Dihydrido(dinitrogen)tris(triphenylphosphine)ruthenium. Dinitrogen Bridging Ruthenium and Boron

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Abstract: Reaction of $[(C_6H_5)_3P]_3RuHCl$ with triethylaluminum and nitrogen in ether gives good yields of $[(C_6H_5)_3P]_3Ru(N_2)H_2$. The nitrogen is reversibly displaced by hydrogen and ammonia and has also been displaced by carbon monoxide, phosphines, benzonitrile, and $N_2B_{10}H_8S(CH_3)_2$. The last reagent gives rise to $[(C_6H_5)_3P]_3Ru(H_2)N_2B_{10}H_8S(CH_3)_2$ in which dinitrogen is bridging boron and ruthenium. Additional examples of such species have been prepared by other routes.

The number of transition metal complexes of molecular nitrogen has increased rapidly since the initial report of $[(H_3N)_5RuN_2]^{2+}$.[1] Species in which dinitrogen acts as a bidentate ligand (*e.g.*, $(H_3N)_5RuN_2Ru(NH_3)_5{}^{4+}$,[2] $[[(C_6H_{11})_3P]_2Ni]_2N_2$,[3] and $[C_6H_5(CH_3)_2P]_4Re(Cl)N_2MoOCl_3P(C_2H_5)(C_6H_5)_2$[4]) have been described as well as those in which dinitrogen is a monodentate ligand.[5] This paper is an elaboration of a preliminary communication[6] concerning $[(C_6H_5)_3P]_3Ru(N_2)H_2$ and also describes a new class of compounds in which dinitrogen is a bidentate ligand bridging ruthenium and boron.

Preparation and Characterization of $(R_3P)_3Ru(N_2)H_2$. The reaction of $[(C_6H_5)_3P]_3RuHCl$[7] with triethylaluminum in ether in a nitrogen atmosphere proceeds smoothly to form $[(C_6H_5)_3P]_3Ru(N_2)H_2$ (I) in 85% yield. This dinitrogen complex is an air-sensitive solid which is stable indefinitely at normal temperature in a nitrogen or argon atmosphere. In solution, stabilization by a nitrogen atmosphere is required; irreversible decomposition occurs slowly in an argon atmosphere. Compound I has been observed spectroscopically in nitrogen-saturated solutions of $[(C_6H_5)_3P]_4RuH_2$, but the presence of the dissociated triphenylphosphine ligand has prevented isolation of the nitrogen complex in a pure state from these solutions.[6]

The infrared spectrum of I is shown in Figure 1; it displays a sharp band at 2147 cm^{-1}, assigned to the N≡N stretching mode, and a doublet assignable to Ru–H at 1947 and 1917 cm^{-1}. Difficulty was experienced in obtaining satisfactory nmr spectra of I because of limited solubility. The much more soluble tri-*p*-tolylphosphine analog II was therefore prepared, using a different synthetic scheme.

$$RuCl_3 + (p\text{-}CH_3C_6H_4)_3P \longrightarrow [(p\text{-}CH_3C_6H_4)_3P]_4RuCl_2 \xrightarrow{HCl}$$

$$[(p\text{-}CH_3C_6H_4)_3P]_3RuCl_2 \xrightarrow[N_2]{NaBH_4} \underset{\text{II}}{[(p\text{-}CH_3C_6H_4)_3P]_3Ru(N_2)H_2}$$

The use of hydrogen chloride to remove a phosphine ligand proved quite satisfactory. Complex II is much more soluble than I in a variety of solvents, including benzene. The ^{1}H nmr spectrum of II (Table I) suggests the structure shown in Figure 2a.

Reactions. Sweeping solutions of I or II with hydrogen or, in somewhat slower displacements, treating I or II with hydrogen in the solid state gives the corresponding tetrahydrides, $[(C_6H_5)_3P]_3RuH_4$ (IIIa) and $(p\text{-}CH_3C_6H_4)_3P]_3RuH_4$ (IIIb). These conversions are readily reversed by exposing the tetrahydrides to nitrogen in solution or as solids. The tetrahydrides are obtained from benzene as crystalline solids if a hydrogen atmosphere is maintained. Confirmation that they are in fact tetrahydrides was obtained by reaction of $[(C_6H_5)_3P]_3RuH_4$ with triphenylphosphine which gave hydrogen (82%) and $[(C_6H_5)_3P]_4RuH_2$. Treatment of the latter with hydrogen chloride then gave additional hydrogen (85% of 2 equiv). The reaction of $[(p\text{-}CH_3C_6H_4)_3P]_3RuH_4$ with triphenylphosphine liberated 85% of 1 equiv of hydrogen.

$$\begin{tikzcd}[column sep=small] \underset{\text{IIIa}}{[(C_6H_5)_3P]_3RuH_4} + (C_6H_5)_3P \arrow[r] & {[(C_6H_5)_3P]_4RuH_2} \arrow[d, "HCl"] & + \underset{82\%}{H_2} \\ & \underset{85\%}{2H_2} & \end{tikzcd}$$

The characterization of IIIa and IIIb as tetrahydrides is in apparent conflict with a recent article[9] which describes the preparation, in a hydrogen atmosphere, of $[(C_6H_5)_3P]_3RuH_2$ and its reaction with nitrogen to form $[(C_6H_5)_3P]_3Ru(N_2)H_2$, identical with I. The latter is reported to lose nitrogen upon treatment with hydrogen or argon in the solid state to re-form $[(C_6H_5)_3P]_3RuH_2$. In our hands, hydrogen converts I to the tetrahydride both in solution and in the solid state, whereas an argon stream was without effect on solid I during a 2-hr period but slowly caused irreversible decomposi-

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[1] A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965).

[2] D. F. Harrison, E. Weissburger, and H. Taube, *Science*, **159**, 320 (1968).

[3] P. W. Jolly and K. Jonas, *Angew. Chem., Int. Ed. Engl.*, 7, 731 1968).

[4] J. Chatt, J. R. Dilworth, G. J. Leigh, and R. L. Richards, *Chem. Commun.*, 955 (1970).

[5] Typical examples of monodentate dinitrogen complexes may be found in (a) A. Sacco and M. Rossi, *Inorg. Chim. Acta*, **2**, 127 (1968); (b) A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *J. Amer. Chem. Soc.*, **93**, 371 (1971); (c) J. Chatt, J. R. Dilworth, and G. J. Leigh, *J. Organometal. Chem.*, **21**, P49 (1970); (d) M. Hidai, K. Tominari, Y. Uchida, and A. Misono, *Chem. Commun.*, 1392 (1969); (e) G. M. Bancroft, M. J. Mays, and B. E. Prater, *ibid.*, 585 (1969).

[6] W. H. Knoth, *J. Amer. Chem. Soc.*, **90**, 7172 (1968).

[7] P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *J. Chem. Soc. A*, 3143 (1968).

[8] T. Ito, S. Kitazume, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, **92**, 3011 (1970).

[9] T. I. Eliades, R. O. Harris, and M. C. Zia, *Chem. Commun.*, 1709 (1970).

