-}C_3H_7$] and $P(CH_3)_2C_6H_5\}$ and RhL_5^+ [$L = P(OR)_3$ ($R = CH_3$ and C_2H_5)] react with the allyl halides C_3H_5X ($X = Cl$ and Br) to give $Rh(\pi\text{-}C_3H_5)L_4^{2+}$ or $RhX(\pi\text{-}C_3H_5)L_3^+$. The product formed is shown to depend on the ligand involved and on the reaction conditions.

Introduction

The addition reactions of small covalent molecules to transition metal complexes having a d^8 configuration are particularly relevant to the mechanisms of homogeneous catalyses involving these systems and as a consequence have received considerable attention.[2,3] These studies have been restricted chiefly to neutral complexes and few such additions have been reported for transition metal cationic species. The only rhodium(I) cations for which addition reactions have been reported are $Rh(R_2PC_2H_4PR_2)_2^+$ ($R = CH_3$[4] and C_6H_5[5]), $Rh[cis\text{-}(C_6H_5)_2AsCH{=}CHAs(C_6H_5)_2]_2^+$,[6] and $Rh(diene)[P(C_6H_5)_3]_2^+$ (diene = cycloocta-1,5-diene and bicyclo[2.2.1]hepta-2,5-diene).[7]

The synthesis of cations of the types RhL_5^+ and RhL_4^+ and a study of their reactivity toward air were reported in earlier publications.[8-10] Thus $\{Rh[P(CH_3)_2C_6H_5]_4\}PF_6$ was shown to react with oxygen from the air to give the adduct $\{Rh[P(CH_3)_2C_6H_5]_4O_2\}PF_6$[10] while $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$ was found to decompose in air to form the arene complex $Rh[P(OCH_3)_3]_2B(C_6H_5)_4$.[9,10] The results of some addition reactions of small covalent molecules to the rhodium(I) cations of the types RhL_4^+ and RhL_5^+ are now reported.

Experimental Section

The syntheses of the compounds $\{Rh[P(OR)_3]_5\}$[anion] [$R = CH_3$ and C_2H_5, anion = $B(C_6H_5)_4$ and PF_6], $[RhL_4]B(C_6H_5)_4$ [$L = P(OR)_3$ ($R = CH_3$, C_2H_5, $i\text{-}C_3H_7$, and C_6H_5) and $P(n\text{-}C_4H_9)_3$], and $\{Rh[P(CH_3)_2C_6H_5]_4\}PF_6$ were reported in previous publications.[8-10] All ligands were obtained commercially. All reactions were performed under an atmosphere of nitrogen. 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-60 and Varian HA-100 instruments. Conductivities were determined using a Van Waters and Rogers Model 31 conductivity bridge. Melting points were obtained with a Kofler hot stage and are corrected. Elemental analyses were performed by the Bernhardt Microanalytical Laboratory, Elbach über Engelskirchen, West Germany, and by Mr. G. J. Roberts, National Chemical Research Laboratory, CSIR, Pretoria, Republic of South Africa.

1. **Carbonyltetrakis(trimethyl phosphite)rhodium(I) Tetraphenylborate.**—Carbon monoxide was passed through a solution of $\{Rh[P(OCH_3)_3]_4\}B(C_6H_5)_4$ (0.6 g, 0.65 mmol) in dichloromethane (*ca.* 5 ml) at room temperature for 5 min. Methanol (*ca.* 10 ml) was added to the solution and the dichloromethane was removed under a stream of carbon monoxide. The complex which separated from solution as white crystals was recrystallized from dichloromethane–methanol under carbon monoxide.

2. **Hexafluorobut-2-ynetetrakis(trimethyl phosphite)rhodium Tetraphenylborate.**—The complex was obtained from $\{Rh[P\text{-}OCH_3)_3]_4\}B(C_6H_5)_4$ and hexafluorobut-2-yne by the procedure described in section 1.

3. **(Dimethyl acetylenedicarboxylate)tetrakis(trimethyl phosphite)rhodium Tetraphenylborate.**—A solution of $\{Rh[P(OCH_3)_3]_4\}B(C_6H_5)_4$ (0.800 g, 0.87 mmol) and dimethyl acetylenedicarboxylate (0.123 g, 0.87 mmol) in dichloromethane (*ca.* 10 ml) was stirred at room temperature for 5 min. The solvent was removed under reduced pressure and the resultant oily solid was washed with methanol and crystallized from dichloromethane–methanol.

4. ***cis*-Dihydridotetrakis(trimethyl phosphite)rhodium(III) Tetraphenylborate.**—The complex was obtained from $\{Rh[P\text{-}OCH_3)_3]_4\}(C_6H_5)_4$ and hydrogen by the procedure described in section 1.

5. ***cis*-Dihydridotetrakis(tri-*n*-butylphosphine)rhodium(III) Tetraphenylborate.**—The complex was obtained from $\{Rh[P(n\text{-}C_4H_9)_3]_4\}B(C_6H_5)_4$ and hydrogen by the procedure described in section 1.

6. ***cis*-Dihydridotetrakis(triphenyl phosphite)rhodium(III) Tetraphenylborate.**—Hydrogen was passed through a solution of $\{Rh[P(OC_6H_5)_3]_4\}B(C_6H_5)_4$ (0.3 g, 0.2 mmol) in dichloromethane (*ca.* 5 ml) at room temperature for 5 min. The presence of *cis*-$\{Rh[P(OC_6H_5)_3]_4H_2\}B(C_6H_5)_4$ in the resultant colorless solution was demonstrated by means of infrared spectroscopy.

7. ***trans*-Bromohydridotetrakis(trimethyl phosphite)rhodium(III) Tetraphenylborate.**—A methanol solution of hydrobromic acid (0.9 mmol) was added to a suspension of $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$ (0.4 g, 0.4 mmol) in methanol (*ca.* 10 ml). The solution was stirred for 5 min and filtered. Addition of sodium tetraphenylboron (0.4 g, 1.2 mmol) in methanol (*ca.* 3 ml) to the filtrate gave white crystals of the compound.

8. ***trans*-Hydridoiodotetrakis(trimethyl phosphite)rhodium-**

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(III) Tetraphenylborate.—The complex was obtained from $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$ (0.4 g, 0.4 mmol), hydriodic acid (0.9 mmol), and sodium tetraphenylboron (0.4 g, 1.2 mmol) by the procedure described in section 7.

9. ***cis*-Dibromotetrakis(trimethyl phosphite)rhodium(III) Tetraphenylborate.**—A methanol solution of hydrobromic acid (1.6 mmol) was added to a suspension of $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$ (0.4 g, 0.4 mmol) in methanol (*ca.* 10 ml) and the resultant solution was stirred at room temperature for 3 hr. Addition of sodium tetraphenylboron (0.5 g, 1.5 mmol) in methanol (*ca.* 5 ml) gave white crystals which were recrystallized from dichloromethane–methanol.

