"twist angle," the angle between the Ir–P(1)–P(2) and Ir–C(1)–C(2) planes, is 5.4 (4)°, a value typical of trigonal-bipyramidal structures containing olefins π-bonded to metals.[20]

Preparation and Properties of Some Cationic Complexes of Rhodium(I) and Rhodium(III)

Richard R. Schrock and John A. Osborn*

Contribution from the Mallinckrodt Laboratory, Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. Received August 29, 1970

Abstract: Cationic complexes of the type $[Rh(diene)L_2]^+$ (diene = 1,5-cyclooctadiene (COD) or norbornadiene (NBD), L = tertiary phosphine or arsine ligand) have been prepared by several routes. These complexes serve as useful intermediates for the synthesis of many other cationic rhodium(I) and rhodium(III) species. Treatment of $[Rh(COD)\{P(C_6H_5)_3\}_2]^+$ with basic phosphines, L, leads to the isolation of the cations $[RhL_4]^+$. Under identical conditions using $[Rh(NBD)\{P(C_6H_5)_3\}_2]^+$, however, the five-coordinate species $[Rh(NBD)L_3]^+$ are produced. Treatment of solutions of $[Rh(NBD)\{P(C_6H_5)_3\}_2]^+$ with molecular hydrogen generates $[Rh\{P(C_6H_5)_3\}_2H_2S_2]^+$ (S = solvent) in situ with the elimination of norbornane. These solutions react with phosphines to give the cations of the type $[RhL_4H_2]^+$ or, alternatively, with carbon monoxide to yield carbonyl complexes such as $[Rh\{P(C_6H_5)_3\}_2(CO)_3]^+$, $[Rh\{P(C_6H_5)_3\}_2CO(S)]^+$ (S = solvent), or $[Rh\{P(C_6H_5)_3\}_3CO]^+$. Further, treatment of the solution-labile species $[Rh\{P(C_6H_5)_3\}_2(CO)_3]^+$ with dienes leads to the isolation of the five-coordinate complexes $[Rh\{P(C_6H_5)_3\}_2(diene)(CO)]^+$. The infrared and nmr ($^1H$ and ^{31}P) of the complexes are discussed. The use of certain complexes as homogeneous catalysts is also briefly investigated.

It is well known that reactions of the dimeric diene complexes of rhodium(I), $[Rh(diene)Cl]_2$, with uncharged monodentate ligands such as triphenylphosphine lead to bridge cleavage and the formation of monomeric species of the type $Rh(diene)P(C_6H_5)_3Cl$.[1–5] We have recently reported[6] that under the appropriate conditions further reaction can also occur in which chloride ion is displaced from the metal by the neutral ligand to form a cationic four-coordinate rhodium(I) complex, viz.

$$Rh(diene)P(C_6H_5)_3Cl \xrightarrow{P(C_6H_5)_3} [Rh(diene)\{P(C_6H_5)_3\}_2]^+ + Cl^-$$
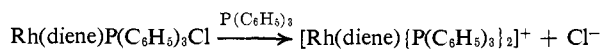
These complexes can be readily isolated from solution by the addition of a suitable precipitating counteranion such as $B(C_6H_5)_4^-$, ClO_4^-, or PF_6^-.

By this route (and, in some cases, by less direct methods) we have prepared a series of cationic diene complexes $[Rh(diene)L_2]^+A^-$, where diene = norbornadiene (NBD) or 1,5-cyclooctadiene (COD); L = tertiary phosphine, phosphite, arsine, or amine; and A = noncoordinating anion. These complexes have some interesting chemical properties. Direct reaction under mild conditions with ligands such as phosphines or carbon monoxide leads to a variety of rhodium(I) complexes, e.g., $[Rh(NBD)\{P(CH_3)_2C_6H_5\}_3]^+$, $[Rh\{P(CH_3)_2C_6H_5\}_4]^+$, and $[Rh\{P(C_6H_5)_3\}_2(CO)_3]^+$. Treat-

ment of solutions of the cationic diene complexes with molecular hydrogen causes reduction of the diene moiety to alkene (and, subsequently, alkane) and species of the type $[RhL_2H_2S_2]^+$ (S = solvent molecule) are produced. These species will react further with phosphines or arsines to yield dihydridorhodium(III) complexes, e.g., $[Rh\{P(CH_3)_3\}_4H_2]^+$, or, alternatively, will react with other dienes to yield rhodium(I)–diene complexes such as $[Rh(1,3\text{-butadiene})\{P(C_6H_5)_3\}_2]^+$. The solvated dihydrido species have also been found to be active catalysts for the homogeneous hydrogenation of a variety of substrates.[6,7] The preparation of the series of catalyst precursors, $[Rh(diene)L_2]^+$, with variation only in the ligand L, has thus enabled a detailed study of the effect of the nature of the ligand L on the catalytic process. The results of this study will be the subject of a subsequent publication.

In this paper the preparations of the cationic species of the type $[Rh(diene)L_2]^+$ and species derived therefrom are described, and the spectroscopic and chemical properties reported. Following our earlier communication of this work,[6] certain of the complexes reported here have been isolated by two other independent research groups.[8–10]

Discussion

The general methods of synthesis and some of the reactions of complexes described in this paper are collected together in the form of flow charts in Figure 1

(1) J. Chatt and L. M. Venanzi, J. Chem. Soc. A, 4735 (1957).
(2) M. A. Bennett and G. Wilkinson, ibid., 1418 (1961).
(3) K. Vrieze, H. C. Volger, and A. P. Pratt, J. Organometal. Chem., 14, 185 (1968).
(4) K. Vrieze, H. C. Volger, and A. P. Pratt, ibid., 15, 195 (1968).
(5) L. Cattalini, R. Ugo, and A. Orio, J. Amer. Chem. Soc., 90, 4800 (1968).
(6) J. R. Shapley, R. R. Schrock, and J. A. Osborn, ibid., 91, 2816 (1969).

(7) R. R. Schrock and J. A. Osborn, Chem. Commun., 567 (1970).
(8) L. M. Haines, Inorg. Nucl. Chem. Lett., 5, 399 (1969).
(9) L. M. Haines, Inorg. Chem., 9, 1517 (1970).
(10) B. F. G. Johnson, J. Lewis, and D. A. White, J. Amer. Chem. Soc., 91, 5186 (1969).

$[RhL'_4H_2]^+$

(b) L'   H₂ (h)

$[RhL_2H_2S_2]^+$ ——L' (c)—— $[RhL_2L'_2H_2]^+$ $[RhL'_4]^+$

diene (d)   (i) L'

(e) H₂

$[Rh(diene)Cl]_2$ —2L'–Cl⁻ (a)— $[Rh(diene)L_2]^+$ ——L' (j)—— $[Rh(diene)L'_3]^+$

diene (f)   NaClO₄   (g) 1, HClO₄   L' (k)
                                  2, 2L

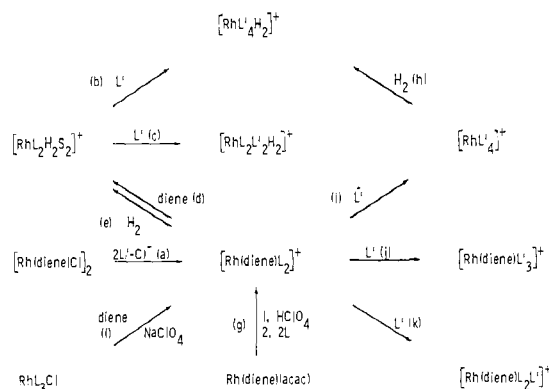RhL_3Cl $Rh(diene)(acac)$ $[Rh(diene)L_2L']^+$

Figure 1. Flow diagram illustrating preparations and reactions of cationic species except carbonyls; NBD = norbornadiene, COD = 1,5-cyclooctadiene, diphos = 1,2-bisdiphenylphosphinoethane, arphos = 1-diphenylarsino-2-diphenylphosphinoethane, S = solvent molecule, acac = acetylacetonate: (a) diene = NBD or COD; L = $P(C_6H_5)_3$, $P(C_6H_5)_2CH_3$, $P(CH_3)_2C_6H_5$, or $NH_2C(CH_3)_3$; (b) L' = $P(CH_3)_2C_6H_5$ or $P(CH_3)_3$; (c) L' = $As(CH_3)_2C_6H_5$; (d) diene = NBD, COD, 1,3-butadiene, or 1,3-cyclohexadiene; (e) diene = NBD; L = $P(C_6H_5)_3$; (f) diene = NBD or COD; L = $P(C_6H_5)_3$; (g) diene = NBD or COD; L = $P(OC_6H_5)_3$, $P(C_6H_5)_2OCH_3$, $As(C_6H_5)_3$ or L_2 = diphos or arphos; (h) L' = $P(CH_3)_2C_6H_5$; (i) diene = COD; L' = $P(C_6H_5)_2CH_3$, $P(CH_3)_2C_6H_5$, or $P(OCH_3)_2C_6H_5$; L = $P(C_6H_5)_3$; (j) diene = NBD; L' = $P(CH_3)_3$, $P(CH_3)_2C_6H_5$ if L = $P(C_6H_5)_3$; L' = $As(CH_3)_2C_6H_5$ if L = $As(C_6H_5)_3$; (k) diene = NBD; L' = $P(CH_3)_2C_6H_5$ or $As(CH_3)_2C_6H_5$ and L_2 = diphos or arphos.

(all complexes except carbonyls) and Figure 4 (carbonyl complexes). The sections below discuss in turn each class of complex prepared and the relevant chemical and spectroscopic properties. Analytical, conductivity, and spectroscopic data can be found in the Experimental Section.

Complexes of the Type $[Rh(diene)L_2]^+$. The complexes of the type $[Rh(diene)L_2]^+$ have been prepared by four different methods. Earlier we reported that cleavage of the complexes $[Rh(diene)Cl]_2$ by ligands such as triphenylphosphine, when carried out in polar media, produces cationic species, $[Rh(diene)\{P(C_6H_5)_3\}_2]^+$, which can be isolated from solution as tetraphenylborate or perchlorate salts.[6] We find, however, contrary to other reports,[8,9] that the cationic complexes can be isolated from a variety of solvents, alcohols not being unique in this respect (see Experimental Section). A combination of spectroscopic and conductivity data indicates the following behavior in solution, viz.

(structure) $\rightleftharpoons^{+L}_{-L}$

(structure) $\rightleftharpoons^{+L}_{-L}$ [(structure)]⁺ + Cl⁻
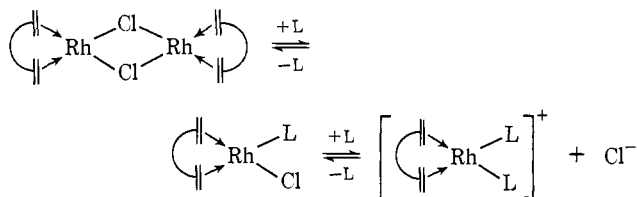
Addition of greater than 1 mol of ligand L (per mole of rhodium) to the dimeric species in polar solvents causes a marked increase in conductivity. The conductivity increase is greatly dependent upon the nature of L. When 2 mol of phosphine, i.e., $P(C_6H_5)_3$, $P(C_6H_5)_2CH_3$, or $P(CH_3)_2C_6H_5$, was added to $[Rh(NBD)Cl]_2$ in acetone, the equivalent conductivity was found to be, respectively, 0, 1, and 15% of the value which would result from total chloride ion dissociation.[11] How-

ever, an identical experiment employing 2 mol of $P(C_6H_{11})_2C_6H_5$ showed ca. 0% equivalent conductivity. Steric effects are therefore important in determining the extent of cation formation.[12] The mechanism of chloride ion displacement by phosphine at rhodium is most likely via the formation of a five-coordinate intermediate, $Rh(diene)L_2Cl$, with subsequent loss of halide ion to form the four-coordinate cationic species. Ionization of halide ion would be favored in polar solvents, but isolation of the cationic species can also be readily achieved in solvents of low polarity by precipitation of the alkali metal halide and/or cationic complex from solution. The ready displacement of halide ion from four-coordinate d^8 complexes to form four-coordinate cationic species appears to be an increasingly distinctive feature of their chemistry.[13] This direct method of diene cation formation is of quite general applicability but, as expected, fails for very weakly nucleophilic and/or sterically hindered ligands, e.g., $As(C_6H_5)_3$.

A second method of isolating the cationic species of the type $[Rh(diene)\{P(C_6H_5)_3\}_2]^+$ involves the treatment of $Rh\{P(C_6H_5)_3\}_3Cl$ with diene in the presence of perchlorate or hexafluorophosphate anion, viz.

$$Rh\{P(C_6H_5)_3\}_3Cl \xrightarrow[-P(C_6H_5)_3]{+diene} Rh(diene)\{P(C_6H_5)_3\}_2Cl \xrightarrow{-Cl^-}$$
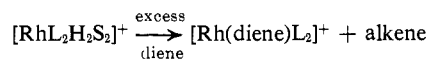$$[Rh(diene)\{P(C_6H_5)_3\}_2]^+$$
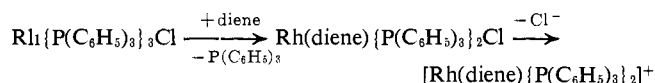
Good yields of the norbornadiene and 1,5-cyclooctadiene complexes can be obtained in this way.

A third, and very general route to cationic diene complexes, is by addition of diene after the reductive elimination of norbornadiene from the readily accessible $[Rh(NBD)L_2]^+$ species. Treatment of a solution of this cation with molecular hydrogen (1 atm, 25°) for a few minutes yields the solvated dihydrido species in situ plus norbornane.

$$[Rh(NBD)L_2]^+ \xrightarrow[S]{H_2} [RhL_2H_2S_2]^+ + \text{norbornane (S = solvent)}$$
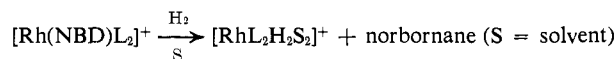
Addition of an excess of the requisite diene under an atmosphere of argon yields the corresponding cationic complex, $[Rh(diene)L_2]^+$.

$$[RhL_2H_2S_2]^+ \xrightarrow[\text{diene}]{\text{excess}} [Rh(diene)L_2]^+ + \text{alkene}$$

By this method the cationic complexes, $[Rh(1,3\text{-butadiene})\{P(C_6H_5)_3\}_2]^+$ and $[Rh(1,3\text{-cyclohexadiene})\{P(C_6H_5)_3\}_2]^+$, are conveniently prepared, but this route can be used to synthesize a wide variety of such diene complexes.

