droxypentaaquochromium(III) ion, and sulfitopentaaquochromium(III) ion; these derived rate constants are given in Table IV. The relative reactivities of aquochromium(III) ion, hydroxychromium(III) ion, and sulfitochromium(III) ion toward thiocyanate ion are approximately 1:30:1500 and toward chloride ion are approximately 1:700:1000.

TABLE IV
SECOND-ORDER RATE CONSTANTS
DEFINED BY THE RATE LAW[a]

$$d[CrX^{2+}]/dt = k[Cr^{III}][X^-] \qquad (t = 25°)$$

Cr^{III} species	$X^- = NCS^-$	$X^- = Cl^-$
$Cr(OH_2)_6^{3+}$	2×10^{-6} [b]	3×10^{-8} [d]
$Cr(OH_2)_5OH^{2+}$	6×10^{-5} [b]	2×10^{-5} [d]
$Cr(OH_2)_5OSO_2^+$	3×10^{-3} [c]	3×10^{-5} [e]

[a] Dimensions of k are l. mol^{-1} sec^{-1}. [b] From ref 20. [c] Calculated from the equilibrium quotient[10] and the rate constant for aquation measured in this work. Value measured directly in this work (see text) agrees with this value. [d] From combining data of ref 19 ($I = 1.0$ *M*) and equilibrium data in R. J. Baltisberger and E. L. King, *J. Amer. Chem. Soc.*, **86**, 795 (1964). [e] Calculated from equilibrium data in the reference cited in *d* and rate of aquation obtained in the present study.

The question of whether the labilizing effect of sulfite is a trans effect, as it is in the sulfur-bondedamminesulfitocobalt(III) species,[2a] was explored in the aquation reactions of isomeric bis(isothiocyanato)-chromium(III) species. There is, at most, slight evidence for the labilizing effect of sulfite ion or hydroxide ion being attributable to a trans effect. Comparing aquation rate constants for the two isomers, the ratio for the uncatalyzed pathways (k_{cis}/k_{trans}) is 2.3/2.8 = 0.82, and for the sulfite-catalyzed pathway the value is 15/5.9 = 2.5. The corresponding ratio for the pathways involving transition states of the composition $\{Cr(OH)(NCS)_2\}^{\ddagger}$ is $2.0 \times 10^{-10}/3.8 \times 10^{-11} = 5.3$. Before a completely rational comparison of these ratios can be made, one would have to know the equilibrium constants for association of sulfite with the two isomeric bis species and also the acid dissociation constant for the isomeric bis species. These values are not known. The problem is complicated further by the possibility of cis bis species forming isomeric species upon associating with sulfite ion or hydroxide ion. Of course, the simple presence of the inverse hydrogen ion concentration term and the sulfite ion concentration term in the rate law for aquation of the trans isomer shows that the effect of neither ion can be solely a trans effect. It would appear, therefore, that oxygen-donating sulfite and hydroxide as ligands exert less of a trans effect than sulfur-donating sulfite as a ligand; this conclusion is consistent with trends in trans-activating ability of ligands discussed by Basolo and Pearson.[29]

The rate law for conversion of $Cr_2(OH)(OSO_2)^{3+}$ to $Cr(OH_2)_6^{3+}$ is consistent with the mechanism

$$Cr_2(OH)(OSO_2)^{3+} + H^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Cr_2OSO_2^{4+} + H_2O$$

$$Cr_2OSO_2^{4+} \xrightarrow{k_3} 2Cr^{3+} + SO_3^{2-}$$

$$Cr_2OSO_2^{4+} + SO_3^{2-} \xrightarrow{k_4} 2Cr^{3+} + 2SO_3^{2-}$$

with a, b, and c of the empirical rate law identified as $a = k_1k_3/(k_2 + k_3)$, $b = k_1k_4Q/(k_2 + k_3)$, and $c = k_4Q/(k_2 + k_3)$, where $Q = [H^+]^2[SO_3^{2-}]/[SO_2]$. The value of k_1 is obtainable from the empirical parameters: $k_1 = b/c = 3.3 \times 10^{-4}$ l. mol^{-1} sec^{-1}. This value of k_1 is only slightly larger than the analogous rate constant for ring opening of $Cr_2(OH)_2^{4+}$, found by Thompson[3b] to be 9×10^{-5} l. mol^{-1} sec^{-1}.