Table I. ^{1}H Nuclear Magnetic Resonance Spectra (High Field)

Compd	Solvent	τ (Ru–H)[a]	J, cps[a]
$[(Tol_3P)]_3Ru(N_2)H_2$[b]	C_6D_6	H_1,[c] 18.1	H_1–P_1, 30 H_1–P_2, 75 H_1–H_2, 6
		H_2,[c] 22.5	H_2–P_1, 27 H_2–P_2, 15
$[(Tol)_3P]_3Ru(NH_3)H_2$[b]	C_6D_6	H_1,[c] 19.75	H_1–P_1, 34 H_1–P_2, 73 H_1–H_2, 6
		H_2,[c] 27.63	H_2–P_1, 26 H_2–P_2, 16
$(Ph_3P)_3Ru(NCC_6H_5)H_2$[d]	C_6D_6	H_1,[e] 18.6	H_1–P_1, 32 H_1–P_2, 88 H_1–H_2, 6
		H_2,[e] 23.8	H_2–P_1, 28 H_2–P_2, 14
$(Ph_3P)_3Ru(CO)H_2$[f]	$CDCl_3$	H_1, 18.67	H_1–P_1, 29 H_1–P_2, 74 H_1–H_2, 6
		H_2, 16.69	H_2–P_1, 30 H_2–P_2, 16
$(Ph_3P)_3RuH(Cl)N_2B_{10}H_6S(CH_3)_2$[d]	$CDCl_3$	15.7[e]	H–P_{cis}, 22 H–P_{trans}, 135
$(Ph_3P)_2Ru(H)(Cl)(NCCH_3)N_2B_{10}H_8S(CH_3)_2$[d]	$CDCl_3$–$(CD_3)_2SO$	20.7[e]	H–P, 19

[a] Numerical subscripts refer to labeling in Figure 2. [b] Determined on a Varian Model HR 220 spectrometer. [c] Referred to external tetramethylsilane. [d] Determined on a Varian Model HA 100 spectrometer. [e] Referred to internal tetramethylsilane. [f] Data taken from ref 7.

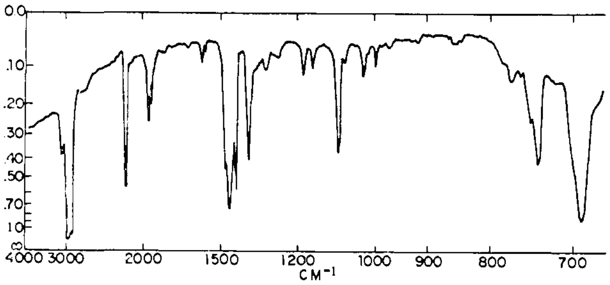

Figure 1. Infrared spectrum (Nujol mull) of $[(C_6H_5)_3P]_3Ru(N_2)H_2$.

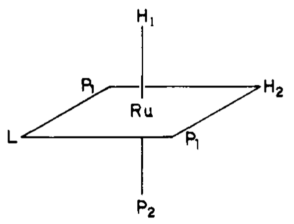

Figure 2. Structures of $(R_3P)_3Ru(N_2)H_2$ and derivatives: (a) L = N_2, (b) L = NH_3, (c) L = CO, (d) L = C_6H_5CN; P = $(C_6H_5)_3P$ or $(p\text{-}CH_3C_6H_4)_3P$.

tion when passed through solutions of I. Heating I to 100° *in vacuo* for 2 hr caused no change; at 140° nitrogen was irreversibly lost. The Ru-H stretching frequency reported for $[(C_6H_5)_3P]_3RuH_2$ (1950 cm^{-1}) is the same that we find for $[(C_6H_5)_3P]_3RuH_4$. The ^{1}H nmr spectrum of IIIb in toluene-d_8 (hydrogen atmosphere) consists of one broad resonance at τ 17.05. No fine structure was noted in the range -50 to $+50°$; some broadening occurred at the lower temperature. Integration of the hydride resonance against the 27 methyl protons gave values of 3.0–3.2 hydridic hydrogens. This low value and the featureless nature of the resonance can be explained by assuming partial dissociation and rapid exchange in solution. Attempts to

$$[(p\text{-}CH_3C_6H_4)_3P]_3RuH_4 \rightleftharpoons [(p\text{-}CH_3C_6H_4)_3P]_3RuH_2 + H_2$$

reduce the dinitrogen in I with lithium aluminum hydride have been unsuccessful.

Treatment of I or IIIa with ammonia, in solution or in the solid state, forms $[(C_6H_5)_3P]_3Ru(NH_3)H_2$ (IV). These reactions are reversible. Compound IV is a bright-yellow air-sensitive solid which is stable in the solid state but which decomposes irreversibly in solution *in vacuo*. Sweeping a solution of II with ammonia gave a solution containing the *p*-tolylphosphine analog of IV, which was used for ^{1}H nmr determinations. The ^{1}H nmr spectrum (Table I) confirmed the structure shown in Figure 2b.

Other reactions involving displacement of nitrogen from I include

$$[(C_6H_5)_3P]_3Ru(N_2)H_2 \xrightarrow{(C_6H_5)_3P} \underset{\text{V}}{[(C_6H_5)_3P]_4RuH_2}$$

$$[(C_6H_5)_3P]_3Ru(N_2)H_2 \xrightarrow{CO} \underset{\text{VI}}{[(C_6H_5)_3P]_3Ru(CO)H_2}$$

$$[(C_6H_5)_3P]_3Ru(N_2)H_2 \xrightarrow{C_6H_5CN} \underset{\text{VII}}{[(C_6H_5)_3P]_3Ru(NCC_6H_5)H_2}$$

The reaction of I with triphenylphosphine is in sharp contrast to the behavior of $[(C_6H_5)_3P]_3Co(N_2)H$, which can be prepared in the presence of excess triphenylphosphine. This difference in behavior may result from the different steric situations. The carbonyl complex VI has been prepared previously[7] by a different route and has been shown (Table I) to have the structure shown in Figure 2c.

The proton nmr spectrum (Table I) of the benzonitrile complex VII establishes it as an analog of the other nitrogen-exchange complexes derived from I (Figure 2d). It has been noted[10] that replacement of

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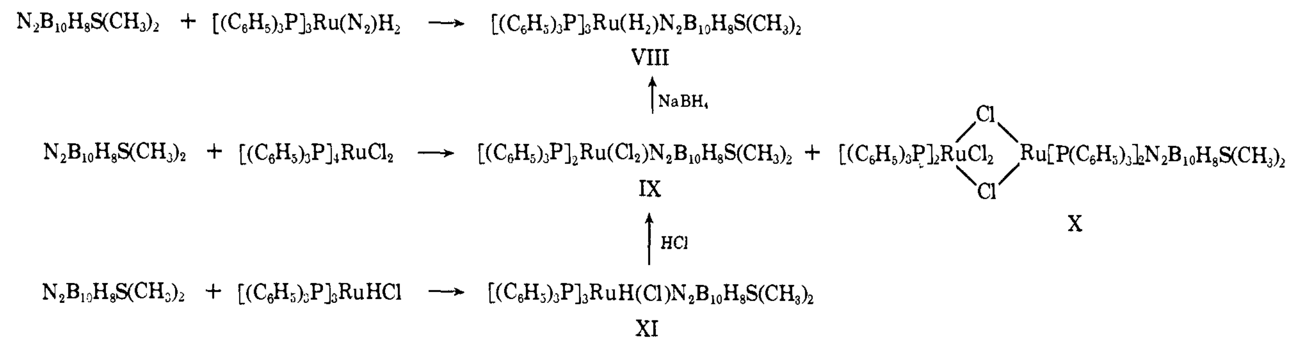
(10) (a) P. C. Ford and R. E. Clarke, *Chem. Commun.*, 1109 (1968); (b) A. Misono, Y. Uchida, M. Hidai, and T. Kuse, *ibid.*, 208 (1969).