10. ***trans*-Dibromotetrakis(trimethyl phosphite)rhodium(III) Tetraphenylborate.**—A dichloromethane solution of bromine (0.42 mmol) was added to a solution of $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$ (0.4 g, 0.4 mmol) in dichloromethane (*ca.* 5 ml) and the resultant solution was stirred at room temperature for 5 min. The solvent and any excess bromine were removed under reduced pressure to give a residue containing two products. *cis*-$\{Rh[P(OCH_3)_3]_4Br_2\}B(C_6H_5)_4$ (0.04 g, 9% yield) was separated from the major product *trans*-$\{Rh[P(OCH_3)_3]_4Br_2\}B(C_6H_5)_4$ (0.27 g, 65% yield) by fractional crystallization from dichloromethane–methanol. The former isomer, which separated first as white plates, was identified by a comparison of its infrared spectrum and melting point with those of an authentic sample. *trans*-$\{Rh[P(OCH_3)_3]_4Br_2\}B(C_6H_5)_4$ separated as yellow needles.

11. ***cis*-Diiodotetrakis(trimethyl phosphite)rhodium(III) Tetraphenylborate.**—The complex was obtained from $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$ (0.3 g, 0.3 mmol) and iodine (0.07 g, 0.3 mmol) by the procedure described in section 3.

12. ***trans*-Iodomethyltetrakis(trimethyl phosphite)rhodium(III) Tetraphenylborate.**—$\{Rh[P(OCH_3)_3]_4\}B(C_6H_5)_4$ (1.0 g, 1.1 mmol) was dissolved in methyl iodide (*ca.* 10 ml) and the solution was allowed to stand at 0° for 48 hr. The methyl iodide was removed under reduced pressure and the residue was washed with methanol and crystallized from methyl iodide–methanol.

13. **Reaction of Allyl Chloride with $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$ to Give π-Allyltetrakis(trimethyl phosphite)rhodium(III) Bis(tetraphenylborate) and π-Allylchlorotris(trimethyl phosphite)rhodium(III) Tetraphenylborate.**—A suspension of $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$ (1.0 g, 1.0 mmol) in allyl chloride (*ca.* 10 ml) was stirred at room temperature for 30 min. The white precipitate of $\{Rh(\pi\text{-}C_3H_5)[P(OCH_3)_3]_4\}[B(C_6H_5)_4]_2$ (0.45 g) that separated from solution was isolated and crystallized from acetone. Allyl chloride was removed from the filtrate under reduced pressure and the residue containing $\{RhCl(\pi\text{-}C_3H_5)[P(OCH_3)_3]_3\}B(C_6H_5)_4$ (0.1 g) was crystallized from dichloromethane–methanol.

14. **Reaction of Allyl Bromide with $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$ to Give $\{Rh(\pi\text{-}C_3H_5)[P(OCH_3)_3]_4\}[B(C_6H_5)_4]_2$ and π-Allylbromotris(trimethyl phosphite)rhodium(III) Tetraphenylborate.**—A suspension of $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$ (1.0 g, 1.0 mmol) in allyl bromide (*ca.* 15 ml) was stirred at room temperature for 2 hr. The two products were isolated by the procedure described in section 13.

15. **Reaction of Allyl Chloride with $\{Rh[P(OCH_3)_3]_4\}B(C_6H_5)_4$ or with $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$ in Methanol to Give $\{Rh(\pi\text{-}C_3H_5)[P(OCH_3)_3]_4\}[B(C_6H_5)_4]_2$.** A suspension of $\{Rh[P(OCH_3)_3]_4\}B(C_6H_5)_4$ (0.35 g, 0.4 mmol) or $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$ (0.4 g, 0.4 mmol), allyl chloride (*ca.* 3 ml), and sodium tetraphenylboron (0.3 g, 0.9 mmol) in methanol (*ca.* 10 ml) was stirred at room temperature for 30 min. The white precipitate that formed was crystallized from acetone.

16. **π-Allyltetrakis(trimethyl phosphite)rhodium(III) Bis(hexafluorophosphate).**—A solution of $\{Rh[P(OCH_3)_3]_5\}PF_6$ (1.0 g, 1.2 mmol), allyl chloride (*ca.* 5 ml), and ammonium hexafluorophosphate (0.4 g, 2.5 mmol) in methanol (*ca.* 10 ml) was stirred at room temperature for 30 min. The methanol and excess allyl chloride were removed under reduced pressure. The residue was washed with methanol and crystallized from dichloromethane–methanol.

17. **Reaction of 2-Methylallyl Chloride with $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$ to Give π-2-Methylallyltetrakis(trimethyl phosphite)rhodium(III) Bis(tetraphenylborate).**—A suspension of $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$ (0.5 g, 0.5 mmol) in 2-methylallyl chloride (*ca.* 10 ml) was stirred at room temperature for 30 min. The white precipitate that formed was isolated and crystallized from acetone.

18. **π-2-Methylallyltetrakis(trimethyl phosphite)rhodium(III) Bis(hexafluorophosphate).**—The complex was obtained from $\{Rh[P(OCH_3)_3]_5\}PF_6$ (0.5 g, 0.6 mmol) and 2-methylallyl chloride (*ca.* 3 ml) by the procedure described in section 16.

19. **π-Allylchlorotris(triethyl phosphite)rhodium(III) Tetraphenylborate.**—A solution of $\{Rh[P(OC_2H_5)_3]_5\}B(C_6H_5)_4$ (1.0 g, 0.8 mmol) in allyl chloride (*ca.* 20 ml) was stirred at room temperature for 2 hr. Allyl chloride was removed under reduced pressure and the residue was extracted with hot methanol. The extract was concentrated to a small volume (*ca.* 10 ml). The white crystals of the complex which formed were recrystallized from methanol.

20. **π-Allyltetrakis(triethyl phosphite)rhodium(III) Bis(tetraphenylborate).**—A suspension of $\{Rh[P(OC_2H_5)_3]_5\}B(C_6H_5)_4$ (1.0 g, 0.8 mmol) or $\{Rh[P(OC_2H_5)_3]_4\}B(C_6H_5)_4$ (0.9 g, 0.8 mmol), allyl chloride (*ca.* 5 ml), and sodium tetraphenylboron (0.6 g, 1.75 mmol) in methanol (*ca.* 15 ml) was stirred at room temperature for 30 min. The methanol and excess allyl chloride were removed under reduced pressure. The residue was washed with methanol and crystallized from acetone–methanol.

21. **π-Allyltetrakis(triethyl phosphite)rhodium(III) Bis(hexafluorophosphate).**—A solution of $\{Rh[P(OC_2H_5)_3]_5\}PF_6$ (0.5 g, 0.5 mmol), allyl chloride (*ca.* 3 ml), and ammonium hexafluorophosphate (0.2 g, 1.2 mmol) in methanol (*ca.* 5 ml) was stirred at room temperature for 30 min. The methanol and excess allyl chloride were removed under reduced pressure and the residue was crystallized from methanol–water.

22. **π-2-Methylallyltetrakis(triethyl phosphite)rhodium(III) Bis(tetraphenylborate).**—The complex was obtained from $\{Rh[P(OC_2H_5)_3]_5\}B(C_6H_5)_4$ (0.5 g, 0.4 mmol), 2-methylallyl chloride (*ca.* 3 ml), and sodium tetraphenylboron (0.3 g, 0.9 mmol) by the procedure described in section 20.

23. **π-Allylchlorotris(triisopropyl phosphite)rhodium(III) Tetraphenylborate.**—Allyl chloride (*ca.* 5 ml) was added to a suspension of $\{Rh[P(O\text{-}i\text{-}C_3H_7)_3]_4\}B(C_6H_5)_4$ (0.5 g, 0.6 mmol) in methanol (*ca.* 10 ml) and the solution stirred at room temperature for 1 hr. The methanol and excess allyl chloride were removed under reduced pressure and the oily residue was crystallized from methanol.