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[29] F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," Wiley, New York, N. Y., 1967, pp 369–375.

CONTRIBUTION FROM THE MALLINCKRODT LABORATORY, DEPARTMENT OF CHEMISTRY,
HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS 02138

π-Bonded Complexes of the Tetraphenylborate Ion with Rhodium(I) and Iridium(I)

BY RICHARD R. SCHROCK AND JOHN A. OSBORN*

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Several complexes of tetraphenylborate ion with Rh(I) and Ir(I) have been isolated in which tetraphenylborate coordinates to the metal *via* a π(h^6)-bonded interaction. The protonation of a π-cyclopentadienyl complex to yield cyclopentadienetetraphenylboratorhodium(I) was found by deuteration studies to give exclusively endo product. The nmr and infrared spectra of these complexes are discussed.

Introduction

Tetraphenylborate ion has been widely used as a counterion for the isolation of cationic species from solution. During our investigation[1,2] of the catalytic properties of the weakly solvated cationic species of the type $Rh(P(C_6H_5)_3)_2H_2S_2^+$ (S = solvent), totally different behavior was found using tetraphenylborate as anion in place of perchlorate or hexafluorophosphate. Further investigation of this anomalous behavior shows that tetraphenylborate can readily coordinate to transition metals *via* a π-bonded interaction of one of

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* To whom correspondence should be addressed.

[1] J. R. Shapley, R. R. Schrock, and J. A. Osborn, *J. Amer. Chem. Soc.*, **91**, 2816 (1969).

[2] R. R. Schrock and J. A. Osborn, *Chem. Commun.*, 567 (1970).

TABLE I

ANALYSES OF COMPOUNDS PREPARED IN THIS WORK

Compound	Color	% C		% H		% other	
		Calcd	Found	Calcd	Found	Calcd	Found
$Rh(norbornadiene)[B(C_6H_5)_4]$[a]	Pale yellow	72.40	72.46	5.49	5.46	2.10	2.30 (B)
						0.00	0.00 (Cl)
$Rh(1,3\text{-butadiene})[B(C_6H_5)_4]$[b]	Yellow	70.62	70.31	5.50	5.61		
$Rh(2,3\text{-dimethyl-1,3-butadiene})[B(C_6H_5)_4]$	Yellow	71.45	71.71	6.00	6.13		
$Rh(cyclopentadiene)[B(C_6H_5)_4]$	Yellow	71.34	70.42	5.37	5.27		
$Rh(1,3\text{-cyclohexadiene})[B(C_6H_5)_4]$[c]	Yellow	71.74	71.12	5.62	5.74		
$Rh(1,5\text{-hexadiene})[B(C_6H_5)_4]$	Yellow	71.45	70.95	6.00	5.93		
$Rh(1,5\text{-cyclooctadiene})[B(C_6H_5)_4]$	Pale yellow	72.47	71.69	6.09	6.01	0.00	0.00 (Cl)
$Rh(1,3,5,7\text{-cyclooctatetraene})[B(C_6H_5)_4]$	Pale yellow	73.03	68.87	5.36	4.35	0.00	0.78 (Cl)[d]
$Rh(ethylene)_2[B(C_6H_5)_4]$	Yellow	70.36	69.99	5.90	5.93	0.00	0.00 (Cl)
$Rh[P(C_6H_5)_3]_2[B(C_6H_5)_4]$	Red-brown	76.12	75.40	5.32	5.54	6.54	6.61 (P)
$Ir(1,5\text{-cyclooctadiene})[B(C_6H_5)_4]$	White	62.03	61.60	5.21	5.49		
$Ir(1,5\text{-hexadiene})[B(C_6H_5)_4]$	White	60.70	60.03	5.09	5.05	1.82	1.77 (B)
						0.00	0.00 (Cl)
$[Rh(\pi\text{-}C_5H_5)(H)(P(C_6H_5)_3)_2]^+BF_4^-$	Yellow	63.10	63.53	4.65	4.84	7.94	8.13 (P)

[a] Molecular weight in 1,2-dichloroethane: calcd, 514; found, 509. [b] Molecular weight: calcd, 476; found, 496. [c] Molecular weight: calcd, 502; found, 515. [d] Sample could not be obtained analytically pure.

