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# PREPARATIONS AND REACTIONS OF SOME HYDRIDODINITROGENTRIALKYLPHOSPHINE COMPLEXES OF RHODIUM(I). THE STRUCTURE OF A DINITROGEN-BRIDGED RHODIUM(I) DIMER, $[RhH(P(i\text{-}Pr)_3)_2]_2(\mu\text{-}N_2)$ *

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## Summary

The reduction of $RhCl_3 \cdot 3\ H_2O$ by sodium amalgam in THF solution under an atmosphere of $N_2$ and in the presence of an excess of a phosphine ligand has resulted in the formation of the hydridodinitrogen complexes $RhH(N_2)(PPh(t\text{-}Bu)_2)_2$ (I), $RhH(N_2)(P(t\text{-}Bu)_3)_2$ (II), and $[RhH(P(cyclo\text{-}C_6H_{11})_3)_2]_2(\mu\text{-}N_2)$ (V), and a hydridotrisphosphine complex $RhH(P(i\text{-}Pr)_3)_3$ (X). The dinitrogen coordination is stable in I but $N_2$ is readily lost from the other dinitrogen complexes, permitting the isolation of three-coordinate hydridobisphosphine rhodium(I) complexes $RhH(P(t\text{-}Bu)_3)_2$ (VII) and $RhH(P(cyclo\text{-}C_6H_{11})_3)_2$ (VIII). Trihydrido complexes $RhH_3L_2$ ($L = PPh(t\text{-}Bu)_2$ (XI), $P(t\text{-}Bu)_3$ (XII), $P(cyclo\text{-}C_6H_{11})_3$ (XIII), and $P(i\text{-}Pr)_3$ (XIV)) have been synthesized by the reaction of the above rhodium(I) compounds with $H_2$. By treatment of the corresponding trihydrido complexes with $N_2$ we have been able to obtain $RhH(N_2)(P(cyclo\text{-}C_6H_{11})_3)_2$ (III) and $RhH(N_2)(P(i\text{-}Pr)_3)_2$ (IV). Loss of $N_2$ from IV results in the formation of $[RhH(P(i\text{-}Pr)_3)_2]_2(\mu\text{-}N_2)$ (VI) and $RhH(P(i\text{-}Pr)_3)_2$ (IX). The crystal and molecular structure of $[RhH(P(i\text{-}Pr)_3)_2]_2(\mu\text{-}N_2)$ (VI) has been determined at −85°C. The compound crystallizes in the triclinic space group $C_i^1\text{-}P\bar{1}$ with two molecules in a cell of dimensions $a$ 12.703(16), $b$ 16.455(16), $c$ 11.389(8) Å, $\alpha$ 90.25(9), $\beta$ 103.87(3), $\gamma$ 97.58(3)°, V 2289 Å$^3$. The final conventional and weighted agreement indices on $F_0$ for $F_0^2 > 3\sigma(F_0^2)$ are 0.051 and 0.060, respectively. The dinitrogen ligand of VI linearly bridges two planar $RhHP_2$ fragments with an N—N separation of 1.134(5) Å and an average Rh—N

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* Dedicated to Professor Joseph Chatt on the occasion of his 65th birthday.

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bond distance of 1.977(6) Å. The dihedral angle between the two $RhHP_2$ fragments is 55.2°. Overall, the dimeric complex effectively has $D_2$ (222) symmetry.

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## Introduction

Recently we demonstrated that phosphine ligands with bulky substituents are capable of stabilizing two-coordinate, fourteen-electron complexes of $d^{10}$ metals [1,2]. The chemistry of isoelectronic, three-coordinate phosphine complexes of $d^8$ metals is of obvious interest, but is virtually unexplored. Three-coordinate rhodium(I) complexes, $RhXL_2$, have been proposed to result from the equilibrium dissociation of a phosphine ligand from the four-coordinate complexes $RhXL_3$ (X = Cl, L = $PPh_3$ [3]; X = H, L = $PPh_3$ [4], 5-phenyl-5*H*-dibenzophosphole [5]) but equilibrium concentrations of the three-coordinate complexes are very small [6,7]. The only isolated three-coordinate $d^8$ complexes of the Co triad previously reported are $[Rh(PPh_3)_3]^+$ [8] and RhX-$(P(c\text{-}C_6H_{11})_3)_2$ (X = Cl, Br, I; c-$C_6H_{11}$ = cyclohexyl) [9].

Our attempts to prepare three-coordinate rhodium(I) compounds using bulky phosphine ligand have led us to the discovery of two types of rhodium hydridodinitrogen compounds, the mononuclear complexes *trans*-$RhH(N_2)L_2$ (L = $PPh(t\text{-}Bu)_2$ (I) [10], $P(t\text{-}Bu)_3$ (II), $P(c\text{-}C_6H_{11})_3$ (III), $P(i\text{-}Pr)_3$ (IV)) and the binuclear dinitrogen bridged compounds $(RhHL_2)_2(\mu\text{-}N_2)$ (L = $P(c\text{-}C_6H_{11})_3$ (V), $P(i\text{-}Pr)_3$ (VI)). We have found that some of the rhodium(I) hydridodinitrogen complexes serve as precursors to the three-coordinate hydrido complexes $RhHL_2$ (L = $P(t\text{-}Bu)_3$ (VII), $P(c\text{-}C_6H_{11})_3$ (VIII), $P(i\text{-}Pr)_3$ (IX)) through a facile dissociation of the coordinated dinitrogen ligand [11—15]. A hydridotrisphosphine complex $RhH(P(i\text{-}Pr_3)_3$, (X) and trihydride complexes $RhH_3L_2$ (L = PPh-$(t\text{-}Bu)_2$ (XI), $P(t\text{-}Bu)_3$ (XII), $P(c\text{-}C_6H_{11})_3$ (XIII), $P(i\text{-}Pr)_3$ (XIV)) have been prepared and utilized as synthetic intermediates. Compounds VII—IX are of considerable interest both in view of their unusual coordination numbers and their ability to catalyze hydrogenation reactions and H—D exchange reactions of organic substrates [16]. In this paper we report the preparations of the hydridodinitrogen complexes and the three-coordinate hydrido complexes, some of their reactions, and the low-temperature structure of the dinitrogen complex $[RhH(P(i\text{-}Pr)_3)_2]_2(\mu\text{-}N_2)$ (VI). A preliminary report of the preparations of some of these compounds has been published [16].