24. **π-Allylchlorotris(dimethylphenylphosphine)rhodium(III) Hexafluorophosphate.**—Allyl chloride (*ca.* 10 ml) was added to a suspension of $\{Rh[P(CH_3)_2C_6H_5]_4\}PF_6$ (0.3 g, 0.4 mmol) in methanol (*ca.* 10 ml) and the mixture was stirred until complete dissolution of the solid (*ca.* 2 hr). The methanol and excess allyl chloride were removed under reduced pressure. The residue was washed with methanol and crystallized from dichloromethane–methanol.

Results and Discussion

The four-coordinate rhodium(I) compound $\{Rh[P(OCH_3)_3]_4\}B(C_6H_5)_4$ was found to add carbon monoxide reversibly to give the complex $\{Rh(CO)[P(OCH_3)_3]_4\}B(C_6H_5)_4$. This latter compound, as well as all other complexes prepared in this study, was characterized by elemental analysis (Table I) and, where appropriate, from nmr spectral intensity data. The conductivity data for these complexes are presented in Table I and are in accord with the proposed formulations.

The solid-state infrared spectrum of $\{Rh(CO)[P(OCH_3)_3]_4\}B(C_6H_5)_4$ contains a single CO stretching band at 1975 cm^{-1} consistent with a monocarbonyl derivative (Table II). The methyl resonance in the nmr spectrum of this compound associated with the trimethyl phosphite ligands occurs as a broad featureless peak (Table III) and thus a structure cannot be assigned on the basis of these data. An attempt was made to synthesize the derivative $\{Rh(CO)_2[P(OCH_3)_3]_3\}B(C_6H_5)_4$ by passing carbon monoxide into a methanol solution of $\{Rh[P(OCH_3)_3]_4\}B(C_6H_5)_4$ under reflux. There was no evidence for the formation of the dicarbonyl cation in this reaction, however. Significantly the cations $Rh(L_2)_2^+$ [$L_2 = (CH_3)_2PC_2H_4P(CH_3)_2$[4] and *cis*-$(C_6H_5)_2AsCH{=}CHAs(C_6H_5)_2$[6]] have been reported to add carbon monoxide reversibly ac-

TABLE I
COLOR, MELTING POINT, CONDUCTIVITY, AND ANALYTICAL DATA

Compound	Color	Mp,[a] °C	Conductivity,[b] ohm^{-1} cm^2 mol^{-1}	Anal, % Calcd C	Calcd H	Calcd Others	Found C	Found H	Found Others
$\{Rh(CO)[P(OCH_3)_3]_4\}B(C_6H_5)_4$	White	77–100	94	46.9	6.0	P, 13.1	46.7	5.9	P, 13.2
$\{Rh[P(OCH_3)_3]_4[C_2(CF_3)_2]\}B(C_6H_5)_4$	White	172–174	84	44.4	5.2	F, 10.6	44.4	5.3	F, 10.5
$\{Rh[P(OCH_3)_3]_4[C_2(CO_2CH_3)_2]\}B(C_6H_5)_4$	Pale yellow	109–110	86	47.5	5.9	P, 11.7	47.5	6.0	P, 11.6
cis-$\{Rh[P(OCH_3)_3]_4H_2\}B(C_6H_5)_4$	White	80–165	77	47.1	6.2	. . .	47.2	6.4	. . .
cis-$\{Rh[P(n\text{-}C_4H_9)_3]_4H_2\}B(C_6H_5)_4$	White	79–81	89	70.2	10.5	. . .	69.8	11.1	. . .
trans-$\{Rh[P(OCH_3)_3]_4HBr\}B(C_6H_5)_4$	White	129–130	86	43.3	5.8	Br, 8.0	43.0	5.8	Br, 8.3
trans-$\{Rh[P(OCH_3)_3]_4HI\}B(C_6H_5)_4$	White	133–134	84	41.3	5.5	I, 12.1	41.2	5.5	I, 12.0
cis-$\{Rh[P(OCH_3)_3]_4Br_2\}B(C_6H_5)_4$	White	147–150	86	40.1	5.3	Br, 14.8	40.4	5.2	Br, 15.1
trans-$\{Rh[P(OCH_3)_3]_4Br_2\}B(C_6H_5)_4$	Yellow	151–153	90	40.1	5.3	Br, 14.8	40.2	5.4	Br, 14.8
cis-$\{Rh[P(OCH_3)_3]_4I_2\}B(C_6H_5)_4$	Orange	154–156	92	36.9	4.8	I, 21.7	37.1	4.9	I, 21.7
trans-$\{Rh[P(OCH_3)_3]_4(CH_3)I\}B(C_6H_5)_4$	Pale yellow	147–149	94	41.9	5.6	I, 12.0	41.7	5.3	I, 11.7
$\{RhCl(C_3H_5)[P(OCH_3)_3]_3\}B(C_6H_5)_4$	White	139–141	86	49.6	6.0	Cl, 4.1	49.3	5.9	Cl, 4.2
$\{RhBr(C_3H_5)[P(OCH_3)_3]_3\}B(C_6H_5)_4$	White	134–136	91	47.2	5.7	Br, 8.7	47.0	5.9	Br, 8.8
$\{Rh(C_3H_5)[P(OCH_3)_3]_4\}[B(C_6H_5)_4]_2$	White	159–161	197	59.2	6.4	Cl, 0.0 P, 9.7	58.8	6.5	Cl, 0.0 P, 9.6
$\{Rh(C_3H_5)[P(OCH_3)_3]_4\}(PF_6)_2$	White	175	217	19.4	4.5	F, 24.5 P, 20.0	19.6	4.6	F, 24.6 P, 19.9
$\{Rh(2\text{-}CH_3C_3H_4)[P(OCH_3)_3]_4\}[B(C_6H_5)_4]_2$	White	158–161	183	59.5	6.5	. . .	59.3	6.6	. . .
$\{Rh(2\text{-}CH_3C_3H_4)[P(OCH_3)_3]_4\}(PF_6)_2$	White	151–152	211	20.4	4.6	F, 24.1 P, 19.7	20.3	4.5	F, 24.2 P, 19.5
$\{RhCl(C_3H_5)[P(OC_2H_5)_3]_3\}B(C_6H_5)_4$	White	121–123	88	54.2	7.1	Cl, 3.6	54.2	7.1	Cl, 3.4
$\{Rh(C_3H_5)[P(OC_2H_5)_3]_4\}[B(C_6H_5)_4]_2$	White	137–138	183	62.3	7.3	Cl, 0.0	62.2	7.4	Cl, 0.0
$\{Rh(C_3H_5)[P(OC_2H_5)_3]_4\}(PF_6)_2$	White	203–204	222	29.5	6.0	F, 20.8	29.8	5.9	F, 20.6
$\{Rh(2\text{-}CH_3C_3H_4)[P(OC_2H_5)_3]_4\}[B(C_6H_5)_4]_2$	White	135–137	182	62.5	7.4	Cl, 0.0	62.3	7.5	Cl, 0.0
$\{RhCl(C_3H_5)[P(O\text{-}i\text{-}C_3H_7)_3]_3\}B(C_6H_5)_4$	White	147	89	57.7	7.9	Cl, 3.2	57.8	8.0	Cl, 3.0
$\{RhCl(C_3H_5)[P(CH_3)_2C_6H_5]_3\}PF_6$	Pale yellow	144–145	120	43.9	5.2	Cl, 4.8	44.2	5.1	Cl, 5.0

[a] All compounds melt with decomposition. [b] Solutions are $\sim 10^{-3}$ *M* in acetone.