Where isolation of required cations was not successful by the above methods, we have used a less direct but useful approach similar to that used by Lewis for the preparation of certain cationic complexes.[10] Treatment of the complex $Rh(diene)(acac)$ (acac = acetylacetonate anion) with 1 mol of perchloric acid followed by addition of 2 mol of ligand L leads to the isolation of the complexes $[Rh(diene)L_2]^+ClO_4^-$ in good yield. This method has been used to prepare complexes such

(11) Based on the known reaction $\frac{1}{2}[Rh(diene)Cl]_2 + 2diphos \rightarrow [Rh(diphos)_2]^+ + Cl^-$.

(12) C. A. Tolman, J. Amer. Chem. Soc., 92, 2956 (1970).

(13) (a) M. J. Church and M. J. Mays, J. Chem. Soc. A, 1938 (1970); (b) ibid., 3074 (1968); (c) H. C. Clark and K. R. Dixon, J. Amer. Chem. Soc., 91, 596 (1969); (d) J. Powell and B. L. Shaw, J. Chem. Soc. A, 774 (1968); (e) see ref 6; see also ref 24.

as [Rh(NBD){As(C₆H₅)₃}₂]⁺, [Rh(COD)(diphos)]⁺, or [Rh(NBD){P(OC₆H₅)₃}₂]⁺ which could not be obtained in satisfactory yield by direct methods and which were of interest in connection with our catalytic studies.

Finally, the mixed-ligand complex [Rh(NBD){P-(C₆H₅)₃}{As(C₆H₅)₃}]⁺ could be prepared from the reaction of [Rh(1,3-butadiene)₂{P(C₆H₅)₃}]⁺ (*vide infra*) with NBD and As(C₆H₅)₃.

The yellow to red crystalline complexes, [Rh(diene)-L₂]⁺A⁻, are all air stable with the exception of the species [Rh(NBD){P(CH₃)₂C₆H₅}₂]⁺ and [Rh(NBD)-{NH₂C(CH₃)₃}₂]⁺ which are slowly decomposed over several weeks. Solutions of the complexes with ClO₄⁻ or PF₆⁻ as counterion are also stable with the exception of the two above and [Rh(1,3-butadiene){P(C₆H₅)₃}₂]⁺ and [Rh(NBD){P(CH₃)₂C₆H₅}₂]⁺ for which ligand redistribution reactions are observed (see Experimental Section). With tetraphenylborate as the anion, however, the solution behavior may be complicated. The complex, [Rh(COD){P(C₆H₅)₃}₂]⁺B(C₆H₅)₄⁻, when dissolved in acetone, is converted into the two species Rh(COD)B(C₆H₅)₄ and Rh{P(C₆H₅)₃}₂B(C₆H₅)₄, both of which contain tetraphenylborate coordinating to the metal *via* a π interaction of an arene ring. Several such complexes have recently been isolated.[14,15] For chemical and catalytic studies of the cationic diene species we have, in general, isolated the perchlorate and/or hexafluorophosphate salts where no marked interaction between cation and anion has been observed.

The infrared spectra of the complexes are unexceptional, showing the presence of uncoordinated anion along with the expected ligand modes. The ¹H and ³¹P nmr spectra are more informative. In the norbornadiene complexes the olefin proton resonances generally appear as a quartet. Irradiation of the methine protons (H$_m$) of the coordinated norbornadiene in [Rh(NBD){P(C₆H₅)₂CH₃}₂]⁺ at τ 5.89 causes collapse of the olefinic quartet at τ 5.28 to a doublet. The symmetric pattern results therefore from a closely overlapping doublet of triplets with $J_{Rh-Hol} \simeq 2$ Hz, and $J_{Hm-Hol} \simeq 2$ Hz (H$_{ol}$ = olefin protons). It may be noted that the olefinic resonance in the four-coordinate cations is considerably downfield (>1 ppm) from that in the corresponding five-coordinate species (*vide infra*).

In the complexes with P(C₆H₅)₂CH₃ as a ligand the methyl resonance shows a complex resonance pattern as illustrated in Figure 2 for [Rh(COD){P(C₆-H₅)₂CH₃}₂]⁺. This pattern can be interpreted as a X′₃A′AX₃ spectrum ($|J_{AA'}| > |J_{AX} - J_{AX'}|$)[16] with the superposition of first-order rhodium to methyl coupling ($J_{Rh-CH₃} \simeq 3$ Hz). Such "virtually coupled" spectra are now well known, and the pattern here is typical for intermediate values of ²J_{P-P} (*i.e.*, 20–50 Hz). Assignments of the stereochemistry of group VIII metal complexes with phosphine ligands have often been based on the value of ²J_{P-P}.[17] Recently it has been shown[18,19] that this approach is not generally
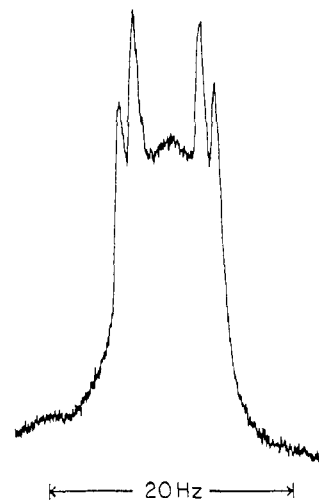
(14) R. R. Schrock and J. A. Osborn, *Inorg. Chem.*, **9**, 2339 (1970).
(15) For the structure of Rh{P(OCH₃)₃}₂B(C₆H₆)₄, see M. J. Nolte, G. Gafner, and L. M. Haines, *Chem. Commun.*, 1406 (1969).
(16) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).
(17) P. R. Brookes and B. L. Shaw, *J. Chem. Soc. A*, 1079 (1967).
(18) D. A. Duddell, J. G. Evans, P. L. Goggin, R. J. Goodfellow, A. J. Rest, and J. G. Smith, *ibid.*, 2134 (1969).
(19) F. B. Ogilvie, R. L. Keiter, G. Wulfsberg, and J. G. Verkade, *Inorg. Chem.*, **8**, 2346 (1969).

Figure 2. τ-8.43 methyl resonance in [Rh(COD){P(C₆H₅)₂CH₃}₂]⁺ at 100 MHz (37°) in CH₂Cl₂.

reliable for other types of metal complexes. For the cationic group VIII complexes described here, where a cis arrangement of phosphines is evident, the value of ²J_{P-P} (or, alternatively, the overall spectral pattern) cannot be used to predict, in a simple manner, such a stereochemistry.

The methyl resonance of the complex [Rh(NBD)-{P(CH₃)₂C₆H₅}₂]⁺ in dichloromethane at 37° consists of a broad unresolved singlet at τ 8.68. However, on cooling the solution to −80°, the resonance shifts upfield to τ 8.73 and is resolved into a virtually coupled pattern (*i.e.*, as in Figure 2). However, the pair of sharp flanking resonances, indicative of rhodium to methyl coupling, could not be satisfactorily resolved. Also, at low temperature three additional resonances of low intensity grew up at τ 6.54 (2), τ 7.03 (4), and τ 8.36 (18). These are identical in position and relative intensity with (respectively) the methine and olefin proton resonances for coordinated NBD and the P(CH₃)₂C₆H₅ methyl resonance in [Rh(NBD){P(CH₃)₂-C₆H₅}₃]⁺ (*vide infra*). Contamination by this species (*ca.* 5%) was present in all our samples of the four-coordinate cation despite many attempts at purification. Line coalescence and broadening found at ambient temperature for the phosphine methyl resonance clearly results from fast intermolecular phosphine exchange occurring between the four- and five-coordinate cations.

The methyl resonance in [Rh(NBD){P(C₆H₅)₂-OCH₃}₂]⁺ is also typical of a virtually coupled X′₃A′AX₃ system ($|J_{AA'}| > |J_{AX} - J_{AX'}|$). The pattern is well resolved but notably there is only one sharp resonance on each side of the central envelope indicating that the rhodium to methyl coupling is quite small (*i.e.*, <*ca.* 0.5 Hz).

The ³¹P spectra of the complexes [Rh(diene)L₂]⁺ (L = phosphine ligand) show only one resonance signal split into a clearly resolved doublet by the interaction with ¹⁰³Rh ($s = ½$, 100%). It may be noted that although shielding of the phosphorus nucleus increases in both the complexed and free ligand in the order P(C₆H₅)₃ < P(C₆H₅)₂CH₃ < P(CH₃)₂C₆H₅, the complexed phosphine resonance occurs at significantly lower fields than that for the free phosphine.[20]

Complexes of the Type [Rh(diene)L$_3$]$^+$ and [RhL$_4$]$^+$ (L = Phosphine or Arsine Ligand). Treatment of solutions of the cation [Rh(NBD){P(C$_6$H$_5$)$_3$}$_2$]$^+$ with P(CH$_3$)$_2$C$_6$H$_5$ or P(CH$_3$)$_3$ leads to displacement of P(C$_6$H$_5$)$_3$ and formation of *five*-coordinate complexes, *e.g.*, [Rh(NBD){P(CH$_3$)$_3$}$_3$]$^+$. In the reaction with P(C$_6$H$_5$)$_2$CH$_3$, although nmr evidence indicates the initial formation of [Rh(NBD){P(C$_6$H$_5$)$_2$CH$_3$}$_3$]$^+$, rapid redistribution of ligands takes place and a mixture of [Rh(NBD){P(C$_6$H$_5$)$_2$CH$_3$}$_2$]$^+$ and [Rh{P(C$_6$H$_5$)$_2$CH$_3$}$_4$]$^+$ is formed in solution. The five-coordinate arsine cation, [Rh(NBD){As(CH$_3$)$_2$C$_6$H$_5$}$_3$]$^+$, could also be readily isolated by displacement of triphenylarsine (but *not* triphenylphosphine) from the corresponding four-coordinate species. Five-coordinate cations of the type [Rh(NBD)(chelate)(L)]$^+$ (chelate = 1,2-bis-diphenylphosphinoethane or 1-diphenylarsino-2-diphenylphosphinoethane are formed on treatment of the species [Rh(NBD)(chelate)]$^+$ with L (L = P(CH$_3$)$_2$C$_6$H$_5$ or As(CH$_3$)$_2$C$_6$H$_5$).

In contrast, if the corresponding 1,5-cyclooctadiene complex [Rh(COD){P(C$_6$H$_5$)$_3$}$_2$]$^+$ is treated in a similar manner with P(C$_6$H$_5$)$_2$CH$_3$, P(CH$_3$)$_2$C$_6$H$_5$, or P(OCH$_3$)$_2$-C$_6$H$_5$), displacement of both 1,5-cyclooctadiene and triphenylphosphine occurs, yielding the cationic species [RhL$_4$]$^+$. Recently Haines has also used this route to prepare several phosphite complexes.[8,9]

If the analogous butadiene complex, [Rh(1,3-butadiene){P(C$_6$H$_5$)$_3$}$_2$]$^+$, is treated with excess butadiene in tetrahydrofuran, the complex, [Rh(1,3-butadiene)$_2$P(C$_6$H$_5$)$_3$]$^+$, may be isolated in up to 50% yield. No other [Rh(diene)$_2$P(C$_6$H$_5$)$_3$]$^+$ species could be obtained. The unique behavior of butadiene in this respect may be due to its steric compactness relative to the larger diene species. On the other hand, electronic factors may make formation of the [Rh(diene)$_2$-P(C$_6$H$_5$)$_3$]$^+$ species more likely if the diene is conjugated.

The ^{1}H nmr spectra of the five-coordinate species show an interesting but rather complex temperature dependence resulting from intramolecular, and in some cases, intermolecular site-exchange processes. The detailed mechanism of such rearrangements in these and other five-coordinate complexes will be the subject of a forthcoming publication. Suffice to say at present that an averaged spectrum is generally observed at room temperature which is consistent with the formulations proposed. Interestingly also, the ^{31}P spectra confirm these observations; *e.g.*, at 37° the complex [Rh(NBD){P(CH$_3$)$_2$C$_6$H$_5$}$_3$]$^+$ shows only *one* ^{31}P resonance (at +5.0 ppm relative to external 85% H$_3$PO$_4$) in which the rhodium to phosphorus coupling is preserved (J_{Rh-P} = 118 Hz).

The ^{1}H resonance spectra for [Rh{P(C$_6$H$_5$)$_2$CH$_3$}$_4$]$^+$ and [Rh{P(CH$_3$)$_2$C$_6$H$_5$}$_4$]$^+$ each show a single, rather broad methyl ^{1}H resonance with poorly resolved multiplet structure throughout the temperature range +40 to −60°. No changes in the spectra were observed when phosphine ligand was added (except for the appearance of a sharp resonance due to free phosphine), indicating intermolecular phosphine exchange to be slow in these species in contrast to most other d^8

complexes of this type. This behavior and the unexpected lack of chemical reactivity of these complexes may result from considerable steric crowding about the rhodium, with, possibly, distortion of the ligands out of a square-planar configuration. The ^{31}P spectra are unexceptional showing the expected doublet structure, even in the presence of free phosphine, arising from ^{103}Rh interaction. These observations confirm the stability of these complexes to dissociation of phosphine ligand.