Scheme I



nitrogen in $[(H_3N)_5RuN_2]^{2+}$ and in $[(C_6H_5)_3P]_3Co(N_2)H$ by organic nitriles gives complexes in which ν_{CN} is lowered from ν_{CN} for the free nitrile, in contrast to the more common increase in ν_{CN} upon complex formation. A similar lowering occurs when benzonitrile (ν_{CN}^{THF} 2222 cm^{-1}) is complexed to form VII (ν_{CN}^{THF} 2185 cm^{-1}).

It was mentioned above that I decomposes in solution unless a stabilizing atmosphere of nitrogen is present. A small amount of $[(C_6H_5)_3P]_4RuH_2$ was isolated from a toluene solution of I which had been swept with argon for 1.5 hr. No other products were identified. However, when an equimolar mixture of I and the analogous ammonia complex IV in tetrahydrofuran was stirred in an argon atmosphere, a yellow, crystalline solid separated. This product was too insoluble for molecular weight determination but elemental analysis suggested $[(C_6H_5)_3P]_5Ru_4(NH_3)_3$ as a simplest formula. This may be a tetrahedral cluster containing three $(C_6H_5)_3PRuNH_3$ moieties derived from IV and one $[(C_6H_5)_5P]_2Ru$ moiety derived from I. There is no infrared indication of hydrogen on ruthenium; the absence of hydridic hydrogen could not be confirmed by nmr because of low solubility. A similar yellow solid comprised only of $(C_6H_5)_3PRuNH_3$ units is obtained if a tetrahydrofuran solution containing only IV is stirred in an argon atmosphere.

Dinitrogen as a Bridging Ligand between Ruthenium and Boron. Treatment of I or II with inner diazonium salts of $B_{10}H_{10}^{2-}$, such as $B_{10}H_8(N_2)_2$[11] and $N_2B_{10}H_8S(CH_3)_2$,[12] has given a new class of complexes in which dinitrogen bridges ruthenium and boron. Compounds containing $N_2B_{10}H_8S(CH_3)_2$ have been prepared as shown in Scheme I.

The conversion of IX to VIII by sodium borohydride requires disproportionation; the other products were not isolated. The chlorine-bridged structure postulated for X is inferred from the stoichiometry.

Similar reactions involving $B_{10}H_8(N_2)_2$ are

$$[(C_6H_5)_3P]_3Ru(N_2)H_2 + B_{10}H_8(N_2)_2 \longrightarrow \underset{\text{XII}}{\{[(C_6H_5)_3P]_3Ru(H_2)N_2\}_2B_{10}H_8}$$

$$\Big\uparrow \text{NaBH}_4 \text{ or } H_2/Pt$$

$$[(C_6H_5)_3P]_3RuHCl + B_{10}H_8(N_2)_2 \longrightarrow \underset{\text{XIII}}{\{[(C_6H_5)_3P]_3RuH(Cl)N_2\}_2B_{10}H_8}$$

$$\Big\downarrow \text{HCl}$$

$$\underset{\text{XIV}}{\{[(C_6H_5)_3P]_2Ru(Cl_2)N_2\}_2B_{10}H_8}$$

Several analogous reactions involving the corresponding tri-*p*-tolylphosphine–ruthenium complexes are described in the Experimental Section.

Complexes XII–XIV oxidize very slowly (months) in air while VIII–XI appear to be stable indefinitely in air. All these are bright-yellow, crystalline solids except for X which is rust colored. The retention of the nitrogen–nitrogen triple bond in these complexes is demonstrated by strong, sharp, infrared absorption in the 2000–2135-cm^{-1} region. The $RuN{\equiv}N{-}B$ moiety is surprisingly stable as shown by its inertness to hydrogen chloride, sodium borohydride, platinum-catalyzed hydrogenolysis, and atmospheric oxidation as well as its retention in the following reactions.

$$\underset{\text{XI}}{[(C_6H_5)_3P]_3RuH(Cl)N_2B_{10}H_8S(CH_3)_2} \xrightarrow{\text{KCN}} \underset{\text{XV}}{K^+[(C_6H_5)_3P]_2RuH(Cl)(CN)N_2B_{10}H_8S(CH_3)_2^-}$$

$$\xrightarrow{\text{CH}_3\text{CN}} \underset{\text{XVI}}{[(C_6H_5)_3P]_2Ru(NCCH_3)(H)(Cl)N_2B_{10}H_8S(CH_3)_2}$$

The structure of XI (Figure 3a) has been determined by ^1H nmr. The labile phosphine is that trans to hydrogen as shown by the structure of XVI (Figure 3b), also determined by ^1H nmr. This is not surprising in view of the strong trans effect of hydrogen in general and recent studies on a related species, $(C_6H_5R_2P)_3RuH(Cl)CO$ (Figure 4), in which the phosphine trans to hydrogen has been found to be labile.[13]

Experimental Section

$[(C_6H_5)_3P]_3Ru(N_2)H_2$. **A.** Ether (300 ml) and $[(C_6H_5)_3P]_3RuHCl \cdot C_6H_5CH_3$[7] (9.82 g, 9.7 mmol) were stirred in a round-bottomed flask which was fitted with a solid carbon dioxide–acetone-cooled condenser. A stream of nitrogen was directed at the surface of the reaction mixture. Triethylaluminum (8 ml, 5.9 mmol) was added. After 4 hr, the nitrogen stream was switched to a bypass at the top of the condenser and the mixture was stirred overnight. Filtration in a nitrogen atmosphere gave 7.6 g (8.3 mmol, 85%) of $[(C_6H_5)_3P]_3Ru(N_2)H_2$ as a slightly off-white, air-sensitive solid. Recrystallization was achieved by stirring the product for 30 min in benzene (80 ml) in a nitrogen atmosphere at ambient temperature, filtering, and diluting the filtrate with hexane (400 ml). Crystalline $[(C_6H_5)_3P]_3Ru(N_2)H_2$ separated slowly (5.8 g, 76% recovery, dec >130°) as a slightly deeper colored solid than the unrecrystallized product.

Anal. Calcd for $[(C_6H_5)_3P]_3Ru(N_2)H_2$: C, 70.7; H, 5.2; N, 3.1; P, 10.1; Ru, 10.9. Found: C, 70.9; H, 5.3; N, 3.2; P, 10.2; Ru, 10.2.

The infrared spectrum is shown in Figure 1. The nitrogen complex was also formed by exposing a small sample of $[(C_6H_5)_3P]_3RuH_4$ to a nitrogen atmosphere for 1.5 hr and by passing nitrogen through solutions of the tetrahydride.

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(11) W. H. Knoth, *J. Amer. Chem. Soc.*, **88**, 935 (1966).

(12) W. H. Knoth, W. R. Hertler, and E. L. Muetterties, *Inorg. Chem.*, 4, 280 (1965).

(13) P. G. Douglas and B. L. Shaw, *J. Chem. Soc. A*, 1556 (1970).