TABLE II
INFRARED DATA

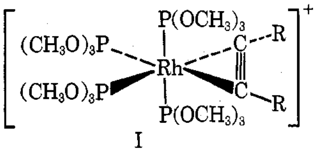
Compound	Freq,[b] cm^{-1} Measured as Nujol mull	Measured in CH_2Cl_2	Assignment
$\{Rh(CO)[P(OCH_3)_3]_4\}B(C_6H_5)_4$	1974	1997	$\gamma(CO)$
$\{Rh[P(OCH_3)_3]_4[C_2(CF_3)_2]\}B(C_6H_5)_4$	1833 s, 1803 sh, 1789 sh	1834 s, 1805 sh, 1792 sh[c]	$\gamma(CC)$
$\{Rh[P(OCH_3)_3]_4[C_2(CO_2CH_3)_2]\}B(C_6H_5)_4$	1806 s, b	1805 s, b	$\gamma(CC)$
	1702 s, 1693 s	1699 s	$\gamma(C{=}O)$
cis-$\{Rh[P(OCH_3)_3]_4H_2\}B(C_6H_5)_4$	1975 b	1976 b	$\gamma(RhH)$
cis-$\{Rh[P(n\text{-}C_4H_9)_3]_4H_2\}B(C_6H_5)_4$	2021 b	2020 b	$\gamma(RhH)$
cis-$\{Rh[P(OC_6H_5)_3]_4H_2\}B(C_6H_5)_4$	*a*	1989 b	$\gamma(RhH)$
trans-$\{Rh[P(OCH_3)_3]_4HBr\}B(C_6H_5)_4$	*a*	2072	$\gamma(RhH)$
trans-$\{Rh[P(OCH_3)_3]_4HI\}B(C_6H_5)_4$	2051	2051	$\gamma(RhH)$

[a] Not measured. [b] Abbreviations: s, strong; sh, shoulder; b, broad. [c] Concerning the appearance of more than one $C{\equiv}C$ stretching band in the infrared spectra of (free) fluorinated acetylenes, see L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1958, p 60.

cording to the scheme

$$Rh(L_2)_2^+ \underset{-CO}{\overset{+CO}{\rightleftharpoons}} Rh(L_2)_2CO^+$$

The acetylenes dimethyl acetylenedicarboxylate and hexafluorobut-2-yne were found to react readily with $\{Rh[P(OCH_3)_3]_4\}B(C_6H_5)_4$ to give the derivatives $\{Rh[P(OCH_3)_3]_4(C_2R_2)\}B(C_6H_5)_4$ (R = CO_2CH_3 and CF_3). The infrared spectra of $\{Rh[P(OCH_3)_3]_4[C_2(CO_2CH_3)_2]\}B(C_6H_5)_4$ and $\{Rh[P(OCH_3)_3]_4[C_2(CF_3)_2]\}B(C_6H_5)_4$ measured as Nujol mulls contain broad peaks at 1806 and 1833 cm^{-1}, respectively (Table II). These are assigned to the $C{\equiv}C$ stretching vibrations of the bonded acetylene. The above frequencies are consistent with the acetylenes being bonded "side-on" to the metal atom and further indicate that appreciable but not extensive back-bonding from the metal into the antibonding orbitals of the acetylene occurs.[11] Structure I is thus proposed for the cations $Rh[P(OCH_3)_3]_4(C_2R_2)^+$ (R = CO_2CH_3 and CF_3).



I

The nmr spectrum of $\{Rh[P(OCH_3)_3]_4[C_2(CF_3)_2]\}B(C_6H_5)_4$ in $CDCl_3$ contains a doublet at τ 6.35 and a triplet at τ 6.48 of equal intensity (Table III). The doublet is assigned to the methyl protons associated with the trimethyl phosphite ligands bonded trans to the acetylene group, while the triplet is assigned to the methyl protons associated with the mutually trans trimethyl phosphites. The assignment is based on previous observations for rhodium complexes containing the ligands $P(CH_3)_2C_6H_5$ and $PCH_3(C_6H_5)_2$ that coupling between trans phosphorus nuclei is strong whereas that between cis phosphorus nuclei is negligible.[12] The methyl resonances of the acetylene $C_2(CO_2CH_3)_2$ and of the trimethyl phosphite ligands in the nmr spectrum

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[11] J. P. Collman and J. W. Kang, *J. Amer. Chem. Soc.*, **89**, 844 (1967).

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

TABLE III

NMR DATA AND ASSIGNMENTS[a]

Compound	Aromatic protons	P–O–CH$_n$– protons	Other protons	Assignments
$\{Rh(CO)[P(OCH_3)_3]_4\}B(C_6H_5)_4$	2.92 m	6.44 s, b		
$\{Rh[P(OCH_3)_3]_4[C_2(CF_3)_2]\}B(C_6H_5)_4$	2.89 m	6.35 d, J_{P-H} = 11.2 6.48 t, J = 11.0[b]		
$\{Rh[P(OCH_3)_3]_4[C_2(CO_2CH_3)_2]\}B(C_6H_5)_4$[c]	2.99 m	6.18 d, J_{P-H} = 11.0 6.31 t, J = 12.3[b]	6.20 s	CH_3 of $C_2(CO_2CH_3)_2$
cis-$\{Rh[P(OCH_3)_3]_4H_2\}B(C_6H_5)_4$	2.96 m	6.46 m, J = 11.6[b]	*d*	
cis-$\{Rh[P(n\text{-}C_4H_9)_3]_4H_2\}B(C_6H_5)_4$	2.91 m	...	8.62 m 21.4 d, J_{P-H} = 126	$P(n\text{-}C_4H_9)_3$ H bonded to Rh
trans-$\{Rh[P(OCH_3)_3]_4HBr\}B(C_6H_5)_4$	2.85 m	6.32,[e] J = 11.8[b]	23.5[f]	H bonded to Rh
trans-$\{Rh[P(OCH_3)_3]_4HI\}B(C_6H_5)_5$	2.92 m	6.34,[e] J = 11.8[b]	21.8[f]	H bonded to Rh
cis-$\{Rh[P(OCH_3)_3]_4Br_2\}B(C_6H_5)_4$	2.93 m	6.18 t, J = 10.7[b] 6.36,[g] J = 11.0[b]		
trans-$\{Rh[P(OCH_3)_3]_4Br_2\}B(C_6H_5)_4$	2.90 m	6.21,[e] J = 11.3[b]		
cis-$\{Rh[P(OCH_3)_3]_4I_2\}B(C_6H_5)_4$	2.72 m	6.20 t, J = 11.2[b] 6.37 d, J_{P-H} = 10.6		
trans-$\{Rh[P(OCH_3)_3]_4(CH_3)I\}B(C_6H_5)_4$	2.95 m	6.37,[e] J = 10.6[b]	9.13,[h] J_{P-H} = 5.2, J_{Rh-H} = 2.1	CH_3 bonded to Rh

[a] τ scale; coupling constants in hertz; measured in $CDCl_3$ at 38°. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad. [b] J is the separation of outer peaks. [c] Measured in $(CD_3)_2CO$. [d] Resonances due to H bonded to Rh not observed. [e] Resonance pattern as shown in Figure 1. [f] Band width of *ca.* 40 Hz. [g] Triplet with broad central component and two sharp outer peaks. [h] Quintet of doublets.

of $\{Rh[P(OCH_3)_3]_4[C_2(CO_2CH_3)_2]\}B(C_6H_5)_4$ occur in the same region. The assignment of these peaks is based on that for the resonances of $\{Rh[P(OCH_3)_3]_4[C_2(CF_3)_2]\}B(C_6H_5)_4$ discussed above. The doublet at τ 6.18 and the triplet at τ 6.31 are associated with the trimethyl phosphite ligands trans to the acetylene and trans to each other, respectively, while the singlet at τ 6.20 is assigned to the equivalent methyl groups of the bonded acetylene (Table III).