Complexes of the Type [RhL$_4$H$_2$]$^+$ and [RhL$_2$L$_2$'H$_2$]$^+$ (L, L' = Phosphine or Arsine Ligand). We have previously noted that treatment of the cationic species [Rh(NBD)L$_2$]$^+$ with molecular hydrogen in a solvent S leads to the formation of the solvated dihydrido species [RhL$_2$H$_2$S$_2$]$^+$. We have isolated such species with L = P(C$_6$H$_5$)$_3$ from a variety of solvents but have been unsuccessful if more basic phosphines are used. However, cations of the type [RhL$_4$H$_2$]$^+$ (L = P(CH$_3$)$_2$C$_6$H$_5$ and P(CH$_3$)$_3$) can be readily isolated by treatment of solutions of [Rh{P(C$_6$H$_5$)$_3$}$_2$H$_2$S$_2$]$^+$ with the appropriate phosphine under hydrogen or, alternatively, by the reaction of certain of the cationic species with molecular hydrogen, *e.g.*, [Rh{P(CH$_3$)$_2$C$_6$H$_5$}$_4$]$^+$. However, [Rh{P(C$_6$H$_5$)$_2$CH$_3$}$_4$]$^+$ and [Rh{P(OCH$_3$)$_2$C$_6$H$_5$}$_4$]$^+$ do not react with molecular hydrogen, illustrating the sensitive nature of such reactions to small changes in the properties of the ligand. The mixed-ligand species [Rh{P(C$_6$H$_5$)$_3$}$_2${As(CH$_3$)$_2$C$_6$H$_5$}$_2$H$_2$]$^+$ was isolated when [Rh{P(C$_6$H$_5$)$_3$}$_2$H$_2$S$_2$]$^+$ was treated with As(CH$_3$)$_2$C$_6$H$_5$. The tetrakisarsinedihydrido complex [Rh{As(CH$_3$)$_2$-C$_6$H$_5$}$_4$H$_2$]$^+$ could only be prepared by the interaction of [Rh(NBD){As(CH$_3$)$_2$C$_6$H$_5$}$_3$]$^+$ with molecular hydrogen in the presence of 1 mol of As(CH$_3$)$_2$C$_6$H$_5$.

The infrared spectra of the dihydrido complexes show, along with the ligand and uncoordinated anion modes, two medium-to-strong bands at *ca.* 2000 cm^{-1} resulting from a metal-to-hydrogen symmetric and asymmetric stretching. In the deuterides these bands appear at *ca.* 1400 cm^{-1} as predicted.

The ^{1}H nmr spectra of the dihydrido cations show a hydride resonance at high field (*ca.* τ 20). The pattern is almost identical for [Rh{P(CH$_3$)$_2$C$_6$H$_5$}$_4$H$_2$]$^+$ and [Rh{P(CH$_3$)$_3$}$_4$H$_2$]$^+$. The accumulated spectrum (40 scans) of the latter is shown in Figure 3a. This pattern is only consistent with a mutually cis arrangement of the hydride ligands. The configuration can be regarded as essentially a seven spin system of the type AA'-MXX'Y$_2$. The calculated best-fit spectrum is shown in Figure 3b. The values of the coupling constants and the method of calculation can be found in the Experimental Section. The spectra were found to be invariant over the temperature range −80 to +90° as well as being unaffected by the presence of free ligand. Hence there is no facile intramolecular rearrangement occurring in these species, unlike the corresponding complexes of the type ML$_4$H$_2$ (M = Fe, Ru; L = phosphine, phosphite, phosphonite, or phosphinite) where ligand site exchange is observed.[21,22] This observation is confirmed by the ^{31}P spectra which show two resonances (relative area 1:1) as expected for a static cis configuration. Interestingly, in both these

(20) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Oxford, England, 1966, p 1052.

(21) F. N. Tebbe, P. Meakin, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 92, 1068 (1970).

(22) P. Meakin, L. J. Guggenberger, J. P. Jesson, D. H. Gerlach, F. N. Tebbe, W. G. Peet, and E. L. Muetterties, *ibid.*, 92, 3482 (1970).
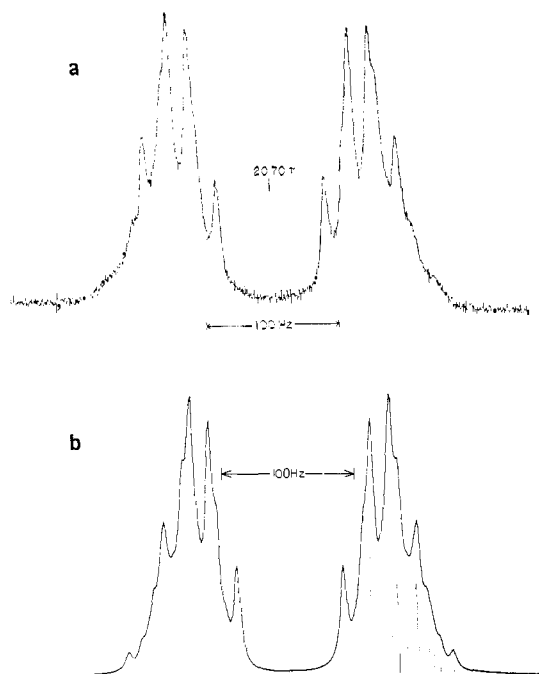
Figure 3. Nmr spectrum of the hydride region of [Rh{P(CH₃)₃}₄-H₂]⁺: (a) observed at 100 MHz in CH₂Cl₂ at 37°, (b) calculated with a Lorentzian line width = 5.0 Hz. (See Experimental Section for calculated coupling constants and their assignments.)

complexes the ³¹P resonance of the phosphorus atoms trans to hydride ligands occurs ca. 10 ppm to higher field than of a phosphorus trans to another phosphorus ligand. This has also been observed in the complexes cis-Fe{P(OC₂H₅)₂C₆H₅}₄H₂² and cis-Ru{P(C₆H₅)₂CH₃}₄H₂.²³ Assignments of the ³¹P resonances were made here on the basis that the mutually trans phosphines appear as basically a doublet ($J_{Rh-P} \simeq$ 100 Hz), whereas the phosphines trans to hydrides show a second-order spectrum resulting from essentially an AA'XX' system.

The ¹H spectrum of [Rh{As(CH₃)₂C₆H₅}₄H₂]⁺ shows a doublet at high field (τ 22.3, J_{Rh-H} = 12.5 Hz) and from infrared data (ν_{Rh-H} = 1995 and 1975 cm⁻¹) is also presumed of a cis configuration.

The mixed dihydrido species [Rh{P(C₆H₅)₃}₂{As-(CH₃)₂C₆H₅}₂H₂]⁺ shows a quartet in the high-field region resulting from an overlapping doublet of triplets (J_{Rh-H} = $^2J_{H-P}$ = 12.0 Hz). The structure of this complex is thus the same as that proposed for [Rh{P(C₆H₅)₃}₂H₂(CH₃CN)₂]⁺ (ref 6) where the arsines occupy the trans positions to the two mutually cis hydride ligands.

Cationic Carbonyl Complexes of Rhodium(I). When a solution of [Rh(COD){P(C₆H₅)₃}₂]⁺ is treated with carbon monoxide (1 atm, 25°), rapid displacement of COD occurs and the tricarbonyl species [Rh{P(C₆H₅)₃}₂-(CO)₃]⁺ (I) (see Figure 4) can be isolated from the CO saturated solution. This method is not satisfactory using the corresponding norbornadiene complex [Rh-(NBD){P(C₆H₅)₃}₂]⁺, since the diene competes favorably with CO for sites on the metal and the reaction does not go readily to completion. However, in the preferred method for preparing I, a solution of [Rh-(NBD){P(C₆H₅)₃}₂]⁺ in acetone is first treated with

(23) K. C. Dewhirst, W. Keim, and C. A. Reilly, Inorg. Chem., 7, 546 (1968).

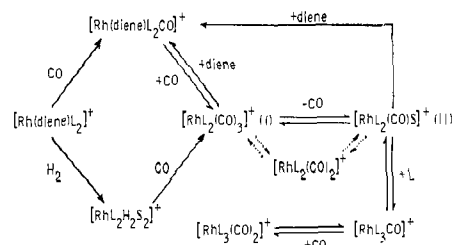Figure 4. Flow diagram illustrating preparation of carbonyl species; L = P(C₆H₅)₃ or P(C₆H₅)₂CH₃, S = solvent molecule.

molecular hydrogen (which generates [Rh{P(C₆H₅)₃}₂-H₂(acetone)₂]⁺ in situ), and then treated with CO.

The tricarbonyl complex I loses CO slowly in the solid state but very readily in solution. When dissolved in solvents such as dimethylformamide, dimethyl-acetamide, acetone, or acetonitrile, CO is evolved and the complexes [Rh{P(C₆H₅)₃}₂(CO)(S)]⁺ (II, S = coordinated solvent) can be isolated as crystalline solids. We have not isolated the intermediate dicarbonyl complex [Rh{P(C₆H₅)₃}₂(CO)₂]⁺. However, the infrared spectrum of I dissolved in dichloromethane shows several bands which are not readily assignable to either I or II, and may indicate the presence of the dicarbonyl species.²⁴ The ease with which I loses two molecules of CO enables the convenient preparation of species containing the [Rh{P(C₆H₅)₃}₂CO]⁺ moiety. Treatment of I with P(C₆H₅)₃ yields [Rh{P(C₆H₅)₃}₃-CO]⁺; if the reaction is carried out in an atmosphere of CO, the five-coordinate complex, [Rh{P(C₆H₅)₃}₃-(CO)₂]⁺, is formed. Similarly, if I is treated with dienes such as norbornadiene or 1,3-butadiene, [Rh-(diene){P(C₆H₅)₃}₂CO]⁺ species are readily isolable. The reactions involving the corresponding complexes with P(C₆H₅)₂CH₃ as ligand follow an identical pattern, except note that the ease of dissociation of CO from these complexes is less marked.

It may be noted that careful analysis of the carbonyl complexes was needed for their unambiguous characterization. In particular we have determined the carbon monoxide content by treating each carbonyl complex with excess 1,2-bisdiphenylphosphinoethane in 2-butanone and measuring the gas evolved in a gas buret. In each case, [Rh(diphos)₂]⁺ was the only rhodium-containing product. Details of the method and results of these analyses are given in the Experimental Section.

The most interesting feature of this series of complexes is the extreme lability of the equilibria involved in their solution chemistry. Solvent, olefin, phosphine, and CO compete for, and exchange at, sites on the three-coordinate [Rh{P(C₆H₅)₃}₂CO]⁺ moiety. We have therefore briefly investigated whether such species have any catalytic potential. The solvated species [Rh{P-(C₆H₅)₃}₂Sₙ]⁺ can be generated in situ by pumping off molecular hydrogen from the dihydrido-species, [Rh{P-(C₆H₅)₃}₂H₂S₂]⁺. Reaction of this rhodium(I) complex with n-heptaldehyde in acetone at 25° yields, rapidly and quantitatively, [Rh{P(C₆H₅)₃}₂(CO)(acetone)]⁺, viz.

(24) W. Hieber and V. Frey, Chem. Ber., 99, 2614 (1966). Hieber formulated the compound produced by the reaction of trans-Rh{P-(C₆H₅)₃}₂(CO)Cl with AlCl₃ in the presence of CO as [Rh{P(C₆H₅)₃}₂-(CO)₂]⁺ ($\nu_{C\equiv O}$ 2017 cm⁻¹). The compound prepared was probably [Rh{P(C₆H₅)₃}₂(CO)₃]⁺.

$$[\mathrm{Rh}\{P(C_6H_5)_3\}_2S_n]^+ + RCHO \longrightarrow$$
$$[\mathrm{Rh}\{P(C_6H_5)_3\}_2(CO)S]^+ + RH$$
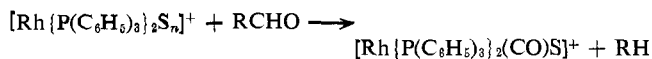
Analysis of the residual solution by glc methods showed that 1 mol of n-hexane (>98% purity) per mole of rhodium had been produced. Heating for several days at temperatures up to 90° produced only very small amounts of additional decarbonylation products (ca. 6 mol/mol of Rh). However, extensive decomposition eventually took place. Identical results were found using the corresponding $P(C_6H_5)_2CH_3$ complexes. The use of the $[\mathrm{Rh}\{P(C_6H_5)_3\}_2(CO)S]^+$ complexes as hydrogenation catalysts was also briefly investigated. Solutions (10^{-3} mM) of these species in tetrahydrofuran at 25° showed very little absorption of hydrogen in the presence of hex-1-ene over several days.

The infrared spectra of the cationic carbonyl complexes show strong absorptions at ca. 2000 cm^{-1} as expected for rhodium(I) carbonyl species. In some cases cations isolated with different counteranions, while showing identical spectra in solution, show significant differences in their solid-state spectra. Appreciable changes in the vibrational spectrum can result from strong cation–anion interactions in the crystal, and in those cases where solution spectra could not be obtained no reliable stereochemical assignment could be made based on the solid-state data alone. In the mull spectrum of $[\mathrm{Rh}\{P(C_6H_5)_3\}_2(CO)_3]^+$, two strong bands appear at 2037 and 2023 cm^{-1}. No satisfactory solution spectrum could be obtained owing to rapid loss of CO. This molecule probably has a distorted bipyramidal structure by comparison with the analogous Co(I) and Ir(I) complexes.[25] The solution-labile species, $[\mathrm{Rh}\{P(C_6H_5)_3\}_3(CO)_2]^+$, as its ClO$_4^-$ or PF$_6^-$ salt, shows only one strong, sharp absorption at 2013 cm^{-1} in the mull spectrum, and a trans trigonal-bipyramidal configuration might be presumed. However, as its B($C_6H_5)_4^-$ salt, the cation shows one strong and two medium absorptions (at 1987, 2013, and 2048 cm^{-1}, respectively) which may result from distortion of this configuration and/or possibly the stabilization of an isomer of lower symmetry. However, an examination of the crystals of this species showed no evidence of different crystal forms. In the corresponding complex $[\mathrm{Rh}\{P(C_6H_5)_2CH_3\}_3(CO)_2]^+$ both the mull and solution spectra show two $\nu_{C=O}$ absorptions and structures with a configuration other than trans trigonal bipyramidal must be considered.