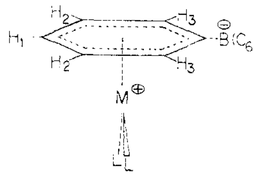

Figure 1.—Idealized sketch of a bonded tetraphenylborate complex.[3]

the phenyl rings (see Figure 1). The preparation of several such complexes is reported here and their nmr and ir spectra are discussed. During the course of this work, the X-ray structure of an analogous complex was communicated[3] which confirms structural assignments which we have proposed here.

Experimental Section

Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach über Engelskirchen, Germany; Galbraith Laboratories Inc., Knoxville, Tenn.; and Amherst Microanalytical Laboratory Inc., Amherst, Mass. Infrared spectra were recorded on a Perkin-Elmer 337 grating spectrometer (4000–400 cm^{-1}). Proton resonance spectra were measured on a Varian Associates HA-100 Instrument. Conductivities were measured with a Model 31 conductivity bridge from Yellow Springs Instrument Co., Inc., Yellow Springs, Ohio. Molecular weights were measured with a Model 301A vapor pressure osmometer from Mechrolab Inc., Mountain View, Calif. Analytical data are collected together in Table I. Spectroscopic data are presented in Tables II and III.

Preparation of the Complexes. Tetraphenylboratobis(triphenylphosphine)rhodium(I), $Rh[B(C_6H_5)_4][P(C_6H_5)_3]_2$.—A solution of $[Rh(C_7H_8)\{P(C_6H_5)_3\}_2]^+[B(C_6H_5)_4]^-$ (1 g) (C_7H_8 = norbornadiene) in dichloromethane (15 ml) was stirred vigorously under an atmosphere of hydrogen for 2 hr. On allowing the solution to stand for a further 12 hr, the product crystallized out as red-brown needles, which were filtered and air dried; yield 0.64 g (70%). The low solubility of the product did not allow recrystallization from any of the common solvents.

Complexes of the Type $Rh(diolefin)[B(C_6H_5)_4]$. Method 1.—The same procedure was used for the following diolefins: norbornadiene, 1,5-cyclooctadiene, 2,3-dimethyl-1,3-butadiene, 1,5-hexadiene, 1,3,5,7-cyclooctatetraene, and 1,3-cyclohexadiene. $RhCl_3 \cdot 3H_2O$ (250 mg) was dissolved in water (1 ml) and $Na[B(C_6H_5)_4]$ (1 g) in methanol (20 ml) was added. The appropriate diolefin (1 ml) was then added and the solution was allowed to stand until crystals were deposited. For 1,5-hexadiene the reaction was essentially complete after *ca.* 1 hr whereas a good yield of the 2,3-dimethylbutadiene product required 10–12 hr. Other dienes were intermediate in behavior. The yellow crystalline products were filtered and air dried; yields *ca.* 70–80%. The complexes could be recrystallized from dichloromethane–ethanol except for the sparingly soluble cyclooctatetraene and 1,5-cyclooctadiene complexes. The analytical data for these complexes are collected in Table I. An alternative procedure permits the reactions to be accelerated by heating the above solutions to *ca.* 50° and, where necessary, using a sealed system.

Method 2—Used for $Rh(1,3\text{-butadiene})[B(C_6H_5)_4]$.—$RhCl_3 \cdot 3H_2O$ (1 g) was dissolved in water (5 ml) and a solution of $NaB(C_6H_5)_4$ (3 g) in methanol (25 ml) was added. 1,3-Butadiene was bubbled through the solution for 4 hr and the resultant solution was allowed to stand overnight at −20°. The yellow crystalline product was filtered and recrystallized from dichloromethane–methanol; yield 460 mg (24%).