Polymeric compounds were formed in the reaction of $\{Rh[P(OCH_3)_3]_4\}B(C_6H_5)_4$ with phenylacetylene in methanol. This contrasts with the corresponding reaction involving $\{Ir[P(OCH_3)_2C_6H_5]_4\}PF_6$ in which the acetylide complex $\{Ir[P(OCH_3)_2C_6H_5]_4(C{\equiv}C\text{-}C_6H_5)H\}PF_6$ is formed.[13]

Hydrogen was found to react readily and irreversibly with $\{Rh[P(n\text{-}C_4H_9)_3]_4\}B(C_6H_5)_4$ to give the dihydride complex $\{Rh[P(n\text{-}C_4H_9)_3]_4H_2\}B(C_6H_5)_4$. In contrast the corresponding reaction involving $\{Rh[P(OCH_3)_3]_4\}B(C_6H_5)_4$ is reversible and the product isolated, *viz.*, $\{Rh[P(OCH_3)_3]_4H_2\}B(C_6H_5)_4$, was only stable under an atmosphere of hydrogen. Further the product obtained from the reaction of $\{Rh[P(OC_6H_5)_3]_4\}B(C_6H_5)_4$ with hydrogen was so unstable under any atmosphere other than hydrogen that it could only be identified as $\{Rh[P(OC_6H_5)_3]_4H_2\}B(C_6H_5)_4$ by means of infrared spectroscopy. The decrease in stability of the dihydrides $[RhL_4H_2]B(C_6H_5)_4$ along the series $P(n\text{-}C_4H_9)_3 > P(OCH_3)_3 > P(OC_6H_5)_3$ may be related to the donor properties of the various ligands with the stronger σ donor $P(n\text{-}C_4H_9)_3$ more readily stabilizing the +3 oxidation state.

The infrared spectra of $[RhL_4H_2]B(C_6H_5)_4$ [L = $P(n\text{-}C_4H_9)_3$, $P(OCH_3)_3$, and $P(OC_6H_5)_3$] contain broad bands at 2021, 1975, and 1989 cm^{-1}, respectively; these are assigned to the Rh–H stretching vibrations (Table II). The above frequencies are consistent with the hydride groups being bonded mutually cis. The corresponding bands in the spectra of compounds containing trans hydridic groups have been shown to occur in the region of 1750–1850 cm^{-1}.[14]

The methyl resonance pattern observed in the nmr spectrum of $\{Rh[P(OCH_3)_3]_4H_2\}B(C_6H_5)_4$ is complex and is not diagnostic of either cis or trans disposition of the hydride groups (Table III). The metal hydride resonance of $\{Rh[P(n\text{-}C_4H_9)_3]_4H_2\}B(C_6H_5)_4$ occurs in the region of τ 20 as a broad doublet separated by 126 Hz (Table III). This splitting is characteristic of coupling between a hydride and a trans phosphorus nucleus and is thus consistent with a cis configuration for the cation.[14] As the derivatives $\{Rh[P(OR)_3]_4H_2\}B(C_6H_5)_4$ are unstable in solution with respect to loss of hydrogen, nmr spectral measurements in the region of τ 20 were unreliable.

$\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$ was found to react with hydrobromic and hydriodic acids to give initially the monohydrides $\{Rh[P(OCH_3)_3]_4HX\}B(C_6H_5)_4$ (X = Br and I). However the dibromide *cis*-$\{Rh[P(OCH_3)_3]_4Br_2\}B(C_6H_5)_4$ was obtained in excellent yield by treating $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$ with an excess of hydrobromic acid for a prolonged reaction time. Addition of bromine to $\{Rh[P(OCH_3)_3]_5\}B(C_6H_5)_4$ gave the trans isomer of $\{Rh[P(OCH_3)_3]_4Br_2\}B(C_6H_5)_4$ together with a small amount of the cis form. In contrast the cis isomer of $\{Rh[P(OCH_3)_3]_4I_2\}B(C_6H_5)_4$ is the sole product of the corresponding iodination reaction. $\{Rh[P(OCH_3)_3]_4\}B(C_6H_5)_4$ was found to react slowly with pure methyl iodide with cleavage of the C–I bond to form the derivative *trans*-$\{Rh[P(OCH_3)_3]_4(CH_3)I\}B(C_6H_5)_4$. The configurations of the cations in these derivatives are assigned on the basis of infrared (Table II) and nmr (Table III) spectral data.

The infrared spectra of the hydrides $\{Rh[P(OCH_3)_3]_4HX\}B(C_6H_5)_4$ (X = Br and I) contain broad peaks at 2072 and 2050 cm^{-1}, respectively, which are assigned to the Rh–H stretching modes. The above frequencies are in accord with the hydride group being bonded trans to the halogen.[4] The metal hydride resonance in the nmr spectrum of $\{Rh[P(OCH_3)_3]_4HBr\}B(C_6H_5)_4$ occurs as a multiplet centered at τ 23.5 and with a band width of *ca.* 40 Hz. The spectrum of $\{Rh[P(OCH_3)_3]_4HI\}B(C_6H_5)_4$ contains a similar hydride resonance pattern. These observations are consistent with a trans configuration for the cations $Rh[P(OCH_3)_3]_4HX^+$ with

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[13] L. M. Haines and E. Singleton, unpublished results.

[14] J. Chatt, R. S. Coffey, and B. L. Shaw, *J. Chem. Soc.*, 7391 (1965).

coupling of *ca.* 10–20 Hz between the hydride and the four equivalent ^{31}P and ^{103}Rh nuclei.[14] However the resonances were poorly resolved and no attempt was therefore made to analyze them. A splitting of the hydride resonance of *ca.* 120 Hz as a result of coupling between the hydride and a trans ^{31}P nucleus is expected for the cations of the type *cis*-Rh[P(OCH$_3$)$_3$]$_4$HX$^+$. A resonance with a pattern of the type shown in Figure 1 is observed in the region of τ 6 in the nmr spectra of the derivatives {Rh[P(OCH$_3$)$_3$]$_4$HX}B(C$_6$H$_5$)$_4$ (X = Br and I) and is assigned to the protons of the trimethyl phosphite groups. This ligand resonance pattern has also been found in the nmr spectra of derivatives of the cations M[P(OCH$_3$)$_{3-x}$(C$_6$H$_5$)$_x$]$_4$$^+$ (M = Rh[10] and Ir;[15] x = 1 and 2) and is characteristic of the four ligands and the metal atom being in the same plane.