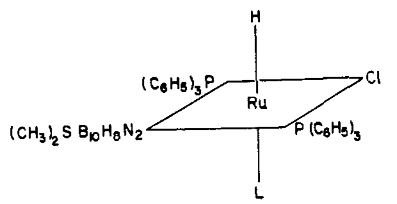

Figure 3. Structure of $[(C_6H_5)_3P]_2Ru(L)(H)(Cl)N_2B_{10}H_8S(CH_3)_2$: (a) L = $(C_6H_5)_3P$, (b) L = CH_3CN.

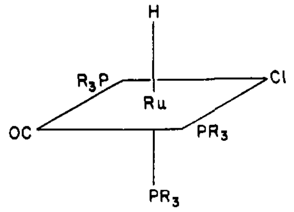

Figure 4. Structure of $(R_3P)_3RuH(CO)Cl$.[13]

B. Anhydrous hydrogen chloride (*ca.* 3 ml) was condensed onto a mixture of $[(C_6H_5)_3P]_3Ru(N_2)H_2$ (0.957 g, 1.04 mmol) and toluene (40 ml) at liquid nitrogen temperature. The mixture was allowed to warm to room temperature. Nitrogen (0.85 mmol, 82%) and hydrogen (1.97 mmol, 95% of 2 equiv) were evolved. In a second experiment it was determined that all the nitrogen and 1 equiv of hydrogen were evolved at temperatures below $-70°$ and that the second equivalent of hydrogen was evolved at substantially higher ($>0°$) temperatures.

C. Argon was passed through a mixture of $[(C_6H_5)_3P]_3Ru(N_2)H_2$ (1 g, 1.1 mmol) and toluene (30 ml) for 1.5 hr. The reaction solution was concentrated to 7 ml *in vacuo* and this residue was diluted with hexane (100 ml). A solid, 0.25 g (*Anal.* Found: C, 63.9; H, 5.2; N, 0.3), precipitated. This solid was dissolved in tetrahydrofuran (15 ml) and nitrogen was bubbled through the solution for 1 hr. No nitrogen complex was formed. Concentration of the filtrate from the initial isolation of the 0.25 g of solid caused the separation of $[(C_6H_5)_3P]_4RuH_2$ (0.15 g) identified by infrared analysis.

D. Toluene (100 ml) and $[(C_6H_5)_3P]_3Ru(N_2)H_2$ (1.48 g, 1.6 mmol) were charged to a flask which was chilled in liquid nitrogen and evacuated. The reaction vessel was warmed to room temperature and stirred for 16 hr. Nitrogen (0.94 mmol, 58%) and a trace of hydrogen (0.02 mmol, 1.2%) were evolved.

E. Tris(triphenylphosphine)ruthenium dinitrogen dihydride was heated at 100° for 2 hr under vacuum. There was no change in the infrared spectrum. The sample was then heated to 140° under vacuum for 2 hr resulting in the loss of the 2147- ($N{\equiv}N$), 1947-, and 1917-cm^{-1} infrared bands. This product did not react with molecular nitrogen during a 16-hr period. Nitrogen was not lost from $[(C_6H_5)_3P]_3Ru(N_2)H_2$ when it was placed in a stream of argon for 2 hr.

F. Hydrogen was passed through a solution of $[(C_6H_5)_3P]_3Ru(N_2)H_2$ (0.2 g, 0.22 mmol) in tetrahydrofuran for 15 min. A precipitate of $[(C_6H_5)_3P]_3RuH_4$ formed (0.1 g, 52%). In a similar experiment, no precipitate formed when argon was used in place of hydrogen.

G. A mixture of triphenylphosphine (0.15 g, 0.57 mmol), $[(C_6H_5)_3P]_3Ru(N_2)H_2$ (0.5 g, 0.55 mmol), and benzene (5 ml) was warmed in a nitrogen atmosphere until a clear solution resulted. Hexane was added until the mixture became cloudy. Cooling caused the separation of crystalline, yellow $[(C_6H_5)_3P]_4RuH_2$ (0.57 g, 90%) identified by infrared analysis.

H. A stream of nitrogen was passed through a flask containing lithium aluminum hydride (0.2 g, 5.2 mmol) and then through 40 ml of 0.05 *M* hydrochloric acid. A solution of $[(C_6H_5)_3P]_3Ru(N_2)H_2$ (1.3 g, 1.4 mmol) in tetrahydrofuran (125 ml) was injected into the first flask. An instantaneous reaction occurred. After 1 hr, titration of the hydrochloric acid solution showed that no volatile base had been evolved. Aqueous tetrahydrofuran was added to the reaction mixture, followed by 30 ml of 10% aqueous sodium hydroxide. The solution (25 ml) was then distilled into standard acid solution. Titration showed that no volatile base had been liberated.

In another experiment, treatment of $[(C_6H_5)_3P]_3Ru(N_2)H_2$ (1.0 g) in tetrahydrofuran (100 ml) with $LiAlH_4$ (0.3 g) resulted in liberation of almost all the complexed nitrogen as molecular nitrogen, identified by mass spectroscopy.

$[(C_6H_5)_3P]_3RuH_4$. A. A mixture of $[(C_6H_5)_3P]_3RuHCl \cdot C_6H_5CH_3$ (6.8 g, 6.7 mmol) and ether (300 ml) was placed in a round-bottomed flask which was fitted with a solid carbon dioxide–acetone-cooled condenser. A stream of hydrogen was directed at the surface of the reaction mixture. Triethylaluminum (6 ml, 4.4 mmol) was added and the mixture was stirred for 2.5 hr. $[(C_6H_5)_3P]_3RuH_4$ (4 g, 67%) was isolated by filtration in an argon atmosphere. Of this, 3 g was placed in toluene (75 ml) through which hydrogen was bubbled continuously. The mixture was heated slowly to 65° to obtain a clear, dark-red solution which was allowed to cool while the hydrogen stream was maintained. Crystalline $[(C_6H_5)_3P]_3RuH_4$ (1.4 g, 47% recovery, dec point 132°) separated as a light-tan solid, unstable in air. In subsequent runs yields of the crude product were as high as 80%. The infrared spectrum (Nujol mull) includes a broad absorption band at 1950 cm^{-1} (Ru–H).

Anal. Calcd for $[(C_6H_5)_3P]_3RuH_4$: C, 72.8; H, 5.5. Found: C, 72.7, 72.7; H, 5.6, 6.1.

B. Hydrogen was bubbled through a mixture of toluene (10 ml) and $[(C_6H_5)_3P]_3Ru(N_2)H_2$ (0.5 g, 0.55 mmol) which was heated to 50° until a clear solution formed. This was allowed to cool while the hydrogen flow was maintained. Crystalline $[(C_6H_5)_3P]_3RuH_4$, identical with that prepared above, separated (0.13 g, 27%).

C. Toluene (15 ml) was condensed onto a mixture of $[(C_6H_5)_3P]_3RuH_4$ (1.19 g, 1.34 mmol) and triphenylphosphine (0.4 g, 1.5 mmol) at liquid nitrogen temperature. The mixture was warmed to room temperature. Hydrogen (1.09 mmol, 81.7%) was evolved and a yellow solid separated. Infrared analysis of the solid showed that it was $[(C_6H_5)_3P]_4RuH_2$. Hydrogen chloride (2 ml) was condensed into the reaction mixture at low temperature. Additional hydrogen (2.28 mmol, 85% of 2 equiv) was evolved.