Method 3—Used for $Rh(C_5H_6)[B(C_6H_5)_4]$.—$Rh(\pi\text{-}C_5H_5)(C_2H_4)_2$ (250 mg) was dissolved in methanol (10 ml) containing $NaB(C_6H_5)_4$ (150 mg) and a 70% aqueous perchloric acid solution (160 mg) was added dropwise with vigorous stirring. Fine yellow crystals formed immediately and, after *ca.* 5 min, were filtered off, washed with methanol and diethyl ether, and dried under vacuum; yield 140 mg (34%). Recrystallization could be carried out from dichloromethane–methanol but some decomposition generally occurred. The yield may be increased slightly (to *ca.* 50%) if the reactants are mixed at −70° in the absence of air and allowed to warm to room temperature.

$Rh(C_5H_5D)[B(C_6H_5)_4]$ was prepared in an analogous manner. $Rh(\pi\text{-}C_5H_5)(C_2H_4)_2$ (100 mg) and $NaB(C_6H_5)_4$ (155 mg) were placed under nitrogen, 1.5 ml of CH_3OD was added, and the mixture was cooled to −70°. A solution of 70% aqueous perchloric acid (70 mg) in 1 ml of CH_3OD was added and the solution was warmed to room temperature. The product was isolated as above.

Method 4—Used for $Rh(C_7H_8)[B(C_6H_5)_4]$.—As an alternative to method 1, the following procedure was also developed. $[Rh(C_7H_8)Cl]_2$ (200 mg) in dichloromethane (4 ml) was added dropwise to a solution of $NaB(C_6H_5)_4$ (284 mg) in methanol (20 ml). Pale yellow crystals quickly deposited, and after 10 min the solution was filtered, and the crystals were washed with methanol and diethyl ether; yield 380 mg (86%). The product could be recrystallized in good yield from dichloromethane–methanol.

Bis(ethylene)tetraphenylboratorhodium(I), $Rh(C_2H_4)_2[B(C_6H_5)_4]$.—This was conveniently prepared by treating a solution as in method 2 (above) with ethylene (in place of butadiene)

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(3) H. J. Nolte, G. Gafner, and L. M. Haines, *Chem. Commun.*, 1406 (1969)

TABLE II

SOLID-STATE INFRARED SPECTRA IN THE 1500–1350-CM^{-1} REGION[a]

Rh(norbornadiene)[B(C_6H_5)$_4$]	1480 s, 1455 s, 1425 s, 1390 s
Rh(1,3-butadiene)[B(C_6H_5)$_4$]	1480 s, 1450 s, 1430 s, 1390 s
Rh(2,3-dimethyl-1,3-butadiene)[B(C_6H_5)$_4$]	1478 s, 1445 s, 1424 s, 1390 m, 1375 s
Rh(cyclopentadiene)[B(C_6H_5)$_4$]	1482 s, 1447 s, 1425 s, 1390 s, 1372 m
Rh(1,3-cyclohexadiene)[B(C_6H_5)$_4$]	1478 s, 1451 s, 1427 s, 1389 s
Rh(1,5-hexadiene)[B(C_6H_5)$_4$]	1490 w, sh, 1480 s, 1440 m, sh, 1425 s, 1390 s
Rh(1,5-cyclooctadiene)[B(C_6H_5)$_4$]	1478 s, 1455 s, 1426 s, 1392 s
Rh(1,3,5,7-cyclooctatetraene)[B(C_6H_5)$_4$]	1480 s, 1450 s, 1426 s, 1389 s
Rh(ethylene)$_2$[B(C_6H_5)$_4$]	1482 m, 1456 s, 1437 w, sh, 1427 s, 1390 m
Rh[P(C_6H_5)$_3$]$_2$[B(C_6H_5)$_4$]	1480 s, 1460 m, 1430 s,[b] 1388 m
Rh[P(OCH_3)$_3$]$_2$[B(C_6H_5)$_4$][c]	1480 s, 1455 s, 1435 m, sh, 1430 s, 1385 m
Ir(1,5-cyclooctadiene)[B(C_6H_5)$_4$]	1480 s, 1450 s, 1425 s, 1390 s
Ir(1,5-hexadiene)[B(C_6H_5)$_4$]	1480 s, 1445 s, 1425 s, 1385 s
Rh[P(OCH_3)$_3$]$_5$$^+$[B($C_6H_5$)$_4$]$^-$ [c]	1480 s, 1455 s, 1430 s
Rh[P(C_6H_5)$_3$]$_2$(norbornadiene)$^+$[B(C_6H_5)$_4$]$^-$ [d]	1480 s, 1435 s[b]
Na^+[B(C_6H_5)$_4$]$^-$	1480 s, 1452 vw, 1425 s, 1390 vw