In the solvated species $[\mathrm{Rh}\{P(C_6H_5)_3\}_2(CO)S]^+$ the ketonic carbonyl frequency in the dimethylformamide, dimethylacetamide, and acetone complexes are all lowered by 25–50 cm^{-1} from that of the uncoordinated solvent. Although "side-on" bonding of the carbonyl group cannot be totally excluded, the magnitude of the frequency lowering is more compatible with bonding to the metal through a lone pair on the oxygen. Moreover, the insensitivity of $\nu_{C=O}$ to a change in the phosphine ligand indicates that the solvent probably occupies a site trans to the carbonyl group on the metal. In the corresponding acetonitrile complexes, marked $\nu_{C=O}$ frequency differences are observed in the mull spectra for salts with different anions, but the solution spectra are identical. Only a single strong carbonyl absorption is observed. Strangely, however, the mull and

solution spectra show two weak acetonitrile absorptions of approximately the same intensity (at 2319 and 2288 cm^{-1} in the mull). At present we have no explanation for this behavior.

Finally it may be noted that the complex [Rh(1,3-butadiene)$\{P(C_6H_5)_3\}_2CO]^+$ shows two bands in the solid state and in solution. Initial ^{1}H nmr data indicate that this results from two energetically similar isomers in equilibrium in solution. Details of this system will be reported subsequently.

The ^{1}H nmr spectra of the solvated species $[\mathrm{Rh}\{P(C_6H_5)_3\}_2(CO)S]^+$ show consistently an upfield shift for the coordinated solvent protons in relation to the signal for the free solvent. Rapid exchange between coordinated and free solvent occurs in solution, as is evident from the sharp, averaged resonance observed when free solvent is present. The dimethylformamide and dimethylacetamide adducts both show nonequivalent methyl groups attached to the nitrogen, as is observed in the uncoordinated species. In the case of $[\mathrm{Rh}\{P(C_6H_5)_2CH_3\}_3CO]^+$, the methyl pattern consists of two resonances (relative areas 2:1) consistent with a square-planar configuration.

The ^{31}P nmr spectrum for $[\mathrm{Rh}\{P(C_6H_5)_2CH_3\}_3CO]^+$ in dichloromethane consists of a double doublet (relative intensity 2; $J_{Rh-P_t} = 120$ Hz, $J_{P_c-P_t} = ca.$ 30 Hz), resulting from the mutually trans phosphorus ligands (P_t), and overlapping this, a less well-resolved, complex pattern due to the unique phosphorus ligand (P_c). Addition of 1 drop of CH_3CN causes immediate collapse of all resonances to a singlet, with loss of rhodium to phosphorus coupling. Fast intermolecular phosphine exchange therefore occurs in the presence of donor solvents. Although the initial spectrum was less well resolved, similar behavior was found for $[\mathrm{Rh}\{P(C_6H_5)_3\}_3CO]^+$.

Interestingly, the ^{31}P spectrum of [Rh(1,3-butadiene)$\{P(C_6H_5)_3\}_2CO]^+$ in dichloromethane shows a doublet resonance, indicating that the dynamic process observed in the ^{1}H nmr spectrum does not result from a phosphine dissociation process.

Experimental Section

All solvents were of reagent grade quality and were used without further purification unless otherwise noted. [Rh(COD)Cl]$_2$ was prepared by the method of Chatt and Venanzi[1] and used without recrystallization. [Rh(NBD)Cl]$_2$ was prepared by the method of Abel,[26] except that the reaction vessel was sealed and heated at 50° for 6 hr. [Rh(NBD)Cl]$_2$ was recrystallized from dichloromethane with methanol. Rh(NBD)(acac) and Rh(COD)(acac) were prepared by a method analogous to that for the preparation of Rh-(ethylene)$_2$(acac) by Cramer.[27]

Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach über Engelskirchen, and Galbraith Laboratories, Inc., Knoxville, Tenn. Routine infrared spectra were measured on a Perkin-Elmer 337 grating spectrometer. Carbonyl frequencies were measured on a Cary-White 90 spectrometer. Spectra were calibrated using a polystyrene film. Conductivity measurements were made in nitromethane at 25° with a Model 31 conductivity bridge manufactured by the Yellow Springs Instrument Co., Inc., Yellow Springs, Ohio. Nmr measurements were made on a Varian HA 100 instrument operating at 37°.

Unless otherwise noted, all compounds were recrystallized by dissolution in minimal dichloromethane and addition of an equal volume of ethanol. Most compounds required stepwise addition of ethyl ether to complete crystallization. The preparations of cat-

(25) M. J. Church and M. J. Mays, *Chem. Commun.*, 435 (1968), and references therein.

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

(27) R. Cramer, *J. Amer. Chem. Soc.*, 86, 217 (1964).

ionic complexes with ClO_4^- or PF_6^- as the anion are entirely analogous, though the experimental procedure and the analysis for only one salt may be given below. Any differences in preparation of the two salts (as in (8)) will be noted. Use of $B(C_6H_5)_4^-$ as the anion was minimized owing to its coordinative tendencies in certain instances (see text and ref 14).

In the procedures below NBD = bicyclo[2.2.1]hepta-2,5-diene (norbornadiene), COD = 1,5-cyclooctadiene, DMF = N,N-dimethylformamide, DMA = N,N-dimethylacetamide, acac = 2,4-pentanedionato anion (acetylacetonate), diphos = 1,2-bisdiphenylphosphinoethane, arphos = 1-diphenylarsino-2-diphenylphosphinoethane. ^{1}H nmr shifts are given in units of τ (s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, m = multiplet); if unspecified the resonance is a broad singlet or a poorly resolved multiplet. Phenyl proton resonances are omitted. ^{31}P nmr shifts were recorded at 40.5 MHz and 37° relative to an external 85% H_3PO_4 standard. Infrared frequencies are in units of reciprocal centimeters (s = strong, m = medium, w = weak, sh = shoulder).

Calculation of the High-Field Nmr Spectrum of $[Rh\{P(CH_3)_3\}_4H_2]$. Transition energies and intensities for the seven-spin $AA'MXX'Y_2$ system (see text) were calculated on an IBM 360 computer with a LAOCN3 program by A. S. Bothner-By and S. Castellano of the Mellon Institute, Pittsburgh, Pa. Line-plotting and -shape routines were done on the Harvard departmental IBM 1620.

LAOCN3 was capable of nine least-squares iterations given line assignments and variable parameters. The eight major peaks (Figure 3a) could be assigned to ±0.5 Hz from the experimental spectrum. Trial and error produced an approximate spectrum whose lines (Figure 3b) were then altered slightly till the shape analysis yielded good agreement with the experimental spectrum. Final assignments were then made and six iterations performed on the IBM 360 with LAOCN3 to yield the coupling constants given below. Errors in the coupling constants were estimated from variations in the solution sets as the best fit set was approached. For the system $[RhH_1H_2P_1P_2P_3P_4]^+$ (octahedral arrangement with $H_1H_2P_1P_2$ in one plane, P_1 trans to H_1), the calculated coupling constants are (Hz): $|J_{Rh-H_{1,2}}| = 14.70$; $|J_{H_{1,2}-P_{3,4}}| = 20.30$; $|J_{P_1-P_2}| = 17.58$ and $|J_{H_1-H_2}| = 8.81$ or vice versa; $J_{H_1-P_1} = \pm149.13$, while $J_{H_1-P_2} = \mp13.24$ or vice versa. The analysis of the $AA'XX'$ system (i.e., the $H_1H_2P_1P_2$ arrangement) does not yield further information regarding the signs and/or magnitudes of the coupling constants. However, based on assignments made for similar d^6 dihydrido species, i.e., $Ru\{P(C_6H_5)_2CH_3\}_4H_2$ and $Ru\{P(C_6H_5)_2CH_3\}_3(CO)H_2$,[23] $[Ir\{P(C_6H_5)_3\}_3(CO)H_2]^+$,[28] and $Ir\{P(C_6H_5)_3\}_3\{Ge(CH_3)_3\}H_2$,[29] the most probable values for the coupling constants are: $J_{Rh-H} = \pm14.5$ (±0.5), $^2J_{H-P_{3,4}} = -20.3$ (±0.5), $^2J_{P_1-P_2} = \pm17.6$ (±0.5), $^2J_{H_1-H_2} = -8.8$ (±0.5), $^2J_{H_1-P_1} = +149$ (±1), and $^2J_{H_1-P_2} = -13.2$ (±0.5).

(1) Preparation of $[Rh(diene)\{P(C_6H_5)_3\}_2]^+B(C_6H_5)_4^-$, diene = NBD or COD. $[Rh(diene)Cl]_2$ (1.00 g) was dissolved in methanol containing 8.0 g of triphenylphosphine. Sodium tetraphenylborate (1.80 g, 1.3 mol) was then added as a solid and stirring continued for 5 min. The suspension was filtered and the solid was washed with benzene and diethyl ether and air-dried; yield 4.04 g of COD salt (95%), 4.00 g of NBD salt (89%). Anal. (COD salt) Calcd for $RhC_{68}H_{62}BP_2$: C, 77.41; H, 5.93; P, 5.87. Found: C, 77.10; H, 5.87; P, 5.83; Λ = 47; (NBD salt) Calcd for $RhC_{67}H_{58}BP_2$: C, 77.45; H, 5.63. Found: C, 77.59; H, 5.75; Λ = 47.

(2) Preparation of $[Rh(COD)\{P(C_6H_5)_3\}_2]^+PF_6^-$ (or ClO_4^-). A mixture of 500 mg of $[Rh(COD)Cl]_2$ dissolved in 10 ml of dichloromethane and 500 mg of KPF_6 dissolved in 10 ml of water was stirred vigorously while 2.0 g of triphenylphosphine was added. After 15 min the dichloromethane layer was removed, washed three times with 10 ml of water, and reduced to ca. 5 ml with a flow of nitrogen. Ethanol (5 ml) was slowly added followed by slow addition of ca. 10 ml of diethyl ether to complete crystallization. The orange crystals were filtered off, washed with benzene and diethyl ether, and air-dried: yield 1.65 g (90%); ^{1}H nmr (CDCl$_3$) 5.39 (4, olefin), 7.58 (m, 8, methylene). Anal. Calcd for $RhC_{44}H_{42}F_6P_3$: C, 60.00; H, 4.81; Cl, 0.00. Found: C, 59.59; H, 5.01; Cl, 0.03; Λ = 74. Preparation of the perchlorate salt gave a similar yield. Anal. Calcd for $RhC_{44}H_{42}ClO_4P_2$: C, 63.27; H, 5.07; P, 7.41. Found: C, 63.49; H, 5.47; P, 7.84; Λ = 73.

(3) Preparation of $[Rh(COD)\{P(C_6H_5)_2CH_3\}_2]^+ClO_4^- \cdot CH_2Cl_2$. $[Rh(COD)Cl]_2$ (720 mg) and 500 mg of sodium perchlorate (slight

excess) were placed in 5 ml of acetone. $P(C_6H_5)_2CH_3$ (1.17 g) was added slowly with stirring. Stirring was continued for 5 min. The suspension was filtered and any solid product washed from the sodium chloride with dichloromethane. The volume of the filtrate was reduced to ca. 10 ml and an equal volume of ethanol was added followed by slow addition of excess diethyl ether. The crystals were filtered off, washed with diethyl ether, and air-dried: yield 1.78 g (86%); ^{1}H nmr (CH$_2$Cl$_2$) 5.36 (4, olefin), 7.64 (8, methylene), 8.43 ("virtually coupled," 6, P-CH$_3$); ^{31}P nmr (CH$_2$Cl$_2$) −10.4 ppm (d, J_{Rh-P} = 141 Hz); the crystals contained 1 mol of dichloromethane of crystallization. Anal. Calcd for $RhC_{35}H_{40}Cl_3O_4P_2$: C, 52.81; H, 5.07; Cl, 13.36; P, 7.78. Found: C, 53.06; H, 5.21; Cl, 12.20; P, 7.19; Λ = 83.

(4) Preparation of $[Rh(COD)\{As(C_6H_5)_3\}_2]ClO_4^-$. Rh(COD)(acac) (250 mg) was placed in 3 ml of tetrahydrofuran and 115 mg of 70% $HClO_4$ in 1 ml of THF was added. Addition of 480 mg of $As(C_6H_5)_3$ yielded an orange solution. Crystals shortly began to form and diethyl ether was added as needed to complete crystallization. The crystals were filtered off, washed with diethyl ether, and air-dried; yield 630 mg (88%); ^{1}H nmr (CDCl$_3$) 5.24 (4, olefin), 7.40 (m, 4, methylene), 7.92 (m, 4, methylene). Anal. Calcd for $RhC_{44}H_{42}As_2ClO_4$: C, 57.26; H, 4.59; Cl, 3.84. Found: C, 56.97; H, 4.74; Cl, 3.85.

(5) Preparation of $[Rh(COD)\{P(OC_6H_5)_3\}_2]^+ClO_4^-$. The compound was prepared as in (4) employing 500 mg of $P(OC_6H_5)_3$: yield 510 mg (74%); ^{1}H nmr (CDCl$_3$) 4.48 (4, olefin), 7.82 (m, 8, methylene). Anal. Calcd for $RhC_{44}H_{42}ClO_{10}P_2$: C, 56.76; H, 4.55; Cl, 3.81. Found: C, 56.87; H, 4.84; Cl, 3.93.

(6) Preparation of $[Rh(COD)(diphos)]^+ClO_4^-$. The preparation was as in (4) employing 310 mg of diphos: yield 420 mg (76%); ^{1}H nmr (CDCl$_3$) 5.05 (4, olefin), ca. 7.6 (m, 8, methylene), ca. 7.6 (m, 4, PC$_2$H$_4$P); ^{31}P nmr (CH$_2$Cl$_2$) −54.6 ppm (d, J_{Rh-P} = 161 Hz). Anal. Calcd for $RhC_{34}H_{36}ClO_4P_2$: C, 57.60; H, 5.12; Cl, 5.00. Found: C, 57.69; H, 5.12; Cl, 4.94.