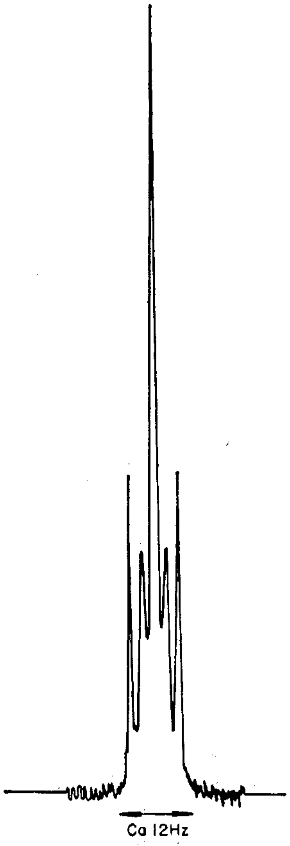


Figure 1.

The nmr spectrum of the yellow form of {Rh[P(OCH$_3$)$_3$]$_4$Br$_2$}B(C$_6$H$_5$)$_4$ also contains a ligand resonance pattern of the type shown in Figure 1 and consistent with a trans configuration for the cation. In contrast the nmr spectrum of the white isomer of {Rh[P(OCH$_3$)$_3$]$_4$Br$_2$}B(C$_6$H$_5$)$_4$ is in accord with cis disposition of the bromide groups. The sharp triplet at τ 6.18 is assigned to the methyl protons associated with the mutually trans trimethyl phosphite groups and the triplet at τ 6.36 with a broad central component and two sharp outer peaks to the methyl protons of the other trimethyl phosphite ligands. This resonance pattern results from strong phosphorus–phosphorus coupling between trans ^{31}P nuclei, weak but not negligible coupling between the ^{31}P nuclei trans to the bromide groups, and negligible coupling between the nonequivalent cis ^{31}P nuclei. The cation Rh[P(OCH$_3$)$_3$]$_4$I$_2$$^+$ is similarly assigned the cis configuration on the basis of its nmr spectrum.

The resonance at τ 9.13 in the nmr spectrum of {Rh[P(OCH$_3$)$_3$]$_4$(CH$_3$)I}B(C$_6$H$_5$)$_4$ corresponds to the methyl group bonded directly to the metal atom and occurs as a well-resolved quintet of doublets. This pattern is consistent with the cation occurring in the trans form, with the methyl protons coupling with four equivalent ^{31}P nuclei (J = 5.2 Hz), and with the ^{103}Rh nucleus (J = 2.1 Hz). The ligand resonance pattern at τ 6.37 is of the type shown in Figure 1 and, as discussed above, is also in accord with a trans configuration for the cation Rh[P(OCH$_3$)$_3$]$_4$(CH$_3$)I$^+$.

Treatment of {Rh[P(OCH$_3$)$_3$]$_5$}B(C$_6$H$_5$)$_4$ with allyl chloride at room temperature in the absence of other solvents gave two products, {RhCl(C$_3$H$_5$)[P(OCH$_3$)$_3$]$_3$}B(C$_6$H$_5$)$_4$ and {Rh(C$_3$H$_5$)[P(OCH$_3$)$_3$]$_4$}[B(C$_6$H$_5$)$_4$]$_2$. The corresponding reaction involving allyl bromide similarly yielded the two derivatives {RhBr(C$_3$H$_5$)[P(OCH$_3$)$_3$]$_3$}B(C$_6$H$_5$)$_4$ and {Rh(C$_3$H$_5$)[P(OCH$_3$)$_3$]$_4$}[B(C$_6$H$_5$)$_4$]$_2$. The dipositive cationic complex is the major product in these reactions however. Further, when methanol was used as the solvent in the reaction of {Rh[P(OCH$_3$)$_3$]$_5$}[anion] [anion = PF$_6$ and B(C$_6$H$_5$)$_4$] with either allyl chloride or allyl bromide, {Rh(C$_3$H$_5$)[P(OCH$_3$)$_3$]$_4$}[anion]$_2$ was the sole product. {Rh(2-CH$_3$C$_3$H$_4$)[P(OCH$_3$)$_3$]$_4$}[B(C$_6$H$_5$)$_4$]$_2$ was obtained by treating {Rh[P(OCH$_3$)$_3$]$_5$}B(C$_6$H$_5$)$_4$ with 2-methylallyl chloride in the absence of other solvents; attempts to isolate the complex {RhCl(2-CH$_3$C$_3$H$_4$)[P(OCH$_3$)$_3$]$_3$}B(C$_6$H$_5$)$_4$ from this reaction were unsuccessful.

In contrast treatment of {Rh[P(OC$_2$H$_5$)$_3$]$_5$}B(C$_6$H$_5$)$_4$ with pure allyl chloride at room temperature yielded {RhCl(C$_3$H$_5$)[P(OC$_2$H$_5$)$_3$]$_3$}B(C$_6$H$_5$)$_4$ only. Significantly when methanol was employed as solvent in the reaction of allyl chloride with {Rh[P(OC$_2$H$_5$)$_3$]$_5$}[anion] [anion = PF$_6$ and B(C$_6$H$_5$)$_4$], {Rh(C$_3$H$_5$)[P(OC$_2$H$_5$)$_3$]$_4$}[anion]$_2$ was formed as the sole product. It is thus possible to prepare the derivatives {RhCl(C$_3$H$_5$)[P(OC$_2$H$_5$)$_3$]$_3$}[anion] and {Rh(C$_3$H$_5$)[P(OC$_2$H$_5$)$_3$]$_4$}[anion]$_2$ selectively by correct choice of the solvent medium. No reaction was observed between {Rh[P(OC$_2$H$_5$)$_3$]$_5$}B(C$_6$H$_5$)$_4$ and 2-methylallyl chloride in the absence of other solvents and using the same conditions as those employed in the corresponding reaction involving allyl chloride. However, 2-methylallyl chloride was found to react readily with {Rh[P(OC$_2$H$_5$)$_3$]$_5$}B(C$_6$H$_5$)$_4$ in methanol to give {Rh(2-CH$_3$C$_3$H$_4$)[P(OC$_2$H$_5$)$_3$]$_4$}[B(C$_6$H$_5$)$_4$]$_2$.

The four-coordinate derivatives {Rh[P(OR)$_3$]$_4$}B(C$_6$H$_5$)$_4$ (R = CH$_3$ and C$_2$H$_5$) were observed to give {Rh(C$_3$H$_5$)[P(OR)$_3$]$_4$}[B(C$_6$H$_5$)$_4$]$_2$ on treatment with allyl chloride in methanol, as observed for the five-coordinate analogs. In contrast the compounds {Rh[P(O-*i*-C$_3$H$_7$)$_3$]$_4$}B(C$_6$H$_5$)$_4$ and {Rh[P(CH$_3$)$_2$C$_6$H$_5$]$_4$}PF$_6$ were found to react with allyl chloride in methanol to form the chloro complexes {RhCl(C$_3$H$_5$)[P(O-*i*-C$_3$H$_7$)$_3$]$_3$}B(C$_6$H$_5$)$_4$ and {RhCl(C$_3$H$_5$)[P(CH$_3$)$_2$C$_6$H$_5$]$_3$}PF$_6$, respectively.