[a] Spectra were measured in Nujol on a Perkin-Elmer 337 grating spectrometer and are accurate to *ca.* ±3 cm^{-1}. The predominant four-band structure is also observed in dichloromethane solution. Abbreviations: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. The last three have been included as references. [b] Peak has sharp shoulders. [c] Prepared as in ref 3. [d] See ref 1.

TABLE III

PROTON NMR SPECTRA OF SOME BONDED TETRAPHENYLBORON COMPOUNDS[a]

	Bonded phenyl ring protons[b]			Diene protons[c]			
	H_1	H_2	H_3	Olefinic	Methyne	Methylene	Methyl
Rh(norbornadiene)[B(C_6H_5)$_4$]	3.38	3.93	3.53	6.35 (4)	6.70 (2)	8.97 (2)	...
Rh(1,3-butadiene)[B(C_6H_5)$_4$]	3.40	3.69	3.30	5.03 (2),[b,d] 7.78 (2),[e] 9.10 (2)[f]	...	...	...
Rh(2,3-dimethyl-1,3-butadiene)[B(C_6H_5)$_4$]	...3.90...[j]		3.22	7.23 (2), 9.17 (2)	...	...	8.01 (6)
Rh(cyclopentadiene)[B(C_6H_5)$_4$]	...3.66...[j]		3.33	4.62 (2),[b] 6.18 (2)	...	7.20 (2)[g]	...
Rh(1,3-cyclohexadiene)[B(C_6H_5)$_4$]	...3.62...[j]		3.26	5.00 (2),[b] 5.98 (2)	...	8.70 (4)[h]	...
Rh[P(OCH_3)$_3$]$_2$[B(C_6H_5)$_4$][i]	3.19	4.16	3.5				

[a] Assignments are in τ values relative to tetramethylsilane at τ 10. [b] Measured in 1,2-dichloroethane. (See Figure 1 for assignments of phenyl protons.) [c] Measured in dichloromethane except where noted. [d] Basically a triplet. [e] A doublet of multiplets. [f] A doublet of triplets with J (doublet) = 9 Hz. [g] A quartet (see text). [h] A broad symmetrical multiplet. [i] See ref 3. [j] Complex overlapping resonances (see text).

for 2 hr. The fine pale yellow crystals were filtered off, washed with methanol and diethyl ether, and air dried; yield 90 mg (20%).

Complexes of the Type Ir(diolefin)[B(C_6H_5)$_4$] (Diolefin = 1,5-Cyclooctadiene or 1,5-Hexadiene).—$IrCl_3 \cdot 3H_2O$ (250 mg) dissolved in water (2 ml) was added to a solution of NaB(C_6H_5)$_4$ (750 mg) in ethanol (12 ml). The appropriate diene (1 ml) was then added and the solution refluxed for 1 hr. On cooling, the fine white crystalline product was filtered off, washed with methanol and diethyl ether, and air dried. Ir(1,5-cyclooctadiene)[B(C_6H_5)$_4$] was obtained in 50% yield (220 mg) and could be recrystallized from dichloromethane–methanol. Ir(1,5-hexadiene)[B(C_6H_5)$_4$] was obtained in 26% yield (110 mg).

Preparation of [Rh(π-C_5H_5)(H)(P(C_6H_5)$_3$)$_2$]$^+$$BF_4^-$.—Rh($\pi$-$C_5H_5$)($C_2H_4$)$_2$ (500 mg) and triphenylphosphine (1.20 g) were placed in 10 ml of methanol under argon and 50% aqueous HBF_4 (0.26 ml) was added slowly with stirring. Yellow crystals formed within 1 min. Diethyl ether (20 ml) was added after 10 min. The mixture was allowed to stand for 10 min and filtered under nitrogen. The product was washed with diethyl ether and dried in a flow of nitrogen; yield 1.39 g (80%). The product slowly decomposed in air over a period of several days.