$[(C_6H_5)_3P]_3Ru(NH_3)H_2$. Ammonia was passed through a mixture of $[(C_6H_5)_3P]_3RuH_4$ (6.7 g, 7.5 mmol) and toluene (120 ml) while the temperature was raised to 65° during a 10-min period. A cloudy, yellow solution was obtained which was allowed to cool while the ammonia stream was maintained. The mixture was filtered in an argon atmosphere. Hexane (300 ml) was added to the filtrate causing the slow separation of $[(C_6H_5)_3P]_3Ru(NH_3)H_2$ (3.9 g, 57%). The infrared spectrum (Nujol mull) included absorptions at 3400 (N–H), 1950, 1900, 1870, and 1600 cm^{-1} (NH_3 def).

Anal. Calcd for $[(C_6H_5)_3P]_3Ru(NH_3)H_2$: C, 71.7; H, 5.5; N, 1.6. Found: C, 71.5; H, 5.7; N, 1.4.

Solutions of $[(C_6H_5)_3P]_3Ru(NH_3)H_2$ in toluene are yellow but require an atmosphere of ammonia to ensure prolonged stability. Brief evacuation of a vessel containing a solution of $[(C_6H_5)_3P]_3Ru(NH_3)H_2$ in toluene caused loss of the yellow color and formation of a dark solution. The introduction of ammonia regenerated the yellow color but the cycle could not be repeated indefinitely. After about ten cycles, reestablishment of the yellow color was less pronounced and after several more cycles was nonexistent.

A solution of $[(C_6H_5)_3P]_3Ru(NH_3)H_2$ in benzene was evaporated in a stream of nitrogen. Infrared analysis of the residue proved it to be $[(C_6H_5)_3P]_3Ru(N_2)H_2$.

$[(C_6H_5)_3P]_5Ru_4(NH_3)_3$. A mixture of $[(C_6H_5)_3P]_3Ru(N_2)H_2$ (0.22 g 0.24 mol), $[(C_6H_5)_3P]_3Ru(NH_3)H_2$ (0.22 g. 0.24 mmol), and tetrahydrofuran (11 ml) was stirred in an argon atmosphere for 1.5 hr. Filtration of the resulting red solution gave a yellow, crystalline solid tentatively identified as $[(C_6H_5)_3P]_5Ru_4(NH_3)_3$. The infrared spectrum (Nujol mull) includes N–H stretching and deformation absorptions and no significant bands in the Ru–H region.

Anal. Calcd for $[(C_6H_5)_3P]_5Ru_4(NH_3)_3$: C, 61.2; H, 4.8; N, 2.4. Found: C, 61.0, 61.3; H, 5.2, 5.2; N, 2.1, 2.3.

$[(C_6H_5)_3PRuNH_3]_4$. A mixture of $[(C_6H_5)_3P]_3Ru(NH_3)H_2$ (1.0 g, 1.1 mmol) and tetrahydrofuran (40 ml) was stirred in an argon atmosphere for 2 hr. Filtration gave $[(C_6H_5)_3PRuNH_3]_4$ as a crystalline, yellow solid (0.1 g, 24%) plus a red filtrate. The yellow solid is stable in air for at least 1 hr in the solid state; solutions slowly become green.

Anal. Calcd for $[(C_6H_5)_3PRuNH_3]_4$: C, 56.8; H, 4.7; N, 3.7. Found: C, 58.7; H, 5.3; N, 3.5.

$[(C_6H_5)_3P]_3Ru(CO)H_2$. Carbon monoxide was bubbled through a solution of $[(C_6H_5)_3P]_3Ru(N_2)H_2$ (5.8 g, 6.3 mmol) in tetrahydrofuran (75 ml) for 15 min. The solution was filtered and ethanol (300 ml) was added to the filtrate. After 30 min the resulting mixture was filtered to obtain crystalline $[(C_6H_5)_3P]_3Ru(CO)H_2$ (4.3 g, 74%). The infrared spectrum (Nujol mull) included an intense carbonyl absorption at 1940 cm^{-1} (lit.[7] value 1940 cm^{-1}).

Anal. Calcd for $[(C_6H_5)_3P]_3Ru(CO)H_2$: C, 72.0; H, 5.2; P, 10.1. Found: C, 72.1; H, 5.3; P, 9.7

$[(C_6H_5)_3P]_3Ru(NCC_6H_5)H_2$. A mixture of $[(C_6H_5)_3P]_3Ru(N_2)H_2$ (2 g, 2.2 mmol), benzonitrile (2 ml), and tetrahydrofuran (30 ml) was stirred in a nitrogen atmosphere for 1.5 hr, forming a clear solution. The addition of hexane (150 ml) caused the slow separation of orange, crystalline $[(C_6H_5)_3P]_3Ru(NCC_6H_5)H_2$ (1.4 g, 64%, mp 208–210°). The infrared spectrum (Nujol mull) exhibited absorption at 2208 cm^{-1} (CN) and bands for Ru–H stretching that were very similar to those in the spectrum of $[(C_6H_5)_3P]_3Ru(N_2)H_2$. In tetrahydrofuran solution ν_{CN} is 2185 cm^{-1}.

$[(p\text{-}CH_3C_6H_4)_3P]_4RuCl_2$. Commercial ruthenium trichloride (9.4 g) was extracted with methanol (500 ml). The extracts were mixed with tri-*p*-tolylphosphine (50 g) and refluxed overnight in a nitrogen atmosphere. The reaction mixture was filtered, and the filter cake was rinsed with methanol and dried to obtain 52 g of $[(p\text{-}CH_3C_6H_4)_3P]_4RuCl_2$, mp 196°.

Anal. Calcd for $[(p\text{-}CH_3C_6H_4)_3P]_4RuCl_2$: C, 72.6; H, 6.1; Cl, 5.1; P, 8.9. Found: C, 73.6; H, 6.2; Cl, 5.0; P, 9.3.

$[(p\text{-}CH_3C_6H_4)_3P]_3RuCl_2$. Hydrogen chloride was passed through a solution of $[(p\text{-}CH_3C_6H_4)_3P]_4RuCl_2$ (20 g, 14.6 mmol) in toluene (200 ml) for 15 min, followed by a nitrogen flush to remove excess hydrogen chloride. The mixture was filtered under nitrogen and the filtrate was diluted to 500 ml with hexane. After the mixture stood for 3 days, filtration gave dark crystals of $[(p\text{-}CH_3C_6H_4)_3P]_3RuCl_2$ (8.0 g, 51%, softens at 130°, dec 150°).

Anal. Calcd for $[(p\text{-}CH_3C_6H_4)_3P]_3RuCl_2$: C, 69.8; H, 5.8; Cl, 6.5; P, 8.6. Found: C, 69.9; H, 6.0; Cl, 6.5; P, 8.6.

$[(p\text{-}CH_3C_6H_4)_3P]_3Ru(N_2)H_2$. A mixture of $[(p\text{-}CH_3C_6H_4)_3P]_3RuCl_2$ (3.6 g, 3.3 mmol), sodium borohydride (1.0 g, 26 mmol), and ethanol (100 ml) was stirred in a nitrogen atmosphere for 3 hr and then filtered. The yellow filter cake was dissolved in benzene (15 ml). The solution was filtered; nitrogen was passed through the filtrate for 5 min and it was diluted with ethanol (100 ml). After 2 hr filtration gave 1.2 g (35%) of $[(p\text{-}CH_3C_6H_4)_3P]_3Ru(N_2)H_2$. Carbonyl-containing impurities separate on longer standing: $\nu_{N{\equiv}N}^{Nujol}$ 2130 cm^{-1}.