(7) Preparation of $[Rh(COD)(arphos)]^+ClO_4^-$. This compound was prepared as in (4) employing 345 mg of arphos: yield 470 mg (80%); ^{1}H nmr (CDCl$_3$) 4.53 (2, olefin), 5.34 (2, olefin), ca. 7.6 (m, 8, methylene), ca. 7.6 (m, 4, PC$_2$H$_4$As); ^{31}P nmr (CH$_2$Cl$_2$) −58.6 ppm (d, J_{Rh-P} = 138 Hz).

(8) Preparation of $[Rh(NBD)\{P(C_6H_5)_3\}_2]^+PF_6^-$ (or ClO_4^-). Method 1. Preparation from $[Rh(NBD)Cl]_2$. $[Rh(NBD)\{P(C_6-H_5)_3\}_2]^+ClO_4^-$. $[Rh(NBD)Cl]_2$ (750 mg) was dissolved in 25 ml of benzene containing 3.0 g of triphenylphosphine. A solution of 500 mg of sodium perchlorate in 7.5 ml of tetrahydrofuran was added, followed shortly by 10 ml of diethyl ether. The suspension was filtered, washed with benzene and diethyl ether, and air-dried. The yellow-orange powder was dissolved off the filter with minimal dichloromethane (ca. 5 ml) and crystallized by addition of ethanol and diethyl ether. The sodium chloride remained on the filter: yield 2.55 g (96%); ^{1}H nmr (CDCl$_3$) 5.43 (4, olefin), 5.86 (2, methine), 8.50 (2, methylene); ^{31}P nmr (CH$_2$Cl$_2$) −28.5 ppm (d, J_{Rh-P} = 155 Hz). Anal. Calcd for $RhC_{43}H_{38}ClO_4P_2$: C, 63.04; H, 4.68; P, 7.56. Found: C, 62.48; H, 4.74; P, 7.37; Λ = 73.

$[Rh(NBD)\{P(C_6H_5)_3\}_2]^+PF_6^-$. $[Rh(NBD)Cl]_2$ (250 mg) was dissolved in a solution of 1.0 g of triphenylphosphine in 8 ml of benzene and 2 ml of tetrahydrofuran. Potassium hexafluorophosphate (200 mg) in 2 ml acetone was added, followed by 5 ml of diethyl ether. The suspension was filtered and the solid was washed with benzene and diethyl ether and air-dried. Recrystallization as above left potassium chloride on the filter and yielded 940 mg (87%) of product. Anal. Calcd for $RhC_{43}H_{38}F_6P_3$: C, 59.80; H, 4.32. Found: C, 59.04; H, 4.37; Λ = 77.

Method 2. Preparation from $Rh\{P(C_6H_5)_3\}_3Cl$. $Rh\{P(C_6H_5)_3\}_3Cl$ (11.5 g), 2.29 g of potassium hexafluorophosphate, and 1.5 ml of norbornadiene were stirred for 2 hr in a mixture of 50 ml of acetone and 10 ml of dichloromethane. The reaction mixture, which consisted of an orange solution and orange precipitate, was filtered and all orange product dissolved away from the potassium chloride with dichloromethane. The combined filtrate was reduced on an evaporator until crystallization set in. Crystallization was completed by the addition of an equal volume of ethanol followed by excess diethyl ether. The filtered orange product was washed with diethyl ether and air-dried. It was recrystallized as in method 1; yield 9.9 g (93%).

An identical preparation employing sodium perchlorate gave a similar yield.

Crystalline samples of $[Rh(NBD)\{P(C_6H_5)_3\}_2]^+A^-$ tend to retain varying amounts of solvent. Solvent of crystallization may be removed by first washing the product with benzene followed by pumping of the sample in vacuo for an extended period.

(28) D. Commereuc, I. Douek, and G. Wilkinson, J. Chem. Soc. A, 1771 (1970).

(29) F. Glockling and M. D. Wilbey, ibid., 1675 (1970).

The preparation of other diene complexes from Rh{P(C$_6$H$_5$)$_3$}$_3$Cl gave very poor yields. The yield of [Rh(COD){P(C$_5$H$_5$)$_3$}$_2$]$^+$ClO$_4^-$ by this method was 59%.

The [Rh(NBD){P(C$_6$H$_5$)$_3$}$_2$]$^+$A$^-$ species prepared in this manner are sometimes slightly impure as judged by their reaction with hydrogen in acetone in the absence of air. A cloudy brownish solution indicates an impure sample. The solution should be pale yellow. Purity could usually be attained by recrystallization from dichloromethane with benzene by sweeping off the dichloromethane with nitrogen. Impure samples seem to result from use of aged or poorly prepared Rh{P(C$_6$H$_5$)$_3$}$_3$Cl.

(9) Preparation of [Rh(NBD){P(C$_6$H$_5$)$_2$CH$_3$}$_2$]$^+$ClO$_4^-$. [Rh-(NBD)Cl]$_2$ and 1.25 g of sodium perchlorate (slight excess) were placed in 20 ml of acetone. After dissolution of the perchlorate, 3.04 g of P(C$_6$H$_5$)$_2$CH$_3$ (2.0 mol) was added very slowly with stirring. Isolation as in (3) after stirring for 5 min yielded 4.31 g (81%) of product: ^{1}H nmr (CDCl$_3$) 5.28 (q, 4, J = 2.2 Hz, olefin), 5.89 (2, methine), 8.54 (2, methylene), 8.40 ("virtually coupled," 6, P–CH$_3$); ^{31}P nmr (CH$_2$Cl$_2$) −12.1 ppm (d, J_{Rh-P} = 159 Hz). *Anal.* Calcd for RhC$_{33}$H$_{34}$ClO$_4$P$_2$: C, 57.02; H, 4.94; P, 8.91. Found: C, 56.22; H, 4.80; P, 8.69; Λ = 77 (PF$_6^-$ salt).

(10) Preparation of [Rh(NBD){P(CH$_3$)$_2$C$_6$H$_5$}$_2$]$^+$ClO$_4^-$. [Rh-(NBD)Cl]$_2$ (1.18 g) and 0.73 g of sodium perchlorate were placed in 5 ml of degassed tetrahydrofuran on a vacuum rack and 1.42 g (2.0 mol) of P(CH$_3$)$_2$C$_6$H$_5$ was slowly added with stirring under argon. After addition was complete and *ca.* 10 min had elapsed, 40 ml of degassed diethyl ether was added in 5-ml aliquots to the cloudy red solution. The orange powder was filtered off and the filtrate discarded. The powder was dissolved off the sintered disk with dichloromethane, leaving sodium chloride behind. The dichloromethane solution was reduced to 5–10 ml *in vacuo* and 35 ml of degassed diethyl ether added in 5-ml portions. The orange crystals which formed were filtered off, washed with benzene and diethyl ether, and air-dried: yield 2.67 g (91%); ^{1}H nmr (CDCl$_3$) 4.94 (4, olefin), 5.82 (2, methine), *ca.* 8.4 (2, methylene), *ca.* 8.6 (broad s, 12, P–CH$_3$); ^{31}P nmr (CH$_2$Cl$_2$) +3.1 ppm (d, J_{Rh-P} = 150 Hz). *Anal.* Calcd for RhC$_{22}$H$_{30}$ClO$_4$P$_2$: C, 48.40; H, 5.29; Cl, 6.21; P, 10.85. Found: C, 47.66; H, 5.45; Cl, 6.23; P, 10.77; Λ = 72 (pales in solution). An identical preparation employing sodium hexafluorophosphate gave a similar yield.

(11) Preparation of [Rh(NBD){As(C$_6$H$_5$)$_3$}$_2$]$^+$ClO$_4^-$·^{1}/$_2$CH$_2$Cl$_2$. Rh(NBD)(acac) (250 mg) and 550 mg of As(C$_6$H$_5$)$_3$ (2 mol) were dissolved, with no color change, in 3 ml of tetrahydrofuran, and 120 mg of 70% HClO$_4$ (1 mol) in 2 ml of tetrahydrofuran was added dropwise. The solution immediately turned deep orange and crystals formed. Diethyl ether was added as needed to complete crystallization and the crystals were filtered off, washed with methanol and diethyl ether, and air-dried: yield 750 mg (90%); ^{1}H nmr ((CD$_3$)$_2$CO) 5.30 (4, olefin), 5.88 (2, methine), 8.55 (2, methylene). The crystals contained *ca.* 0.5 mol of dichloromethane of crystallization. *Anal.* Calcd for RhC$_{43.5}$H$_{39}$As$_2$Cl$_2$O$_4$: C, 55.03; H, 4.14; Cl, 7.47. Found: C, 55.93; H, 4.49; Cl, 6.70; Λ = 74.

(12) Preparation of [Rh(NBD){P(OC$_6$H$_5$)$_3$}$_2$]$^+$ClO$_4^-$. The preparation was as in (11), except that the acid was added before the dropwise addition of 530 mg (2 mol) of P(OC$_6$H$_5$)$_3$: yield 476 mg (67%); ^{1}H nmr (ClCH$_2$CH$_2$Cl) 4.90 (4, olefin), (CH$_2$Cl$_2$) 6.26 (2, methine), 8.39 (2, methylene); ^{31}P nmr (CH$_2$Cl$_2$) −108.2 ppm (d, J_{Rh-P} = 260 Hz). *Anal.* Calcd for RhC$_{43}$H$_{35}$ClO$_{10}$P$_2$: C, 56.44; H, 4.19; Cl, 3.87; P, 6.77. Found: C, 57.05; H, 4.40; Cl, 3.79; P, 6.64; Λ = 78.

(13) Preparation of [Rh(NBD){P(C$_6$H$_5$)$_2$OCH$_3$}$_2$]$^+$ClO$_4^-$. The compound was prepared as in (12) employing 355 mg of P(C$_6$H$_5$)$_2$-OCH$_3$; yield 250 mg (42%) after recrystallization. Crystallization of the product from the reaction mixture was slow and attempts to speed it up were thwarted by formation of an oil. Standing at −20° for 2 days yielded clumps of crystals which appeared to collapse upon drying. Recrystallization was performed from dichloromethane with diethyl ether at −20°. The crystals were filtered off, washed with diethyl ether, and air-dried: ^{1}H nmr (CDCl$_3$) 4.82 (4, olefin), 5.87 (2, methine), 8.27 (2, methylene), 6.80 ("virtually coupled", 6, P–OCH$_3$). *Anal.* Calcd for RhC$_{33}$-H$_{34}$ClO$_6$P$_2$: C, 54.52; H, 4.71; Cl, 4.88; P, 8.52. Found: C, 55.47; H, 5.21; Cl, 4.77; P, 8.66.

(14) Preparation of [Rh(NBD)(diphos)]$^+$ClO$_4^-$. The procedure was as in (12) employing 338 mg of diphos (1 mol): yield 500 mg (85%); ^{1}H nmr (ClCH$_2$CH$_2$Cl) 4.66 (4, olefin), (CH$_2$Cl$_2$) 5.77 (2, methine), 8.16 (2, methylene), 7.63 (dd, 4, J = 18.5 and 1.1 Hz, PC$_2$H$_4$P). *Anal.* Calcd for RhC$_{33}$H$_{32}$ClO$_4$P$_2$: C, 57.19; H, 4.66;

Cl, 5.12; P, 8.94. Found: C, 56.24; H, 4.53; Cl, 5.08; P, 9.00; Λ = 78.

(15) Preparation of [Rh(NBD)(arphos)]$^+$ClO$_4^-$. The compound was prepared as in (12) employing 365 mg of arphos: yield 550 mg (91%); ^{1}H nmr (CDCl$_3$) 4.70 (4, olefin), 5.72 (2, methine), 8.26 (2, methylene), *ca.* 7.5 (m, 4, PC$_2$H$_4$As). *Anal.* Calcd for RhC$_{33}$H$_{32}$-AsClO$_4$P: C, 53.79; H, 4.38; Cl, 4.81. Found: C, 53.28; H, 4.49; Cl, 5.21.

(16) Preparation of [Rh(NBD){NH$_2$C(CH$_3$)$_3$}$_2$]$^+$PF$_6^-$. [Rh(NBD)-Cl]$_2$ (250 mg) and KPF$_6$ (250 mg) were placed in a mixture of 5 ml of dichloromethane and 5 ml of water, and 1 ml of NH$_2$C(CH$_3$)$_3$ was added. The mixture was stirred vigorously for 10 min. The dichloromethane layer was removed, washed with water, dried with sodium sulfate, and reduced to *ca.* 2 ml on an evaporator. Diethyl ether was added slowly to produce yellow needles which were filtered off, washed with diethyl ether, and air-dried: yield 282 mg (63%); ^{1}H nmr (CDCl$_3$) 5.86 (q, 4, J = 2.4 Hz, olefin), 6.15 (2, methine), *ca.* 8.7 (2, methylene), 7.64 (4, −NH$_2$), 8.76 (s, 18, CH$_3$). *Anal.* Calcd for RhC$_{15}$H$_{30}$F$_6$N$_2$P: C, 37.05; H, 6.22; N, 5.76. Found: C, 37.49; H, 6.25; N, 6.15.

(17) Preparation of [Rh(NBD){P(C$_6$H$_5$)$_3$}{As(C$_6$H$_5$)$_3$}]$^+$ClO$_4^-$·^{1}/$_2$CH$_2$Cl$_2$. [Rh(1,3-butadiene)$_2${P(C$_6$H$_5$)$_3$}]$^+$ClO$_4^-$ (500 mg) (see (34)), 1.0 g of As(C$_6$H$_5$)$_3$, and 0.25 ml of norbornadiene were dissolved in 2 ml of dichloromethane to yield an orange solution which was allowed to stand for a few minutes. The product crystallized upon slow addition of excess ethanol. The orange crystals were filtered off, washed with diethyl ether, and air-dried: yield 610 mg (83%); ^{1}H nmr [(CH$_3$)$_2$CO] 5.32 (4, olefin), 5.92 (2, methine), 8.48 (2, methylene); the crystals contained *ca.* 0.5 mol of dichloromethane. *Anal.* Calcd for RhC$_{43.5}$H$_{39}$AsCl$_2$O$_4$P: C, 54.91; H, 4.13; Cl, 3.73. Found: C, 53.96; H, 4.08; Cl, 3.54; Λ = 73.