The nature of the bonding of the allyl group in the complexes {RhX(C$_3$H$_5$)[P(OR)$_3$]$_3$}B(C$_6$H$_5$)$_4$ (X = Cl, R = CH$_3$, C$_2$H$_5$, *i*-C$_3$H$_7$; X = Br, R = CH$_3$) could not be established from nmr data as the resonances asso-

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

TABLE IV

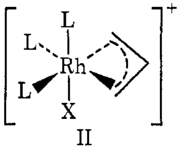
NMR DATA AND ASSIGNMENTS FOR ALLYL DERIVATIVES[a]

Compound	Aromatic protons	P–O–CH$_n$– protons	Other protons	Assignments
$\{RhCl(C_3H_5)[P(OCH_3)_3]_3\}B(C_6H_5)_4$	2.86 m	6.35 t,[b] $J = 11.1$[c] 6.69 d, $J_{P-H} = 11.6$	5.03 m, 5.82[d]	C_3H_5
$\{RhBr(C_3H_5)[P(OCH_3)_3]_3\}B(C_6H_5)_4$	2.83 m	6.27 t,[b] $J = 11.0$[c] 6.61 d, $J_{P-H} = 11.1$	4.97 m, 5.76[d]	C_3H_5
$\{Rh(C_3H_5)[P(OCH_3)_3]_4\}(PF_6)_2$[e]		5.95[f]	[g]	
$\{Rh(2\text{-}CH_3C_3H_4)[P(OCH_3)_3]_4\}(PF_6)_2$[e]		5.97[f]	7.65 s, b[g]	CH_3 of $2\text{-}CH_3C_3H_4$
$\{RhCl(C_3H_5)[P(OC_2H_5)_3]_3\}B(C_6H_5)_4$	2.86 m	5.88[h] 6.23 q, $J_{P-H} = J_{H-H} = 6.8$	4.84 m, 6.58 m 8.74 t, $J_{H-H} = 6.8$ 8.86 t, $J_{H-H} = 6.8$	C_3H_5 CH_3 of $P(OC_2H_5)_3$
$\{Rh(C_3H_5)[P(OC_2H_5)_3]_4\}[B(C_6H_5)_4]_2$[e]	3.01 m	5.68 m	8.55 t, $J_{H-H} = 7.1$[g] 8.62 t, $J_{H-H} = 7.1$	CH_3 of $P(OC_2H_5)_3$
$\{Rh(2\text{-}CH_3C_3H_4)[P(OC_2H_5)_3]_4\}[B(C_6H_5)_4]_2$[e]	3.01 m	5.65 m	7.63 s, b[g] 8.55 t, $J_{H-H} = 7.1$ 8.60 t, $J_{H-H} = 7.1$	CH_3 of $2\text{-}CH_3C_3H_4$ CH_3 of $P(OC_2H_5)_3$
$\{RhCl(C_3H_5)[P(O\text{-}i\text{-}C_3H_7)_3]_3\}B(C_6H_5)_4$	2.84 m	5.76 m	8.61 d, $J_{H-H} = 6.2$[g] 8.66 d, $J_{H-H} = 6.0$	CH_3 of $P(O\text{-}i\text{-}C_3H_7)_3$
$\{RhCl(C_3H_5)[P(CH_3)_2C_6H_5]_3\}PF_6$	2.42 m	...	4.70 m, 5.84 m 8.21 d, $J = 9.5$ 8.67 d, $J = 10.0$	C_3H_5 CH_3 of $P(CH_3)_2C_6H_5$

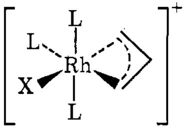
[a] τ scale; coupling constants in hertz; measured in $CDCl_3$ at 38°. Abbreviations: s, singlet; d, doublet; t, triplet; q, quintet; m, multiplet; b, broad. [b] Triplet with broad central component and two sharp outer peaks. [c] J is the separation of outer peaks. [d] Triplet of triplets. [e] Measured in $(CD_3)_2CO$. [f] Multiplet of sharp singlets. [g] Resonances due to protons of C_3H_5 or C_3H_4 of $2\text{-}CH_3C_3H_4$ not observed. [h] Quintet ($J_{H-H} = 7.0$) of triplets with broad central components and two sharp outer peaks ($J = 7.0$[c]).

ciated with the C_3H_5 group occur in the same region as those corresponding to the protons associated with the group P–O–CH$_n$– (Table IV). $\{RhCl(C_3H_5)[P(CH_3)_2C_6H_5]_3\}PF_6$ was insufficiently soluble in $CDCl_3$ or $(CD_3)_2CO$ for its nmr spectrum to be measured in either of these solvents, while the allyl resonances in the nmr spectrum recorded in $(CD_3)_2SO$ are partially obscured by those due to trace amounts of water in the solvent. It is assumed, however, that the cations of the type $RhX(C_3H_5)L_3^+$ are six-coordinate and thus the allyl group is necessarily π bonded to the metal atom. The absence of peaks in the region of 1610 cm^{-1} in the infrared spectra of these derivatives is consistent with this proposal.

Two structures are possible for six-coordinate species of the type $RhX(C_3H_5)L_3^+$, *viz.*, II and III. The nmr spectral intensity data for the derivatives $\{RhX(C_3H_5)[P(OR)_3]_3\}B(C_6H_5)_4$ ($X = Cl$, $R = CH_3$, C_2H_5, $i\text{-}C_3H_7$; $X = Br$, $R = CH_3$) and $\{RhCl(C_3H_5)[P(CH_3)_2C_6H_5]_3\}PF_6$ (Table IV) demonstrate that the cations contain two equivalent ligands and one nonequivalent ligand, consistent with these structures. The structures of these cations were established uniquely on the basis of the assumption that coupling between the trans ^{31}P nuclei is strong but that between cis ^{31}P nuclei is either negligible or is appreciable but not strong. For instance the nmr spectrum of $\{RhCl(C_3H_5)[P(CH_3)_2C_6H_5]_3\}PF_6$ which contains two doublets corresponding to the methyl protons and of relative intensity 2:1 is readily explained in terms of structure II, with negligible phosphorus–phosphorus coupling between the two equivalent ^{31}P nuclei. The spectrum of $\{RhCl(C_3H_5)[P(OCH_3)_3]_3\}B(C_6H_5)_4$ contains a triplet with a broad central component and two sharp outer peaks centered at τ 6.35 and a doublet at τ 6.69 of relative intensities 2:1. These features favor structure II and are in accord with appreciable but not strong phosphorus–phosphorus coupling between the two equivalent ^{31}P nuclei and negligible coupling between these two ^{31}P nuclei and the ^{31}P nucleus of the nonequivalent trimethyl phosphite ligand. A similar coupling pattern is observed in the nmr spectra of $\{RhBr(C_3H_5)[P(OCH_3)_3]_3\}B(C_6H_5)_4$ and $\{RhCl(C_3H_5)[P(OC_2H_5)_3]_3\}B(C_6H_5)_4$ and on this basis structure II is favored. The resonance associated with the group P–O–CH< in the nmr spectrum of $\{RhCl(C_3H_5)[P(O\text{-}i\text{-}C_3H_7)_3]_3\}B(C_6H_5)_4$ occurs as a broad multiplet and thus provides no evidence for the structure of the cation.