Anal. Calcd for $[(p\text{-}CH_3C_6H_4)_3P]_3Ru(N_2)H_2$: C, 72.5; H, 6.3; N, 2.7; P, 8.9. Found: C, 72.5; H, 6.0; N, 2.2; P, 9.0.

A solution of $[(p\text{-}CH_3C_6H_4)_3P]_3Ru(N_2)H_2$ (0.74 g, 0.7 mmol) in benzene (20 ml) was swept with hydrogen for 15 min to form $[(p\text{-}CH_3C_6H_4)_3P]_3RuH_4$. Excess hydrogen was removed. A solution of triphenylphosphine (0.8 g, 3.1 mmol) in benzene (15 ml) was added. Hydrogen (0.62 mmol, 89%) was liberated.

$\{[(C_6H_5)_3P]_3RuH(Cl)N_2\}_2B_{10}H_8$. A solution of $[(C_6H_5)_3P]_3RuHCl\cdot C_6H_5CH_3$ (3.1 g, 0.3 mmol) and $B_{10}H_8(N_2)_2$[11] (0.25 g, 0.14 mmol) in dichloromethane (40 ml) was stirred in a nitrogen atmosphere. A crystalline, yellow precipitate of $\{[(C_6H_5)_3P]_3RuH(Cl)N_2\}_2B_{10}H_8\cdot CH_2Cl_2$ (2.5 g, 80%) separated slowly: $\nu_{N{\equiv}N}^{Nujol}$ 2080 cm^{-1}.

Anal. Calcd for $\{[(C_6H_5)_3P]_3RuH(Cl)N_2\}_2B_{10}H_8\cdot CH_2Cl_2$: C, 62.0; H, 4.9; B, 5.1; Cl, 6.7; N, 2.7; P, 8.8. Found: C, 62.1; H, 4.9; B, 5.6; Cl, 7.3; N, 2.6; P, 8.8.

The product was unchanged after brief exposure to air but darkened over several months.

The dichloromethane of solvation was removed by dissolving the solvate (3.5 g) in hot tetrahydrofuran (250 ml) followed by partial concentration of the solution on an evaporator. The recovery was 1.9 g (57%) of the unsolvated compound as a yellow solid, dec 205–211°, darkens at 155–195°.

Anal. Calcd for $\{[(C_6H_5)_3P]_3RuH(Cl)N_2\}_2B_{10}H_8$: C, 64.1; H, 5.0; B, 5.3; Cl, 3.5; N, 2.8; P, 9.2. Found: C, 64.2; H, 5.6; B, 5.2; Cl, 3.6; N, 2.9; P, 8.5.

$\{[(C_6H_5)_3P]_3Ru(H_2)N_2\}_2B_{10}H_8$. A. A solution of $B_{10}H_8(N_2)_2$ (0.35 g, 2.0 mmol) and $[(C_6H_5)_3P]_3Ru(N_2)H_2$ (3.6 g, 4.0 mmol) in tetrahydrofuran (80 ml) was stirred in a nitrogen atmosphere for 20 min. The solution was filtered and the filtrate was poured into hexane (300 ml) to precipitate $\{[(C_6H_5)_3P]_3Ru(H_2)N_2\}_2B_{10}H_8$ as a yellow solid (3.4 g, 87%) which was soluble in tetrahydrofuran, benzene, and dioxane and insoluble in petroleum ether, methylcyclohexane, alcohol, and ether. Preliminary purification was achieved by dissolution in tetrahydrofuran and reprecipitation with alcohol. Part (0.5 g) of the material thus obtained was dissolved in benzene (15 ml) Stirring this solution for several hours caused the separation of yellow, crystalline solid (0.3 g, dec point 111–113°). A new infrared band (675 cm^{-1}) was present after the crystallization and the product may be solvated with benzene λ_{max}^{THF} 352 mμ (ε 97,600); $\nu_{N{\equiv}N}^{Nujol}$ 2060 cm^{-1}.

Anal. Calcd for $\{[(C_6H_5)_3P]_3Ru(H_2)N_2\}_2B_{10}H_8\cdot C_6H_6$: C, 67.3; H, 5.4; B, 5.3; N, 2.9; P, 9.1. Found: C, 67.3; H, 5.4; B, 5.8; N, 2.7; P, 8.8.

B. A mixture of $\{[(C_6H_5)_3P]_3RuH(Cl)N_2\}_2B_{10}H_8$ (0.5 g, 0.47 mmol) and sodium borohydride (0.2 g, 0.53 mmol) in alcohol (50 ml) was stirred in a nitrogen atmosphere overnight. The mixture was filtered; the filter cake was washed with alcohol to obtain 0.4 g (85%) of $\{[(C_6H_5)_3P]_3Ru(H_2)N_2\}_2B_{10}H_8$ (dec 113–115°), identical with that prepared above. Chlorine was absent as shown by elemental analysis.

C. A mixture of $\{[(C_6H_5)_3P]_3RuH(Cl)N_2\}_2B_{10}H_8\cdot CH_2Cl_2$ (0.7 g), 5% Pt on carbon (0.1 g), and tetrahydrofuran (30 ml) was stirred for 3 hr while a slow stream of hydrogen was passed through. The mixture was heated to boiling briefly after the first 10 min. Filtration, followed by dilution of the filtrate with petroleum ether, gave $\{[(C_6H_5)_3P]_3Ru(H_2)N_2\}_2B_{10}H_8$, identified by infrared analysis.

$\{[C_6H_5)_3P]_2Ru(Cl_2)N_2\}_2B_{10}H_8$. Hydrogen chloride was passed through a solution of $\{[(C_6H_5)_3P]_3Ru(H_2)N_2\}_2B_{10}H_8$ (1.9 g, 1 mmol) in tetrahydrofuran. The temperature rose to 63° and the hydrogen chloride flow was maintained until the temperature fell to 43°. The excess hydrogen chloride was swept out with a stream of nitrogen and the solution was evaporated The residue was extracted with acetonitrile Dilution of the acetonitrile extract with ethanol precipitated $\{[(C_6H_5)_3P]_2Ru(Cl_2)N_2\}_2B_{10}H_8$ (0.5 g, 31%, dec 240°): $\nu_{N{\equiv}N}^{Nujol}$ 2110 cm^{-1}.

Anal. Calcd for $\{[(C_6H_5)_3P]_2Ru(Cl_2)N_2\}_2B_{10}H_8$: C, 55.2; H, 4.4; Cl, 9.1; N, 3.6; P, 7.9. Found: C, 55.0; H, 4.3; Cl, 9.1; N, 4.2; P, 7.9.

$[(C_6H_5)_3P]_3Ru(H_2)N_2B_{10}H_6S(CH_3)_2$. A mixture of $[(C_6H_5)_3P]_3Ru(N_2)H_2$ (3.0 g, 3.3 mmol) and $N_2B_{10}H_8SCH_3$[12] (0.75 g, 3.6 mmol) in tetrahydrofuran (100 ml) was stirred in a nitrogen atmosphere for 1 hr. Filtration gave 2.5 g (69%) of $[(C_6H_5)_3P]_3Ru(H_2)N_2B_{10}H_8S(CH_3)_2$ as a yellow solid (mp 141–142°, dec 143°): $\nu_{N{\equiv}N}^{Nujol}$ 2060 cm^{-1}.