(18) Preparation of [Rh(1,3-cyclohexadiene){P(C$_6$H$_5$)$_3$}$_2$]$^+$ClO$_4^-$. [Rh(NBD){P(C$_6$H$_5$)$_3$}$_2$]$^+$ClO$_4^-$ (500 mg) was placed in 10 ml of tetrahydrofuran and degassed on a vacuum rack. Hydrogen (1 atm) was introduced and the suspension stirred vigorously for 0.5 hr to yield a pale yellow solution. 1,3-Cyclohexadiene (0.25 ml) was added, causing immediate formation of a deep red color followed by precipitation of a red-orange powder. The product was filtered off and excess diethyl ether added to the filtrate followed by filtration to remove residual product. The two yields were combined, washed with diethyl ether, and dried in air to yield 463 mg (94%) of product: ^{1}H nmr (CDCl$_3$) 4.30 (2, olefin), 5.99 (2, olefin), 8.80 (m, 4, methylene). *Anal.* Calcd for RhC$_{42}$H$_{38}$ClO$_4$P$_2$: C, 62.49; H, 4.75; P, 7.67. Found: C, 61.94; H, 4.81; P, 7.73; Λ = 74.

(19) Preparation of [Rh(1,3-butadiene){P(C$_6$H$_5$)$_3$}$_2$]$^+$PF$_6^-$. A preparation identical with (18) was carried out, employing 500 mg of [Rh(NBD){P(C$_6$H$_5$)$_3$}$_2$]$^+$PF$_6^-$ and 1,3-butadiene; it gave 430 mg (90%) of product: ^{1}H nmr [(CD$_3$)$_2$CO sealed under N$_2$] 4.19 (t, 2, J = 7–8 Hz, olefin), 7.12 (broad s, 2, olefin), 8.21 (d, 2, J = *ca.* 10 Hz, olefin); spectrum shows *ca.* 25% disproportionation to [Rh(1,3-butadiene)$_2$P(C$_6$H$_5$)$_3$]$^+$; the complex is red and disproportionates if recrystallization is attempted. *Anal.* Calcd for RhC$_{40}$-H$_{36}$F$_6$P$_3$: C, 58.12; H, 4.39. Found: C, 58.25; H, 4.39; Λ = 74 (pales in solution).

(20) Preparation of [Rh(NBD){P(CH$_3$)$_2$C$_6$H$_5$}$_3$]$^+$PF$_6^-$. P(CH$_3$)$_2$-C$_6$H$_5$ (1.73 g, 3 mol) was added to 3.72 g of [Rh(NBD){P(C$_6$H$_5$)$_3$}$_2$]$^+$-PF$_6^-$ in 20 ml of acetone with stirring. The complex dissolved to yield an orange solution. Excess ethanol was added to complete crystallization. The yellow crystals were filtered off, washed thoroughly with diethyl ether, and air-dried: yield 2.96 g (94%); ^{1}H nmr (CH$_2$Cl$_2$) 6.54 (2, methine), 7.03 (4, olefin), 8.80 (2, methylene), 8.36 (broad s, 18, P–CH$_3$); ^{31}P nmr (CH$_2$Cl$_2$) +5.0 ppm (d, J_{Rh-P} = 118 Hz). *Anal.* (ClO$_4^-$ salt) Calcd for RhC$_{31}$H$_{41}$-ClO$_4$P$_3$: C, 52.51; H, 5.84; Cl, 5.00; P, 13.10. Found: C, 52.50; H, 6.23; Cl, 5.75; P, 12.89; Λ = 76 (PF$_6^-$ salt).

(21) Preparation of [Rh(NBD){P(CH$_3$)$_3$}$_3$]$^+$PF$_6^-$. [Rh(NBD)-{P(C$_6$H$_5$)$_3$}$_2$]$^+$PF$_6^-$ (2.65 g) was placed in 10 ml of acetone and the mixture frozen with liquid nitrogen on a vacuum line. After evacuation of the vessel 0.762 g of P(CH$_3$)$_3$ was frozen in and the mixture warmed to room temperature and stirred for 10 min. The volume was reduced to *ca.* 5 ml, the vessel removed from the line, and 10 ml of diethyl ether slowly added to yield yellow crystals which were filtered off, washed with diethyl ether, and air-dried: yield 1.65 g (95%); ^{1}H nmr (CH$_2$Cl$_2$) 6.52 (2, methine), 7.03 (4, olefin), 8.74 (2, methylene), 8.59 (m, 27, P–CH$_3$); ^{31}P nmr (CH$_2$Cl$_2$) +15.2 ppm (d, J_{Rh-P} = 120 Hz). *Anal.* Calcd for RhC$_{16}$H$_{35}$F$_6$P$_4$: C, 33.82; H, 6.21; P, 21.80. Found: C, 34.62; H, 6.22; P, 20.77; Λ = 87.

(22) Preparation of [Rh(NBD){As(CH₃)₂C₆H₅}₃]⁺ClO₄⁻. [Rh-(NBD){As(C₆H₅)₃}₂]⁺ClO₄⁻ (418 mg) was dissolved in 1 ml of dichloromethane and 260 mg of As(CH₃)₂C₆H₅ (3.1 mol) added. Methanol (1 vol) was added after 10 min, followed by stepwise addition of diethyl ether to yield yellow crystals which were filtered off, washed with diethyl ether, and air-dried: yield 345 mg (93%); ¹H nmr (CDCl₃) 6.44 (2, methine), 6.79 (4, olefin), 8.77 (2, methylene), 8.52 (s, 18, As–CH₃). *Anal.* Calcd for RhC₃₁H₄₁As₃ClO₄: C, 44.82; H, 4.91; Cl, 4.22. Found: C, 44.75; H, 4.97; Cl, 4.02.

(23) Preparation of [Rh(NBD)(diphos){P(CH₃)₂C₆H₅}]⁺ClO₄⁻. [Rh(NBD)(diphos)]⁻ClO₄⁻ (130 mg) was dissolved in 1 ml of dichloromethane, and P(CH₃)₂C₆H₅ was added until the color lightened to orange. Addition of 1 ml of methanol and excess diethyl ether yielded gold crystals which were filtered off, washed with methanol and diethyl ether, and air-dried: yield 135 mg (87%); ¹H nmr (CH₂Cl₂) 6.44 (6, methine and olefin), 8.74 (2, methylene), *ca.* 7.5 (broad m, 4, PC₂H₄P), 8.98 (d, 6, *J* = 6–7 Hz, P–CH₃). *Anal.* Calcd for RhC₄₁H₄₃ClO₄P₃: C, 59.26; H, 5.22; Cl, 4.27. Found: C, 59.44; H, 5.47; Cl, 4.48.

(24) Preparation of [Rh(NBD)(diphos){As(CH₃)₂C₆H₅}]⁺ClO₄⁻. The preparation was as in (23) with 230 mg of [Rh(NBD)(diphos)]⁺-ClO₄⁻ and 62 mg of As(CH₃)₂C₆H₅: yield 270 mg (93%); ¹H nmr (CH₂Cl₂) 6.28 (6, methine and olefin), 8.69 (2, methylene), 7.55 (v br d, 4, *J* = 9 Hz, PC₂H₄P), 9.11 (s, 6, As–CH₃). *Anal.* Calcd for RhC₄₁H₄₃AsClO₄P₂: C, 55.86; H, 4.69; Cl, 4.12. Found: C, 55.62; H, 5.03; Cl, 3.90.

(25) Preparation of [Rh(NBD)(arphos){P(CH₃)₂C₆H₅}]⁺ClO₄⁻. The compound was prepared as in (23) with 250 mg of [Rh(NBD)-(arphos)]⁺ClO₄⁻ and 48 mg of P(CH₃)₂C₆H₅: yield 260 mg (89%); ¹H nmr (CDCl₃) 6.09 (2, olefin), 6.41 (2, methine), 6.82 (2, olefin), 8.71 (2, methylene), 7.96 (4, AsC₂H₄P), 8.84 (d, 3, *J* = 7 Hz, P–CH₃), 9.01 (d, 3, *J* = 7 Hz, P–CH₃); ³¹P nmr (CH₂Cl₂) +14.1 ppm (d, *J*ₐₕ₋ₚ = 125 Hz, P(CH₃)₂C₆H₅), −63.9 ppm (d, *J*ₐₕ₋ₚ = 135 Hz, arphos). *Anal.* Calcd for RhC₄₁H₄₃AsClO₄P₂: C, 55.86; H, 4.69; Cl, 4.12. Found: C, 55.71; H, 5.05; Cl, 3.91.

(26) Preparation of [Rh(NBD)(arphos){As(CH₃)₂C₆H₅}]⁺ClO₄⁻. This was prepared as in (23) with 390 mg of [Rh(NBD)(arphos)]⁺-ClO₄⁻ and 96 mg of As(CH₃)₂C₆H₅: yield 435 mg (90%); ¹H nmr (CH₂Cl₂) 6.31 (6, methine and olefin), 8.68 (2, methylene), *ca.* 7.5 (v br, 4, PC₂H₄As), 9.03 (s, 6, As–CH₃). *Anal.* Calcd for RhC₄₁H₄₃As₂ClO₄P: C, 53.15; H, 4.46; Cl, 3.92. Found: C, 53.29; H, 4.77; Cl, 3.70.

(27) Preparation of [Rh{P(C₆H₅)₂CH₃}₄]⁺PF₆⁻. [Rh(COD){P-(C₆H₅)₃}₂]⁺PF₆⁻ (500 mg) was placed in 2 ml of acetone and 0.5 g of P(C₆H₅)₂CH₃ added. An immediate color change to deep red took place. Excess ethanol was added to complete crystallization. The red-orange crystals were filtered off, washed with diethyl ether, and air-dried: yield 550 mg (93%); ¹H nmr (CDCl₃) 9.76 (m, 12, P–CH₃); ³¹P nmr (CH₂Cl₂) −2.7 ppm (d, *J*ₐₕ₋ₚ = 136 Hz). *Anal.* Calcd for RhC₅₂H₅₂F₆P₅: C, 59.54; H, 5.00; P, 14.76. Found: C, 59.26; H, 5.24; P, 14.77; Λ = 74.

(28) Preparation of [Rh{P(CH₃)₂C₆H₅}₄]⁺PF₆⁻. The preparation was as in (27) with 0.35 ml of dimethylphenylphosphine. Filtration and drying were done under a flow of nitrogen: yield 405 mg (90%); ¹H nmr (CH₂Cl₂) 8.84 (m, 24, P–CH₃); ³¹P nmr (CH₂Cl₂) +4.3 ppm (d, *J*ₐₕ₋ₚ = 132 Hz). *Anal.* Calcd for RhC₃₂H₄₄F₆P₅: C, 48.01; H, 5.54; P, 19.35. Found: C, 47.99; H, 5.52; P, 19.25.

[Rh{P(CH₃)₂C₆H₅}₄]⁺PF₆⁻ does not seem to be air sensitive over a short period of time but does eventually become tan in color if left exposed to the air for several days.

(29) Preparation of [Rh{P(OCH₃)₂C₆H₅}₄]⁺PF₆⁻. [Rh(COD)-{P(C₆H₅)₃}₂]⁺PF₆⁻ (400 mg) was placed in 3 ml of acetone and 0.35 ml of P(OCH₃)₂C₆H₅ added to yield an orange solution. Addition of diethyl ether caused crystallization to take place. The crystals were filtered off, washed with diethyl ether, and air-dried: yield 405 mg (96%); ¹H nmr (CDCl₃) 6.80 ("virtually coupled," 24, P–O–CH₃); ³¹P nmr (CH₂Cl₂) −148.0 ppm (d, *J*ₐₕ₋ₚ = 170 Hz). *Anal.* Calcd for RhC₃₂H₄₄F₆O₈P₅: C, 41.40; H, 4.78; P, 16.68. Found: C, 41.46; H, 5.17; P, 16.66.

(30) Preparation of [Rh{P(CH₃)₂C₆H₅}₄H₂]⁺PF₆⁻. [Rh{P(CH₃)₂-C₆H₅}₄]⁺PF₆⁻ (500 mg) was dissolved in 2 ml of dichloromethane and treated with hydrogen until pale yellow to colorless (very rapid). Slow addition of diethyl ether produced white crystals which were filtered off, washed with diethyl ether, and air-dried: yield 400 mg (89%); ¹H nmr (CH₂Cl₂) 20.29 (see text, 2, *J*ₐₕ₋ₕ = 13.0 Hz, *J*ₕ₋Pₐₓᵢₐₗ = 17.0 Hz, Rh–H₂), 8.52 (m, 24, P–CH₃); ³¹P nmr (CH₂Cl₂) +1.2 ppm (d, *J*ₐₕ₋ₚ = 100 Hz, Pₐₓᵢₐₗ), +12.1 ppm (second order, Pₑqᵤₐₜₒᵣᵢₐₗ); ir (Nujol) 2010 (m, br, Rh–H). *Anal.* Calcd for

RhC₃₂H₄₆F₆P₅: C, 47.89; H, 5.78; P, 1930. Found: C, 48.54; H, 5.80; P, 18.86.