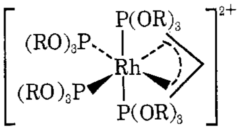


II



III

The determination of the nature of the rhodium–allyl bond in the compounds $\{Rh(2\text{-}RC_3H_4)[P(OCH_3)_3]_4\}[anion]_2$ [$R = H$, CH_3, anion $= PF_6$, $B(C_6H_5)_4$] and $\{Rh(2\text{-}RC_3H_4)[P(OC_2H_5)_3]_4\}[anion]_2$ [$R = H$, anion $= PF_6$, $B(C_6H_5)_4$; $R = CH_3$, anion $= B(C_6H_5)_4$] from the nmr spectral data was again not possible (Table IV). The allyl resonances in the spectra were partly obscured by the resonances corresponding to the protons associated with the P–O–CH$_n$– groups. Furthermore the peaks corresponding to the methyl of the methylallyl group in the nmr spectra of the complexes $\{Rh(2\text{-}CH_3C_3H_4)[P(OR)_3]_4\}[anion]_2$ [$R = CH_3$, C_2H_5, anion $= B(C_6H_5)_4$; $R = CH_3$, anion $= PF_6$] are broad and ill defined, suggesting either dynamic behavior or dissociation of the allyl group in solution. It is assumed however that the dipositive cations are six-coordinate with the allyl group being π bonded (structure IV). The observation that the solid-state infrared spectra of these derivatives contain no bands that can be associated with a σ-bonded allyl group is consistent with this structure.

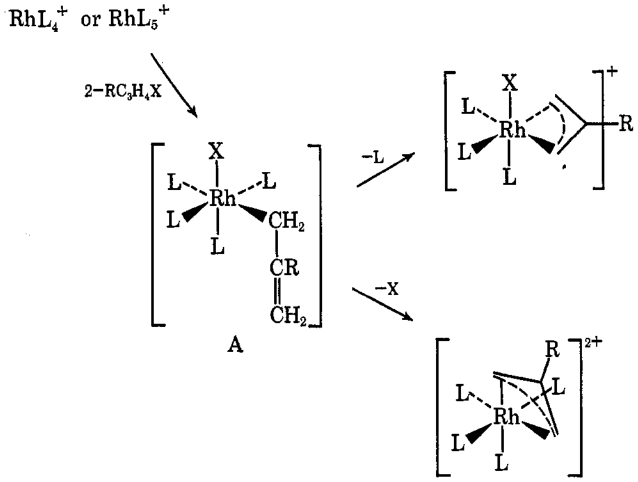


IV

The resonances associated with the P–O–CH$_n$–

groups in the nmr spectra of these derivatives are very complex and are thus not further discussed. However, the ligand methyl resonances in the spectra of the derivatives $\{Rh(2\text{-}RC_3H_4)[P(OC_2H_5)_3]_4\}[anion]_2$ occur as two triplets of equal intensity, which is consistent with structure IV.

The reactions of the cations $Rh[P(OR)_3]_5^+$ (R = CH_3, C_2H_5) and RhL_4^+ $\{L = P(OR)_3$ [R = CH_3, C_2H_5, $i\text{-}C_3H_7$], $P(CH_3)_2C_6H_5\}$ with allyl halides, $2\text{-}R'C_3H_4X$, can be rationalized in terms of a general mechanism involving a σ-allyl species, A, as intermediate, *viz.*



The unbonded olefinic group in the intermediate A effects either displacement of the halide group to give a dipositive cation $Rh(\pi\text{-}2\text{-}R'C_3H_4)L_4^{2+}$ or replacement of a neutral ligand to form the unipositive cation $RhX(\pi\text{-}2\text{-}R'C_3H_4)L_3^+$. Attempts were made to isolate the proposed σ-allyl intermediates but these were unsuccessful; this is attributed to the high intramolecular reactivity of these species. However, the preferential formation of the dipositive cations $Rh(\pi\text{-}2\text{-}R'C_3H_4)[P(OR)_3]_4^{2+}$ (R′ = H, CH_3; R = CH_3, C_2H_5) in methanol is consistent with the proposed mechanism; methanol being a powerful ionizing solvent promotes the displacement of a halide group in preference to a neutral ligand from the intermediate A. It is interesting that, of the cations RhL_4^+ and RhL_5^+ treated with allyl halides, only those containing the ligands $P(OCH_3)_3$ and $P(OC_2H_5)_3$ gave dipositive cations of the type $Rh(\pi\text{-}2\text{-}RC_3H_4)L_4^{2+}$. The reaction of allyl chloride with the cations RhL_4^+ [L = $P(O\text{-}i\text{-}C_3H_7)_3$, $P(CH_3)_2C_6H_5$] using methanol as solvent gave the chloro species $RhCl(\pi\text{-}C_3H_5)L_3^+$ as the sole products.

Halogen displacement, similar to that proposed above, has been reported for a series of iridium–σ-allyl complexes.[16] Thus $IrCl_2(\sigma\text{-}C_3H_5)(CO)[P(CH_3)_2C_6H_5]_2$ has been found to be converted to the cationic complex $\{IrCl(\pi\text{-}C_3H_5)(CO)[P(CH_3)_2C_6H_5]_2\}B(C_6H_5)_4$ in methanol in the presence of sodium tetraphenylboron. The conversion of σ- to π-allyl complexes as a result of ligand replacement by the olefinic group of the σ-allyl group is well established. For instance $Mn(CO)_5(\sigma\text{-}C_3H_5)$ readily loses carbon monoxide on heating to give the π-allyl derivative $Mn(CO)_4(\pi\text{-}C_3H_5)$.[17] However, few examples are known in which the olefinic group of a σ-allyl group effects either ligand replacement or halogen displacement in the same molecule. A pertinent example is the reaction of the cobalt(I) complex $Co(\pi\text{-}C_5H_5)(CO)_2$ with allyl iodide in tetrahydrofuran to give the two products $[Co(\pi\text{-}C_3H_5)(\pi\text{-}C_5H_5)(CO)]I$ and $CoI(\pi\text{-}C_3H_5)(\pi\text{-}C_5H_5)$.[18]

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Platinum(II)–Olefin Complexes Containing Amino Acids. II. Preparation and Structure of Chloro(L-prolinato)(olefin)platinum(II) Complexes[1]

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Received November 23, 1970

Seven complexes of the type PtCl(L-prolinato)(olefin) have been synthesized, and their diastereoisomers isolated by crystallization from suitable solvents. The absolute configurations of these isomers have been elucidated from their CD spectra. The rate of racemization of diastereoisomers has been related to the relative strength of the metal–olefin bond.

An enantiomeric pair is produced when an olefin such as propylene or *trans*-2-butene coordinates to a metal through a π bond. In 1964, Paiaro and Panunzi[2] examined such an isomerism by resolving diastereoisomers of the type *trans*-$PtCl_2$((*R*)- or (*S*)-α-phenethylamine)(olefin).[3] However, the diastereoisomers of this type often give an oily product and are difficult to isolate in a crystalline form. In the previous paper,[4] we have reported the preparation and structure of several platinum(II)–ethylene complexes containing various amino acids. These olefin complexes containing amino acids can be prepared and their diastereoisomers can be iso-

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[1] This work was supported by American Chemical Society–Petroleum Research Fund unrestricted research grant (3318–C3,5).

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