Anal. Calcd for $[(C_6H_5)_3P]_3Ru(H_2)N_2B_{10}H_8S(CH_3)_2$: C, 61.4; H, 5.6; B, 9.9; N, 2.6; P, 8.5; S, 2.9. Found: C, 60.3; H, 5.6; B, 9.8; N, 2.6; P, 8.1; S, 2.2.

No decomposition was apparent after exposure to air for several months.

$[(C_6H_5)_3P]_3RuH(Cl)N_2B_{10}H_8S(CH_3)_2$. $[(C_6H_5)_3P]_3RuHCl\cdot C_6H_5CH_3$ (2.5 g, 2.5 mmol) was added to a solution of $N_2B_{10}H_8S(CH_3)_2$ (0.5 g, 2.4 mmol) in dichloromethane (50 ml) in a nitrogen atmosphere. A small amount of additional $N_2B_{10}H_8S(CH_3)_2$, sufficient to turn the color of the reaction mixture from red to brown yellow, was added. Alcohol (150 ml) was then added slowly, precipitating a dingy yellow solid. This was redissolved in dichloromethane (50 ml) in a nitrogen atmosphere. The solution was filtered. The filtrate was diluted slowly with alcohol (150 ml) precipitating $[(C_6H_5)_3P]_3RuH(Cl)N_2B_{10}H_8S(CH_3)_2$ as a crystalline, yellow solid (2 g, 71%, mp 175–177°) which was stable in air for at least several months: $\nu_{N{\equiv}N}^{Nujol}$ 2095 cm^{-1}.

Anal. Calcd for $[(C_6H_5)_3P]_3RuH(Cl)N_2B_{10}H_8S(CH_3)_2$: C, 59.5; H, 5.3; B, 9.6; Cl, 3.1; N, 2.5; S, 2.8. Found: C, 59.6; H, 5.5; B, 9.8; Cl, 3.2; N, 2.5; S, 2.9.

The proton nmr spectrum in $CDCl_3$ displayed a hydride signal at τ 15.7 which was split into two triplets ($J_{H-P_{cis}}$ = 22 cps, $J_{H-P_{trans}}$ = 135 cps) consistent with an octahedral structure in which the chlorine and the bridging N_2 group are mutually trans.

$[(C_6H_5)_3P]_2Ru(Cl_2)N_2B_{10}H_8S(CH_3)_2$. A solution of $[(C_6H_5)_3P]_4RuCl_2$ (8 g, 6.5 mmol) and $N_2B_{10}H_8S(CH_3)_2$ (2 g, 9.7 mmol) in toluene (200 ml) was stirred for 3 days in a nitrogen atmosphere. Filtration gave 4.8 g (82%) of $[(C_6H_5)_3P]_2Ru(Cl_2)N_2B_{10}H_8S(CH_3)_2$ which was washed with benzene and petroleum ether and dried at 80°: $\nu_{N{\equiv}N}^{Nujol}$ 2135 cm^{-1}.

Anal. Calcd for $[(C_6H_5)_3P]_2Ru(Cl_2)N_2B_{10}H_8S(CH_3)_2$: C, 50.5; H, 4.9; B, 12.0; Cl, 7.8; N, 3.1; P, 6.9; S, 3.5. Found: C, 49.8; H, 4.7; B, 12.8; Cl, 7.0; N, 2.8; P, 6.0; S, 3.8.

Recrystallization from dimethyl sulfoxide with heating to 65° (70° is about the highest temperature that can be used without decomposition) gave $[(C_6H_5)_3P]_2Ru(Cl_2)N_2B_{10}H_8S(CH_3)_2\cdot(CH_3)_2SO$ identical by infrared analysis with that prepared below. Heating this product caused softening at about 100° and decomposition at about 190°.

B. Hydrogen chloride was passed through a solution of $[(C_6H_5)_3P]_3RuH(Cl)N_2B_{10}H_8S(CH_3)_2$ (3 g, 2.7 mmol) in tetrahydrofuran (200 ml). The temperature rose to 60° and the hydrogen chloride flow was maintained until the temperature fell to 40°. Nitrogen was then passed through the mixture until not quite all the solvent had evaporated. Filtration gave 2.4 g (98%) of crude $[(C_6H_5)_3P]_2Ru(Cl_2)N_2B_{10}H_8S(CH_3)_2$ as a yellow solid which was identical by infrared analysis with that obtained above. Proton nmr analysis confirmed the presence of only two triphenylphosphine ligands per dimethyl sulfide group. Recrystallization of 0.2 g of the crude product from 1.2 ml of $(CH_3)_2SO$, with heating to 70° only, gave 80 mg of bright-yellow $[(C_6H_5)_3P]_2Ru(Cl_2)N_2B_{10}H_8S(CH_3)_2 \cdot (CH_3)_2SO$, identical by infrared analysis and melting point behavior with that prepared above. The dimethyl sulfoxide is apparent in the infrared.

Anal. Calcd for $[(C_6H_5)_3P]_2Ru(Cl_2)N_2B_{10}H_8S(CH_3)_2 \cdot (CH_3)_2SO$: C, 48.9; H, 5.1; B, 11.1; Cl, 7.2; N, 2.9; P, 6.3; S, 6.5. Found: C, 49.0; H, 4.8; B, 11.2; Cl, 7.3; N, 2.9; P, 6.0; S, 8.0.

C. A mixture of $[(C_6H_5)_3P]_2Ru(Cl_2)N_2B_{10}H_8S(CH_3)_2$ (1.5 g, 1.7 mmol) and $NaBH_4$ (0.7 g, 18 mmol) in alcohol (150 ml) was stirred overnight in a nitrogen atmosphere. Filtration and analysis of the filter cake (1.25 g) showed reduction was incomplete (Cl: found, 6.5). The filter cake (1.2 g) was treated with an additional 1.0 g of $NaBH_4$ in refluxing alcohol under nitrogen for 1.5 hr. The mixture was filtered; the filter cake (0.8 g) was rinsed with alcohol and dried. Extraction with toluene at 70° followed by dilution of the extracts with ethanol gave crystalline $[(C_6H_5)_3P]_3Ru(H_2)N_2B_{10}H_8S(CH_3)_2$, identified by decomposition point (140–147°), infrared, nmr, and elemental analysis.