(31) Preparation of [Rh{P(CH₃)₃}₄H₂]⁺PF₆⁻. [Rh(NBD){P-(C₆H₅)₃}₂]⁺PF₆⁻ (790 mg) was placed in 10 ml of acetone, degassed on a vacuum rack, and treated with hydrogen until yellow (*ca.* 15 min). After freezing the yellow solution in liquid nitrogen and evacuating the vessel, 350 mg of P(CH₃)₃ (5 mol) was frozen in and the solution allowed to warm to room temperature. Hydrogen (1 atm) was introduced and the solution stirred overnight to yield a very pale yellow solution which was reduced to *ca.* 2 ml *in vacuo.* Hydrogen (1 atm) was again added, and the cream-colored product precipitated with diethyl ether. The product was filtered off under hydrogen and recrystallized from dichloromethane with diethyl ether: yield 430 mg (85%); ¹H nmr (CH₂Cl₂) 20.70 (see text, 2, *J*ₐₕ₋ₕ = 15.0 Hz, *J*ₕ₋Pₐₓᵢₐₗ = 20.0 Hz, Rh–H₂), 8.51 (m, 36, P–CH₃); ³¹P nmr (CH₂Cl₂) +11.9 ppm (d, *J*ₐₕ₋ₚ = 96 Hz, Pₐₓᵢₐₗ), 22.8 ppm (second order, Pₑqᵤₐₜₒᵣᵢₐₗ); ir (Nujol) 1965 (m, br, Rh–H), νₘ₋ₕ/νₘ₋D = 1.39. *Anal.* Calcd for RhC₁₂H₃₈F₆P₅: C, 26.01; H, 6.91. Found: C, 26.01; H, 6.89. *Caution:* the ClO₄⁻ salt detonated upon being struck with a hammer. Due care should be exercised in preparing potentially explosive perchlorate salts.

(32) Preparation of [Rh{As(CH₃)₂C₆H₅}₄H₂]⁺ClO₄⁻. [Rh(NBD)-{As(CH₃)₂C₆H₅}₃]⁺ClO₄⁻ (199 mg) and 43 mg of As(CH₃)₂C₆H₅ were placed in 5 ml of acetone on a vacuum line. The solution was freeze degassed and stirred overnight under hydrogen. The volume of the solution was reduced to *ca.* 1 ml. An nmr of this solution showed a doublet in the hydride region (*ca.* τ 22) with *J* = 12.5 Hz. The sample was reduced to dryness and dissolved in 1 ml of methanol. An off-white solid could be persuaded to form by the very slow addition of diethyl ether. A total of 160 mg of this solid was filtered off, washed with diethyl ether, and air-dried. The product could not be obtained analytically pure, but ir and nmr analyses confirmed the presence of the dihydride species: nmr (CH₂Cl₂) 22.31 (d, 2, *J*ₐₕ₋ₕ = 12.5 Hz, Rh–H₂); ir (Nujol) 1995 (m) and 1975 (m, Rh–H).

(33) Preparation of [Rh{P(C₆H₅)₃}₂{As(CH₃)₂C₆H₅}₂H₂]⁺PF₆⁻. A procedure identical with (31) was used, with 570 mg of [Rh(NBD)-{P(C₆H₅)₃}₂]⁺PF₆⁻ and 300 mg of As(CH₃)₂C₆H₅, yielding 470 mg (63%) of the product after recrystallization from dichloromethane with diethyl ether in the presence of hydrogen: ¹H nmr (CH₂Cl₂) 21.80 (q, 2, *J*ₐₕ₋ₕ = 12.0 Hz, *J*ₕ₋Pₐₓᵢₐₗ = 12.0 Hz, Rh–H₂), 9.05 (s, 12, As–CH₃); ³¹P nmr (CH₂Cl₂) −42.0 ppm (d, *J*ₐₕ₋ₚ = 105 Hz); ir (Nujol) 2045 (m) and 2130 (m, Rh–H). *Anal.* Calcd for RhC₅₂-H₅₄As₂F₆P₃: C, 55.09; H, 4.36. Found: C, 54.79; H, 4.37.

The product yellows slightly in solution in the absence of hydrogen or in the solid state *in vacuo* or air. The peach-colored crystals become white if placed under hydrogen for a few minutes. This behavior in the solid state is apparently indefinitely reversible.

(34) Preparation of [Rh(1,3-butadiene)₂{P(C₆H₅)₃}]⁺ClO₄⁻. [Rh-(NBD){P(C₆H₅)₃}₂]⁺ClO₄⁻ (1 g) was placed in 10 ml of acetone and the solution degassed on a vacuum line. The solution was then treated with hydrogen until yellow. The excess hydrogen was pumped off at room temperature and substituted with 1,3-butadiene to yield a red solution. After stirring for 5 min the volume was reduced to *ca.* 5 ml and 20 ml of tetrahydrofuran added (not peroxide free). Butadiene was then condensed in at 0° to yield a pale red solution and pale yellow crystals and powder after *ca.* 10 min. The product was filtered off and recrystallized from dichloromethane with methanol and diethyl ether to yield 0.35 g (49%) of pale yellow crystals of the product: ¹H nmr [(CD₃)₂CO] 3.91 (br t, 4, *J* = *ca.* 7 Hz), 6.43 (d, 4, *J* = 7.0 Hz), 9.16 (t, 4, *J* = 10.5 Hz). *Anal.* Calcd for RhC₂₆H₂₇ClO₄P: C, 54.50; H, 4.75. Found: C, 54.39; H, 5.04; Λ = 79 (PF₆⁻ salt).

The yield may be increased slightly by an analogous procedure using a few drops of hydrogen peroxide solution in tetrahydrofuran. Possibly removal of the dissociated triphenylphosphine from the reaction equilibrium by formation of the oxide aids the formation of the product.

On the Preparation of Carbonyl Species [Rh(L)ₓ(CO)ᵧ(S)ᵤ]⁺A⁻. The methods of preparation are equally applicable to salts with PF₆⁻, ClO₄⁻, or B(C₆H₅)₄⁻ as anions. Compounds employing each of the three anions were not always prepared, and any significant variations in preparative procedures will be noted.

Determination of Carbon Monoxide Content. The apparatus consisted of two small bulbs (*ca.* 3 ml) joined at right angles to each other and to a male joint such that a liquid in one bulb could be poured onto a solid in the other by rotation about the connecting joint to the gas buret. In a typical determination *ca.* 0.25 mmol of the sample and *ca.* 1 mmol of diphos were placed in one bulb along with a small stirring bar. 2-Butanone (1 ml) was placed in

the other bulb and frozen in liquid nitrogen, after which the apparatus was evacuated. Warming to room temperature equilibrated the 2-butanone throughout the apparatus. The pressure was slowly raised to 750 mm by introduction of argon. The reaction was then initiated by pouring the 2-butanone onto the reaction mixture. The mixture was stirred vigorously and the volume of gas given off measured. The known compound, $Rh\{P(C_6H_5)_3\}_2$-(CO)Cl, was used as a standard for the CO determinations; 105% of the theoretical CO was evolved. CO evolutions are given at the end of the analytical data. CO evolution for other reactions were measured in order to further confirm the CO content of specific compounds.

(35) Preparation of [Rh$\{$P(C$_6$H$_5$)$_3\}_2$(CO)$_3$]$^+$A$^-$. Method 1. [Rh-(COD)$\{$P(C$_6$H$_5$)$_3\}_2$]$^+$B(C$_6$H$_5$)$_4^-$ (500 mg) was placed in 5 ml of acetone and treated with CO to a volume of ca. 1 ml. Crystallization was completed with ethanol. The product was filtered off under CO, washed with diethyl ether, and dried in a stream of CO: yield 410 mg (89%); ir (Nujol) 2037 (s) and 2023 (s, C≡O). The product must be recrystallized in the presence of CO. Anal. Calcd for RhC$_{63}$H$_{50}$BO$_3$P$_2$: C, 73.40; H, 4.89; P, 6.00. Found: C, 73.77; H, 4.98; P, 6.11; evolved CO = 105% of theory; +P-(C$_6$H$_5$)$_3$ → [Rh$\{$P(C$_6$H$_5$)$_3\}_3$(CO)$_2$]$^+$ + CO, 94% of theory.

Method 2. [Rh(NBD)$\{$P(C$_6$H$_5$)$_3\}_2$]$^+$PF$_6^-$ (1.50 g) was treated with hydrogen in 10 ml of acetone on a vacuum line as in previous preparations (31, 33, and 34). The yellow solution was then allowed to react with CO for 5 min, and 50 ml of diethyl ether was slowly added to yield pale yellow crystals. Isolation as in method 1 gave 1.40 g (94%) of product. Anal. (ClO$_4^-$ salt) Calcd for RhC$_{39}$H$_{30}$-ClO$_7$P$_2$: C, 57.75; H, 3.73. Found: C, 57.47; H, 4.02; + DMA → [Rh$\{$P(C$_6$H$_5$)$_3\}_2$(CO)(DMA)]$^+$ + 2CO, 95% of theory; +CH$_3$CN → [Rh$\{$P(C$_6$H$_5$)$_3\}_2$(CO)(CH$_3$CN)]$^+$ + 2CO, 102% of theory.

Method 1 may be used with any anion, but method 2 is restricted to PF$_6^-$ or ClO$_4^-$ salts owing to the coordinating ability of tetraphenylboron (see ref 14).

(36) Preparation of [Rh$\{$P(C$_6$H$_5$)$_3\}_2$(CO)(S)]$^+$A$^-$; S = DMA, DMF, Acetone, or Acetonitrile. [Rh$\{$P(C$_6$H$_5$)$_3\}_2$(CO)$_3$]$^+$ClO$_4^-$ (250 mg) was placed in 1-2 ml of dichloromethane and a few drops of DMA added. Bubbling nitrogen through the solution for a few minutes removed the last of the evolved CO. Addition of an equal volume of ethanol followed by diethyl ether gave yellow crystals which were filtered off, washed with diethyl ether, and air-dried: yield 250 mg (97%); ^{1}H nmr (CDCl$_3$) 7.50 (s, 3, N-CH$_3$), 7.60 (s, 3, N-CH$_3$), 8.70 (s, 3, C-CH$_3$); ir (Nujol) 1984 (s, C≡O), 1605 (s, C=O), (CH$_2$Cl$_2$) 1996 (s, C≡O), 1604 (s, C=O). Anal. Calcd for RhC$_{41}$H$_{39}$ClNO$_6$P$_2$: C, 58.47; H, 4.67; N, 1.66; P, 7.35. Found: C, 57.99; H, 5.12; N, 1.66; P, 6.40; Λ = 69.

The procedure is entirely analogous for the preparation of other solvent adducts and for other anions. Samples could be freed of excess solvent by recrystallization from dichloromethane with ether. An exception is [Rh$\{$P(C$_6$H$_5$)$_3\}_2$(CO)(acetone)]$^+$B(C$_6$H$_5$)$_4^-$, which could not be obtained without one additional acetone as solvent of crystallization. The complexes could be prepared directly from [Rh(COD)P$\{$(C$_6$H$_5$)$_3\}_2$]$^+$A$^-$ after reaction with CO, but not as satisfactorily from [Rh(NBD)$\{$P(C$_6$H$_5$)$_3\}_2$]$^+$A$^-$ (see text). Anal. ([Rh$\{$P(C$_6$H$_5$)$_3\}_2$(CO)(DMF)]$^+$ClO$_4^-$) Calcd for RhC$_{40}$H$_{37}$ClNO$_6$P$_2$: C, 58.02; H, 4.50; N, 1.69. Found: C, 57.76; H, 4.50; N, 1.69; Λ = 75; evolved CO = 107% of theory. ^{1}H nmr (CDCl$_3$) 3.69 (s, 1, CHO), 7.68 (s, 3, N-CH$_3$), 7.88 (s, 3, N-CH$_3$); ir (Nujol) 1994 (s, C≡O), 1652 (s, C=O), (CH$_2$Cl$_2$) 2000 (s, C≡O), 1650 (s, C=O). Anal. ([Rh$\{$P(C$_6$H$_5$)$_3\}_2$(CO)(acetone)]$^+$ClO$_4^-$) Calcd for RhC$_{40}$H$_{36}$ClO$_6$P$_2$: C, 59.08; H, 4.47. Found: C, 58.97; H, 4.58; Λ = 77; evolved CO = 105% of theory; +P-(C$_6$H$_5$)$_3$ → [Rh$\{$P(C$_6$H$_5$)$_3\}_3$(CO)]$^+$ + no evolved CO. ^{1}H nmr (CDCl$_3$) 8.40 (s, 6, -CH$_3$); ir (Nujol) 1998 (s, C≡O), 1664 (m, C=O), (CH$_2$Cl$_2$) 2003 (s, C≡O), 1663 (m, C=O). Anal. ([Rh$\{$P(C$_6$H$_5$)$_3\}_2$(CO)(CH$_3$CN)]$^+$ClO$_4^-$) Calcd for RhC$_{39}$H$_{33}$ClNO$_5$P$_2$: C, 58.85; H, 4.18; Cl, 4.45; N, 1.76. Found: C, 60.02; H, 4.31; Cl, 4.96; N, 1.77; evolved CO = 106% of theory. ^{1}H nmr (CDCl$_3$) 8.47 (s, 3, -CH$_3$); ^{31}P nmr (CH$_2$Cl$_2$) −29.4 ppm (d, J_{Rh-P} = 119 Hz); ir (Nujol) 2016 (m, sh, C≡O) and 1985 (s, C≡O), 2319 (w, C≡N), and 2288 (w, C≡N), (CH$_2$Cl$_2$) 2016 (s, C≡O). The tetraphenylborate salt showed only a $\nu_{C=O}$ 2016-cm^{-1} band in Nujol.

(37) Preparation of [Rh$\{$P(C$_6$H$_5$)$_3\}_3$CO]$^+$A$^-$. The procedure is analogous to (36), employing excess triphenylphosphine. The yields are nearly quantitative. Recrystallization must be carried out in the presence of excess triphenylphosphine and the absence of strongly coordinating solvents. Anal. (ClO$_4^-$ salt) Calcd for RhC$_{55}$H$_{45}$ClO$_5$P$_3$: C, 64.93; H, 4.46; P, 9.13. Found: C,

65.13; H, 4.95; P, 8.80; Λ = 75; evolved CO = 108% of theory. Ir (Nujol) 2029 (s, C≡O), (CH$_2$Cl$_2$) 2029 (s, C≡O).