The preparation of **[Rh(π-C_5H_5)(D)(P(C_6H_5)$_3$)$_2$]$^+$$ClO_4^-$** is analogous, employing 107 mg of Rh(π-C_5H_5)(C_2H_4)$_2$ and 250 mg of triphenylphosphine in 2 ml of CH_3OD and 70 mg of 70% $HClO_4$ in 1 ml of CH_3OD.

Results and Discussion

We have previously reported[1] that treatment of acetone solutions of complexes of the type [Rh(C_7H_8)(P(C_6H_5)$_3$)$_2$]$^+$$A^-$ (where A^- = ClO_4^-, PF_6^-) with molecular hydrogen yields colorless crystalline salts of the cation RhH_2(P(C_6H_5)$_3$)$_2$$S_2^+$ (S = solvent molecule). This and related species have been found to function as homogeneous hydrogenation catalysts for the reduction of olefins,[1] ketones,[2] acetylenes, and diolefins.[4] If, however, tetraphenylborate is used as the counterion, the catalytic behavior observed is greatly altered and can be totally impaired. It was found that hydrogenation of an acetone solution of the complex [Rh(C_7H_8)(P(C_6H_5)$_3$)$_2$]$^+$[B(C_6H_5)$_4$]$^-$ yields sparingly soluble red-brown needles for which analyses indicate the formulation Rh[P(C_6H_5)$_3$]$_2$[B(C_6H_5)$_4$]. Infrared data indicate the absence of coordinated solvent while showing the presence of triphenylphosphine and tetraphenylborate. Although its low solubility precluded further characterization, the infrared spectrum did show two additional bands (Table II) which further studies show to be characteristic of a π-bonded interaction between one of the phenyl rings of the tetraphenylborate and the metal.

An acetone solution of the analogous complex, [Rh(1,5-cyclooctadiene)(P(C_6H_5)$_3$)$_2$]$^+$[B(C_6H_5)$_4$]$^-$, was found on standing, to yield two crystalline compounds,

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[4] R. R. Schrock and J. A. Osborn, to be submitted for publication.

$Rh[P(C_6H_5)_3]_2[B(C_6H_5)_4]$ and the pale yellow $Rh(1,5\text{-cyclooctadiene})[B(C_6H_5)_4]$. Further, treatment of a solution of $[Rh(C_7H_8)Cl]_2$ with a methanol solution of $NaB(C_6H_5)_4$ was found to yield yellow crystals of the species $Rh(C_7H_8)[B(C_6H_5)_4]$. A more general route to such complexes is described in the Experimental Section, which involves treatment of an aqueous methanolic solution of $RhCl_3 \cdot 3H_2O$ with diolefin in the presence of tetraphenylborate ion. The analogous iridium complexes can be prepared in a similar manner preferably by refluxing the solutions.

The cyclopentadiene complex, $Rh(C_5H_6)[B(C_6H_5)_4]$, could not be isolated by the methods described above. However, on treatment of the complex $Rh(\pi\text{-}C_5H_5)(C_2H_4)_2$[5] with aqueous perchloric acid in methanol in the presence of tetraphenylborate ion, gas was evolved and yellow crystals of the desired complex were deposited. If the reaction was carried out in acetone-d_6 in an nmr tube, the sharp singlet resonance at τ 4.66 identified ethylene as the gaseous product. This resonance disappeared upon gently flushing the solution with argon. During the reaction no intermediate metal alkyl was detected and no butenes were found in the products.[6] When the reaction was performed in methanol-d_1 using perchloric acid (in CH_3OD), the product, $Rh(C_5H_5D)[B(C_6H_5)_4]$, contained deuterium only at the endo position (see ir and nmr sections). This result indicates that, in this case, transfer of a proton to the π-cyclopentadienyl moiety to form a cyclopentadiene complex occurs *intramolecularly via* a transient *π-cyclopentadienyl metal–hydrido species*. In tentative support of this mechanism we have isolated a stable metal-hydrido species from a closely similar reaction; *i.e.*, treatment of $Rh(\pi\text{-}C_5H_5)(C_2H_4)_2$ in methanol with tetrafluoroboric acid in the presence of 2 mol of triphenylphosphine yields yellow crystals of $[Rh(\pi\text{-}C_5H_5)(H)(P(C_6H_5)_3)_2]^+BF_4^-$. The perchlorate salt may be prepared in an identical manner using perchloric acid.