$\{[(C_6H_5)_3P]_2RuCl_2\}_2N_2B_{10}H_8S(CH_3)_2$. A solution of $[(C_6H_5)_3P]_4RuCl_2$ (10 g, 8.2 mmol) and $N_2B_{10}H_8S(CH_3)_2$ (2 g, 9.7 mmol) in toluene (200 ml) was stirred in a nitrogen atmosphere for 19 hr. Filtration gave 2.8 g (38%) of yellow $[(C_6H_5)_3P]_2Ru(Cl_2)N_2B_{10}H_8S(CH_3)_2$ (A). The filtrate was stirred an additional 16 hr. Filtration gave an orange-red solid (B) which was extracted with tetrahydrofuran, leaving 1.7 g (23%) of yellow $[(C_6H_5)_3P]_2Ru(Cl_2)N_2B_{10}H_8S(CH_3)_2$. Addition of petroleum ether to the tetrahydrofuran extracts precipitated orange $\{[(C_6H_5)_3P]_2RuCl_2\}_2N_2B_{10}H_8S(CH_3)_2$ (0.7 g, 11%). A second, similar run was made with an initial stirring period of 20 hr. Filtration gave 3.8 g (51%) of yellow $[(C_6H_5)_3P]_2Ru(Cl_2)N_2B_{10}H_6S(CH_3)_2$. The filtrate was combined with the filtrate from the isolation of solid B and the combined filtrates were stirred for 3 days Filtration gave 1.6 g (12%) of orange $\{[(C_6H_5)_3P]_2RuCl_2\}_2N_2B_{10}H_8S(CH_3)_2$. The addition of petroleum ether (400 ml) to the filtrate precipitated 4.8 g (37%) more of the same product. Part of this product (4.3 g) was dissolved in 45 ml of hot tetrahydrofuran. The mixture was filtered; ethanol was added until the cloud point was reached and the mixture was allowed to cool. A rust-colored solid, $\{[(C_6H_5)_3P]_2RuCl_2\}_2N_2B_{10}H_8S(CH_3)_2$, separated (1.3 g, 30% recovery): $\nu_{N\;N}^{Nujol}$ 2110 cm^{-1}.

Anal. Calcd for $\{[(C_6H_5)_3P]_2RuCl_2\}_2RuN_2B_{10}H_8S(CH_3)_2$: C, 55.5; H, 4.7; B, 6.8; Cl, 8.9; P, 7.7. Found: C, 56.0; H, 4.6; B, 6.8; Cl, 8.6; P, 7.2.

$[(p\text{-}CH_3C_6H_4)_3P]_2Ru(Cl_2)N_2B_{10}H_8S(CH_3)_2$. A mixture of $[(p\text{-}CH_3C_6H_4)_3P]_4RuCl_2$ (10 g, 7.2 mmol) and $N_2B_{10}H_8S(CH_3)_2$ (2 g, 9.7 mmol) in toluene (100 ml) was stirred for 1 hr. Filtration gave 4.5 g (63%) of yellow $[(p\text{-}CH_3C_6H_4)_3P]_2Ru(Cl_2)N_2B_{10}H_8S(CH_3)_2$. Longer reaction times caused contamination with precipitated orange $\{[(p\text{-}CH_3C_6H_4)_3P]_2RuCl_2\}_2N_2B_{10}H_8S(CH_3)_2$. Extraction of 1.3 g of the product with dichloromethane (25 ml) followed by the addition of ethanol (50 ml) to the extract gave 0.55 g of yellow crystalline $[(p\text{-}CH_3C_6H_4)_3P]_2Ru(Cl_2)N_2B_{10}H_8S(CH_3)_2$ (dec >150°): $\nu_{N\equiv N}^{Nujol}$ 2125 cm^{-1}.

Anal. Calcd for $[(CH_3C_6H_4)_3P]_2Ru(Cl_2)N_2B_{10}H_8S(CH_3)_2$: C, 53.5; H, 5.7; Cl, 7.2; N, 2.8; P, 6.3; S, 3.3. Found: C, 53.7; H, 5.7; Cl, 7.4; N, 2.7; P, 6.1; S, 3.2.

$\{[(p\text{-}CH_3C_6H_4)_3P]_2RuCl_2\}_2N_2B_{10}H_8S(CH_3)_2$. A mixture of $[(p\text{-}CH_3C_6H_4)_3P]_4RuCl_2$ (8.7 g, 6.2 mmol) and $N_2B_{10}H_8S(CH_3)_2$ (0.6 g, 3 mmol) in toluene (100 ml) was stirred for 3 hr. Filtration gave 3 g (63%) of orange-red $\{[(p\text{-}CH_3C_6H_4)_3P]_2RuCl_2\}_2N_2B_{10}H_8S(CH_3)_2$ (dec 160–169°): $\nu_{N\equiv N}^{Nujol}$ 2105 cm^{-1}.

Anal. Calcd for $\{[(CH_3C_6H_4)_3P]_2RuCl_2\}_2N_2B_{10}H_8S(CH_3)_2$: C, 58.5; H, 5.6; B, 6.1; Cl, 8.0; N, 1.6; P, 7.0; S, 1.8. Found: C, 59.4; H, 6.1; B, 5.8; Cl, 8.0; N, 1.6; P, 6.2; S, 1.1.

The proton nmr spectrum confirms the presence of four $(CH_3C_6H_4)_3$ groups per dimethyl sulfide.

$[(C_6H_5)_3P]_2RuH(Cl)(CN)N_2B_{10}H_8S(CH_3)_2^-$. A solution of KCN (0.4 g, 8 mmol) in water (4 ml) was added to $[(C_6H_5)_3P]_3RuH(Cl)N_2B_{10}H_8S(CH_3)_2$ (1 g, 0.9 mmol) in tetrahydrofuran (30 ml) and the mixture was stirred 7 min. The layers were separated and the tetrahydrofuran layer was diluted with ethanol (55 ml). Concentration of this solution to about 30 ml caused the separation of 0.3 g (30%) of crystalline $K^+[(C_6H_5)_3P]_2RuH(Cl)(CN)N_2B_{10}H_8S(CH_3)_2^-$. The infrared spectrum includes a strong band at 2035 cm^{-1} ($N\equiv N$, with a shoulder at 2080), a sharp band at 2125 cm^{-1} (CN), and a weak band at 1970 cm^{-1} (Ru–H).

Anal. Calcd for $K[(C_6H_5)_3P]_2RuH(Cl)(CN)N_2B_{10}H_8S(CH_3)_2$: C, 50.2; H, 4.9; B, 11.6; Cl, 3.8; K, 4.2; N, 4.5; P, 6.6. Found: C, 49.6; H, 5.0; B, 11.7; Cl, 3.3; K, 3.1; N, 4.3; P, 6.0.

$[(C_6H_5)_3P]_2Ru(H)(Cl)(CH_3CN)N_2B_{10}H_8S(CH_3)_2$. A mixture of $N_2B_{10}H_8S(CH_3)_2$ (2.4 g, 1.2 mmol) and $[(C_6H_5)_3P]_3RuHCl \cdot C_6H_5CH_3$ (10 g, 9.9 mmol) in dichloromethane (200 ml) was stirred for 30 min in a nitrogen atmosphere and then filtered. The filtrate was diluted with acetonitrile (400 ml) and left undisturbed overnight. Filtration gave 6.5 g (72%) of bright-yellow, crystalline $[(C_6H_5)_3P]_2Ru(H)(Cl)(CH_3CN)N_2B_{10}H_8S(CH_3)_2$: dec 150–160°; $\nu_{N\equiv N}^{Nujol}$ 2030 cm^{-1}.

Anal. Calcd for $[(C_6H_5)_3P]_2Ru(H)(Cl)(CH_3CN)N_2B_{10}H_8S(CH_3)_2$: B, 11.9; C, 52.9; H, 5.3; Cl, 3.9; N, 4.6; P, 6.8. Found: B, 11.5; C, 52.3; H, 5.4; Cl, 4.0; N, 4.4; P, 6.8.

The proton nmr spectrum as determined in $CDCl_3$–$(CD_3)_2SO$ includes a triplet hydride signal at τ 20.7 (J = 19 cps).