(38) Preparation of [Rh$\{$P(C$_6$H$_5$)$_3\}_3$(CO)$_2$]$^+$A$^-$. The procedure is identical with (37) except that CO must be continually bubbled through the solution during isolation. Recrystallization must be carried out in the presence of excess triphenylphosphine and CO and the absence of strongly coordinating solvents. Anal. (B(C$_6$H$_5$)$_4^-$ salt) Calcd for RhC$_{80}$H$_{65}$BO$_2$: C, 75.94; H, 5.18; P, 7.34. Found: C, 75.84; H, 5.10; P, 7.34; Λ = 47; evolved CO = 110% of theory. Ir (Nujol) 2048 (m, C≡O) 2013 (m, C≡O), 1987 (s, C≡O). Other salts showed only a 2013-cm^{-1} band in Nujol.

(39) Preparation of [Rh$\{$P(C$_6$H$_5$)$_2$CH$_3\}_2$(CO)(S)]$^+$ClO$_4^-$; S = DMF or DMA. [Rh(COD)$\{$P(C$_6$H$_5$)$_2$CH$_3\}_2$]$^+$ClO$_4^-$ (1.0 g) was placed in 2 ml of dichloromethane and allowed to react with CO until a light yellow solution was obtained. Ethanol (1 ml) was added along with 20 drops of DMF. The solution was bubbled with argon for 15 min to remove evolved CO. Addition of excess diethyl ether caused crystallization of yellow needles which were filtered off, washed with diethyl ether, and air-dried: yield 810 mg (82%); ^{1}H nmr (CDCl$_3$) 3.27 (s, 1, -CHO), 7.54 (s, 3, N-CH$_3$), ca. 7.8 (s, 3, N-CH$_3$) overlapping with ca. 7.84 (6, P-CH$_3$); ir (Nujol) 1971 (s, C≡O), 1644 (m, C=O), (CH$_2$Cl$_2$) 1994 (s, C≡O), 1650 (m, C=O). Anal. Calcd for RhC$_{30}$H$_{33}$ClNO$_6$P$_2$: C, 51.19; H, 4.73; N, 1.99; P, 8.80. Found: C, 50.34; H, 4.64; N, 2.03; P, 9.18.

The DMA adduct preparation is identical: ^{1}H nmr (CH$_2$Cl$_2$) 7.50 (s, 3, N-CH$_3$), 7.58 (s, 3, N-CH$_3$), 8.71 (s, 3, C-CH$_3$), 7.84 (br s, 6, P-CH$_3$); ir (CH$_2$Cl$_2$) 1993 (s, C≡O), 1604 (m, C=O). Anal. Calcd for RhC$_{31}$H$_{35}$ClNO$_6$P$_2$: C, 51.86; H, 4.91; Cl, 4.94; N, 1.95. Found: C, 51.18; H, 4.85; Cl, 4.80; N, 1.89; evolved CO = 107% of theory.

(40) Preparation of Rh$\{$P(C$_6$H$_5$)$_2$CH$_3\}_3$CO]$^+$ClO$_4^-$. [Rh$\{$P-(C$_6$H$_5$)$_2$CH$_3\}_2$(CO)(DMF)]$^+$ClO$_4^-$ (300 mg) was placed in 1 ml of acetone and 0.085 ml of P(C$_6$H$_5$)$_2$CH$_3$ added. Ethanol (1 ml) was added, followed by slow addition of excess diethyl ether to precipitate gold crystals which were filtered off, washed with diethyl ether, and air-dried: yield 310 mg (88%); ^{1}H nmr (CH$_2$Cl$_2$) 8.26 (t, 6, J = 2.6 Hz, cis-P-CH$_3$ to C≡O), 8.48 (d, 3, J = 7.6 Hz, trans-P-CH$_3$); ^{31}P nmr (CH$_2$Cl$_2$) −10.6 ppm (dd, J_{Rh-P} = 120 Hz, $J_{P_c-P_t}$ = ca. 30 Hz, cis-P to C≡O), trans P to C≡O signal complex and overlapping (see text); ir (Nujol) 2008 (s, C≡O), (CH$_2$Cl$_2$) 2023 (s, C≡O). Anal. Calcd for RhC$_{40}$H$_{39}$ClO$_5$P$_3$: C, 57.80; H, 4.73; P, 11.17. Found: C, 57.61; H, 5.08; P, 11.48; Λ = 75; evolved CO = 102% of theory.

(41) Preparation of [Rh$\{$P(C$_6$H$_5$)$_2$CH$_3\}_3$(CO)$_2$]$^+$ClO$_4^-$. The procedure was identical with (40) except that CO was bubbled through the solution during isolation; yield 337 mg (92%); ir (Nujol) 2017 (s, C≡O) and 1975 (s, C≡O), (CH$_2$Cl$_2$) 2027 (s, C≡O), and 1980 (s, C≡O). Anal. Calcd for Rh C$_{41}$H$_{39}$ClO$_6$P$_3$: C, 57.32; H, 4.58; P, 10.82. Found: C, 56.54; H, 4.78; P, 10.88; Λ = 77; evolved CO = 109% of theory.

(42) Preparation of [Rh(NBD)$\{$P(C$_6$H$_5$)$_3\}_2$(CO)]$^+$ClO$_4^-$. [Rh-(NBD)$\{$P(C$_6$H$_5$)$_3\}_2$]$^+$ClO$_4^-$ (400 mg) was placed in 2 ml of dichloromethane containing 0.5 ml of norbornadiene and treated with CO until pale yellow. The solution was swept with argon for a few minutes to sweep off excess CO. The addition of 1 vol of methanol followed by the slow addition of diethyl ether caused the formation of yellow crystals which were filtered off, washed with diethyl ether, and air-dried: yield 380 mg (92%); ^{1}H nmr (CDCl$_3$) 6.00 (4, olefin), 6.60 (2, methine), 8.68 (2, methylene); ir (Nujol) 2012 (s, C≡O), (CH$_2$Cl$_2$) 2020 (s, C≡O). Anal. Calcd for RhC$_{44}$-H$_{38}$ClO$_5$P$_2$: C, 62.39; H, 4.52; Cl, 4.19; P, 7.31. Found: C, 62.65; H, 4.42; Cl, 4.26; P, 6.86; Λ = 71; evolved CO = 109% of theory.

(43) Preparation of [Rh(1,3-butadiene)$\{$P(C$_6$H$_5$)$_3\}_2$(CO)]$^+$ClO$_4^-$. [Rh$\{$P(C$_6$H$_5$)$_3\}_2$(CO)$_3$]$^+$ClO$_4^-$ (250 mg) was dissolved in 1 ml of dichloromethane and allowed to react with butadiene for 10 min. Addition of 2 ml of ethanol followed by diethyl ether caused formation of pale yellow crystals of the product. These were filtered off, washed with diethyl ether, and air-dried: yield 208 mg (84%); ^{1}H nmr (CH$_2$Cl$_2$) 3.90 (br s, 2), 7.20 (br s, 2), 9.54 (br t, 2, J = 9.0 Hz); ir (Nujol) 2044 (s, C≡O) and 1991 (m, C≡O), (CH$_2$Cl$_2$) 2050 (s, C≡O) and 1999 (m, C≡O). Anal. Calcd for RhC$_{41}$H$_{38}$-ClO$_5$P$_2$: C, 60.87; H, 4.49; Cl, 4.38; P, 7.66. Found: C, 60.95; H, 4.76; Cl, 5.16; P, 7.71; Λ = 74.

(44) Preparation of [Rh(NBD)$\{$P(C$_6$H$_5$)$_2$CH$_3\}_2$(CO)]$^+$ClO$_4^-$. [Rh-(NBD)$\{$P(C$_6$H$_5$)$_2$CH$_3\}_2$]$^+$ClO$_4^-$ (300 mg) was placed in 5 ml of tetrahydrofuran containing 1 ml of NBD. CO was bubbled through the solution until all material was dissolved to yield a yellow solution. Argon was bubbled through the solution for 10

min. Ethanol (1 ml) was added, followed by excess diethyl ether to yield yellow-orange crystals which were filtered off, washed with diethyl ether, and air-dried: yield 279 mg (90%); ^{1}H nmr (CDCl$_3$) 6.22 (4, olefin), 6.50 (2, methine), 8.75 (2, methylene), 8.18 (m, 6, P–CH$_3$); ir (Nujol) 2028 (s, C≡O), (CH$_2$Cl$_2$) 2019 (s, C≡O). *Anal.* Calcd for RhC$_{34}$H$_{34}$ClO$_5$P$_2$: C, 56.49; H, 4.74; Cl, 4.90. Found: C, 57.02; H, 4.88; Cl, 5.32; Λ = 72.

(45) Preparation of [Rh(1,3-butadiene){P(C$_6$H$_5$)$_2$CH$_3$}$_2$(CO)]$^+$-ClO$_4^-$. [Rh(NBD){P(C$_6$H$_5$)$_2$CH$_3$}$_2$]$^+$ClO$_4^-$ (500 mg) was placed in 3 ml of acetone and treated with CO until a light yellow solution was obtained. Ethanol (2 ml) was added and butadiene was bubbled through the solution for 10 min. Slow addition of diethyl ether produced pale yellow crystals of the product which were filtered off, washed with diethyl ether, and air-dried: yield 438 mg (89%); ^{1}H nmr (CH$_2$Cl$_2$) 3.98 (2), 7.36 (2), and 9.42 (2), all

br, 8.08 (d, 6, J = 8.0 Hz, P–CH$_3$); ^{31}P (CH$_2$Cl$_2$) −12.1 ppm (d, $J_{Rh–H}$ = 133 Hz); ir (Nujol) 2031 (s, C≡O) and 1986 (m, C≡O), (CH$_2$Cl$_2$) 2048 (s, C≡O) and 1993 (m, C≡O). *Anal.* Calcd for RhC$_{31}$H$_{32}$ClO$_5$P$_2$: C, 54.36; H, 4.71; P, 9.04. Found: C, 54.48; H, 5.05; P, 8.91.

Chemistry of Bis[π-(3)-1,2-dicarbollyl]metalates. Protonation and Boron Substitution

M. Frederick Hawthorne,* Leslie F. Warren, Jr., Kenneth P. Callahan, and Neill F. Travers

Contribution No. 2691 from the Department of Chemistry, University of California, Los Angeles, California 90024. Received September 17, 1970

Abstract: The "sandwich"-bonded {bis[π-(3)-1,2-dicarbollyl]iron(II)}$^{2-}$ ion is protonated in strongly acidic media to form what may prove to be the analog of protonated ferrocene. This species readily reacts with dialkyl sulfides to form B-substituted bis(dicarbollyl)iron(II) and -(III) species. Analogous reactions have been carried out employing bis(dicarbollyl)iron(III) and -cobalt(III) anions. The preparation, characterization, and structures of these complexes are discussed.

The synthesis and properties of transition metal complexes analogous to metallocenes and employing the ligands (3)-1,2-B$_9$C$_2$H$_{11}^{2-}$ and (3)-1,7-B$_9$C$_2$H$_{11}^{2-}$ have been reported previously.[1–3] Certain aspects of the chemistry of some of these novel compounds have also appeared, *e.g.*, bromination,[1] Lewis acid–base reactions,[2] and electrophilic substitution.[4] We now wish to report further studies which deal with the protonation and B substitution of some metalates of the (3)-1,2-B$_9$C$_2$H$_{11}^{2-}$ ion.

The Protonation of Ferrocene and Its Bis(dicarbollyl) Analog

Bis(cyclopentadienyl)iron(II), ferrocene, is protonated in strongly acidic media such as sulfuric acid, boron trifluoride hydrate, or hydrogen chloride–aluminum chloride. The ^{1}H nmr spectrum of this species[5] contains a broad high-field resonance at +2.09 ppm (relative to tetramethylsilane = 0.00) which Rosenblum, *et al.*,[5] have assigned to a proton bonded to the iron atom. From Ballhausen and Dahl's theoretical model of the isoelectronic molecule (π-C$_5$H$_5$)$_2$ReH[6] and related

compounds, it was suggested that the cyclopentadienyl ring planes in protonated ferrocene are inclined, and that the unique proton is coordinated to the central of three hybrid metal orbitals as indicated in structure **1**.
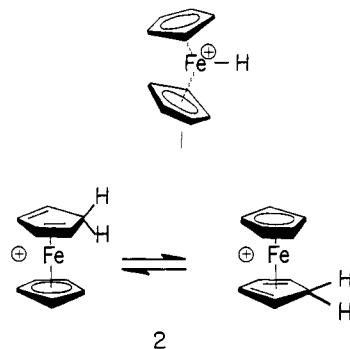
In this light, recent work[7] with a ring-tilted ferrocene, 1,1'-dimethyleneferrocene, indicates that ring-tilt distortion of the ferrocene nucleus is accompanied by an increase in Lewis basicity.

Ware and Traylor,[8] on the other hand, have suggested that the high-field resonance in the ^{1}H nmr spectrum of ferrocene in strong acid solution is consistent with a rapidly equilibrating σ complex, **2**. Such a structure as **2**, or its equivalent, is indeed required to explain the rapid acid-catalyzed deuteration of ferrocene.[9] It ap-

(1) M. F. Hawthorne, *et al.*, *J. Amer. Chem. Soc.*, **90**, 879 (1968).
(2) L. F. Warren, Jr., and M. F. Hawthorne, *ibid.*, **92**, 1157 (1970).
(3) L. F. Warren, Jr., and M. F. Hawthorne, *ibid.*, **90**, 4823 (1968).
(4) (a) J. N. Francis, Ph.D. Thesis, University of California, Riverside, 1969; (b) M. R. Churchill, K. Gold, J. N. Francis, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 1222 (1969); (c) J. N. Francis and M. F. Hawthorne, *Inorg. Chem.*, **10**, 594 (1971).
(5) T. J. Curphey, J. O. Santer, M. Rosenblum, and J. H. Richards, *J. Amer. Chem. Soc.*, **82**, 5249 (1960).
(6) C. J. Ballhausen and J. P. Dahl, *Acta Chem. Scand.*, **15**, 1333 (1961).

(7) H. L. Lentzner and W. E. Watts, *Chem. Commun.*, 26 (1970).
(8) J. C. Ware and T. G. Traylor, *Tetrahedron Lett.*, 1295 (1965).
(9) M. Rosenblum and F. W. Abbate, *Advan. Chem. Ser.*, No. 62, 532 (1967).