Attempts to prepare $Rh(CO)_2B(C_6H_5)_4$ by routes analogous to those described above have been unsuccessful although impure materials containing both carbonyls and tetraphenylborate have been isolated.

All soluble $\pi(h^6)$-tetraphenylborate compounds were found to be nonconducting in dichloromethane and/or acetone solutions. Slow decomposition occurs however on standing. The molecular weights of the most soluble complexes in 1,2-dichloroethane were normal.

Infrared Data.—The Nujol mull (and solution) infrared spectra show bands in the region 1500–1350 cm^{-1} characteristic for coordinated tetraphenylborate. Uncomplexed tetraphenylborate ion generally shows only two *strong* bands at *ca.* 1480 and 1425 cm^{-1}. These result from in-plane skeletal C–C stretching modes of the phenyl ring. In coordinated tetraphenylborate, two *additional* strong bands appear at *ca.* 1460 and 1390 cm^{-1}. The position of these bands is almost invariant from one complex to another and is diagnostic for such complexes. Otherwise the infrared spectra (4000–400 cm^{-1}) are unexceptional showing the expected ligand modes. Notably, the cyclopentadiene complex, $Rh(C_5H_6)[B(C_6H_5)_4]$, shows a broad, strong absorption at *ca.* 2820 cm^{-1}, characteristic of the exo carbon to hydrogen stretching frequency as is found in other complexes of this type.[7] In the deuterated complex, $Rh(C_5H_5D)[B(C_6H_5)_4]$, the strong exo carbon to hydrogen stretching frequency is still present (although now slightly shifted to 2800 cm^{-1}) along with a weak but clearly observable band at 2190 cm^{-1} resulting from the carbon to deuterium stretching frequency at the endo position.

The hydrido complex, $[Rh(\pi\text{-}C_5H_5)(H)(P(C_6H_5)_3)_2]^+BF_4^-$, shows, apart from the expected ligand modes, a band at 2045 cm^{-1} due to the metal–hydrogen stretching frequency. In the corresponding deuteride complex, the metal–deuteride stretching frequency is obscured by ligand modes, although it may be noted that the band at 2045 cm^{-1} is no longer present.

Nuclear Magnetic Resonance Data.—Uncoordinated tetraphenylborate ion shows a complex resonance pattern centered at τ 2.9. In the spectra of coordinated tetraphenylborate complexes, a similar resonance pattern of relative intensity 15 is also observed at the same position, but there is a further resonance pattern between τ 3.0 and 4.2 of relative intensity 5. This is the position expected for an arene group bonded to a metal *via* a $\pi(h^6)$ interaction.[8] The structure of this resonance pattern varies markedly from one complex to another which again is typical of monosubstituted arene derivatives.[9] The nmr data of several of these complexes are collected together in Table III. The assignments of the resonances is based on the labeling of the π-bonded phenyl ring introduced in Figure 1. In the case of $Rh(C_7H_8)[B(C_6H_5)_4]$ the resonances H_1, H_2, and H_3 were clearly resolved into a first-order pattern (Figure 2) with $J_{12} \approx J_{23} \approx$ 6.5 Hz and with J_{13} too small to be observed (<0.5 Hz). Similarly the nmr spectrum of $Rh(1,3\text{-butadiene})[B(C_6H_5)_4]$ can be interpreted on a first-order basis (even though H_1 and H_3 overlap) since J_{13} is negligible and H_2 is well separated from both H_1 and H_3. Other complexes showed more complex spectra resulting from H_1 and H_2 second-order interactions and detailed analysis was not attempted.

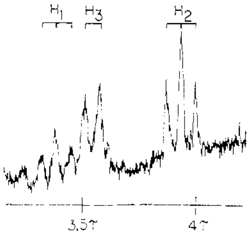

Figure 2.—The 100-MHz nmr spectrum of $Rh(\text{norbornadiene})B(C_6H_5)_4)$ showing bonded phenyl ring protons.

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Other details of the nmr spectra are generally unexceptional. However the methylene protons in Rh(h^4-C_5H_6)[$B(C_6H_5)_4$] show an interesting pattern resulting from coupling to the vicinal olefin protons of the h^4-C_5H_6 moiety. An AB quartet (centered at τ 7.20) is observed for the endo and exo protons (peak separations each 14.5 Hz; $|J_{AB}|$ = 14.5 Hz, $|\nu_0\delta_{AB}|$ = 25.1 Hz). However, only the two highest field lines of this quartet are further split into triplet patterns ($J \approx$ 2.0 Hz). Irradiation of the olefinic resonance at τ 6.18 causes collapse of the triplets to singlets. This splitting therefore results from coupling of either the endo or exo proton with the two equivalent olefinic protons on the adjacent carbon atoms. A study of a model of the system shows that the out-of-plane bending of methylene carbon in the complex (*i.e., ca.* 36°[10]) results in a much smaller dihedral angle between the endo proton and the vicinal olefin protons. Moreover the carbon–exo proton bond becomes closely orthogonal to those bonds. From the Karplus relationship,[11] it is clear that it is the endo proton which is strongly coupled to the olefin proton and thus its position can be qualitatively identified with the two upfield resonances; *i.e.*, the endo resonance occurs upfield of the exo resonance. The nmr spectrum of the deuterated complex is totally consistent with this assignment; *i.e.*, only a singlet (relative intensity 1) at τ 7.08 is present in the methylene region. This is precisely the predicted position and pattern of the exo proton resonance with complete deuteration at the endo position.

Finally, the hydrido species [Rh(π-C_5H_5)(H)P(C_6H_5)$_3$)$_2$]$^+BF_4^-$ shows, apart from expected ligand resonances (*e.g.*, π-C_5H_5 at τ 4.80), a doublet of triplets at τ 20.4 in dichloromethane resulting from the metal hydride resonance (J_{Rh-H} = 16.5 Hz; $^2J_{H-P}$ = 28.0 Hz).

Structural Considerations.—The spectroscopic data on these complexes can be best accomodated by assuming tetraphenylborate ion is coordinating to the metal *via* one of its phenyl rings in a π-bonding interaction. The X-ray structure[3] of a complex of similar formulation, Rh(P(OCH_3)$_3$)$_2$B(C_6H_5)$_4$, shows such an interaction to occur although the bonding deviates slightly from the idealized scheme presented in Figure 1. The phenyl ring is puckered slightly (*ca.* 6°) into a boat form so that the metal is somewhat closer (*ca.* 0.1 Å) to the four carbon atoms attached to H_2 and H_3 than the two other unique carbon atoms. However, the bonding may be best regarded as involving an h^6 interaction using all six π electrons of the phenyl ring in bonding to the metal. The metal would then formally achieve the inert gas configuration and the compounds can thus be considered isoelectronic with known complexes of the type Rh(π-C_5H_5)(diolefin). This approach gains tentative support in that the complexes show certain properties typical of coordinative saturation; *e.g.*, Rh(C_7H_8)[$B(C_6H_5)_4$] can be recovered unchanged from dichloromethane solution after treatment with carbon monoxide. This observation also mitigates against a formulation involving a phenyl migration from the tetraphenylborate ion to the metal, *i.e.*, Rh(diene)(C_6H_5)[$B(C_6H_5)_3$], since this species might be expected to interact readily with carbon monoxide. Overall, the complexes must be formally regarded as mesoionic species,[12] since no direct interaction exists between the negatively charged boron atom and the central metal.

Finally, tetraphenylborate ion forms complexes analogous to those of the cyclopentadienyl anion and thus should have an extensive coordination chemistry; *e.g.*, complexes such as Fe[$B(C_6H_5)_4$]$_2$, Mn(CO)$_3$-[$B(C_6H_5)_4$], and Co(CO)$_2$[$B(C_6H_5)_4$] might have reasonable stability. Such possibilities are now under active study.

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[10] M. R. Churchill and R. Mason, *Proc. Roy. Soc., Ser. A*, **279**, 191 (1964).

[11] See ref 9, p 678.

[12] A referee has suggested that "zwitterionic" or "betaine-like" might also be appropriate.