## Results and discussion

*Complexes with phenyldi-t-butylphosphine, $PPh(t\text{-}Bu)_2$.* Earlier [10] we reported the properties and the molecular structure of *trans*-$RhH(N_2)$-$(PPh(t\text{-}Bu)_2)_2$ (I), prepared by the reduction of $RhCl_3 \cdot 3\ H_2O$ with sodium amalgam (Na/Hg) in the presence of the free phosphine ligand and $N_2$. It is probable that the hydrido ligand in I and in the hydrido compounds described below is derived from the solvent, tetrahydrofuran (THF). Precedents for such a hydride abstraction are the formation of *cis*-$PtH_2(R_2P(CH_2)_2PR_2)$ (R = t-Bu, *l*-menthyl) [17] from the reduction of the corresponding dichloride with

Na/Hg in THF, and the formation of $RuH(OH)(PPh_3)_2(THF)_2$ from $RuCl_2(PPh_3)_3$ and NaOH in THF [18]. Low-valent transition metal complexes are known to abstract hydrogen from THF in the metal-catalyzed hydrogen transfer hydrogenation of olefins [19]. Compound I can also be obtained by two alternative routes, the reaction of *trans*-$RhCl(CH_2{=}CH_2)(PPh(t\text{-}Bu)_2)_2$ with n-BuLi and an anion exchange reaction of $[RhH_2(Sol)_2(PPh(t\text{-}Bu)_2)_2][ClO_4]$ (Sol = solvent) with $OH^-$. This latter reaction probably involves the formation of $[RhH_2(Sol)_2(PPh(t\text{-}Bu)_2)_2][OH]$ followed by the reductive elimination of water to give $RhH(PPh(t\text{-}Bu)_2)_2$, which coordinates $N_2$.

The dinitrogen complexes prepared with the other phosphine ligands (vide infra) are unstable with respect to loss of the dinitrogen ligand. Compound I, however, is very stable, perhaps because of the lower basicity of $PPh(t\text{-}Bu)_2$ relative to the trialkylphosphine ligands. The coordinated dinitrogen ligand of I can be displaced by other coordinating ligands; for instance, treatment of I with $H_2$ affords the trihydride, $RhH_3(PPh(t\text{-}Bu)_2)_2$ (XI).

*Complexes with tri-t-butylphosphine, $P(t\text{-}Bu)_3$.* Reduction of $RhCl_3 \cdot 3\,H_2O$ with Na/Hg in the presence of $P(t\text{-}Bu)_3$ gives the hydridodinitrogen compound *trans*-$RhH(N_2)(P(t\text{-}Bu)_3)_2$ (II). This complex is stable at —30°C under $N_2$, but at room temperature it gradually loses the coordinated dinitrogen ligand to give a dark brown solid, $RhH(P(t\text{-}Bu)_3)_2$ (VII). The dissociation is rapid in benzene or hexane solution. Immediately after the preparation of a hexane solution of II under one atmosphere of $N_2$ the N≡N and Rh—H stretching bands can be seen in the infrared spectrum at 2145 and 2060 $cm^{-1}$, respectively (see Table 1). The $^1H$ NMR spectrum shows no hydride signal, however, even at —70°C. We interpret this result in terms of a rapid equilibration between II and VII (eq. 1) since VII prepared separately in pure form does exhibit a hydride signal.

$$\underset{(II)}{RhH(N_2)(P(t\text{-}Bu)_3)_2} \rightleftharpoons \underset{(VII)}{RhH(P(t\text{-}Bu)_3)_2} + N_2 \qquad (1)$$

Consistently we have obtained the three-coordinate compound VII as brown air-sensitive crystals by recrystallization of II from hexane under an argon atmosphere. Molecular weight measurements have confirmed its monomeric nature in benzene solution. The mass spectrum shows the expected parent peak (*m/e* 508) and fragments corresponding to stepwise loss of butene from the t-butyl groups of the phosphine ligands. The IR and $^1H$ NMR spectra, respectively, show a Rh—H stretching band at 2065 $cm^{-1}$ and a hydride signal at $\delta$ —13.9 (double triplet, $J$(H—P) 18.8 Hz, $J$(H—Rh) 10.5 Hz). Virtual coupling is observed in the t-butyl proton NMR signal ($\delta$ 1.47 (triplet), $^3J$(H—P) + $^5J$(H—P) 11.4 Hz); thus a near *trans* disposition of the phosphine ligands in the complex is likely. The resultant T-shaped structure could be ascribed to the large steric bulk of the phosphine (cone angle 182° [20]). However, as pointed out elsewhere [21], the cone angle is not necessarily an accurate measure of the effective steric demand of trialkylphosphines, as a considerable amount of "squeezing" of the phosphine substituents appears to be possible [1]. Based on extended Hückel calculations, Komiya et al. [22] predict a T-shaped structure as the most stable molecular geometry of diamagnetic $d^8$ three-coordinate com-

TABLE 1

SPECTRAL DATA OF THE DINITROGEN COMPOUNDS

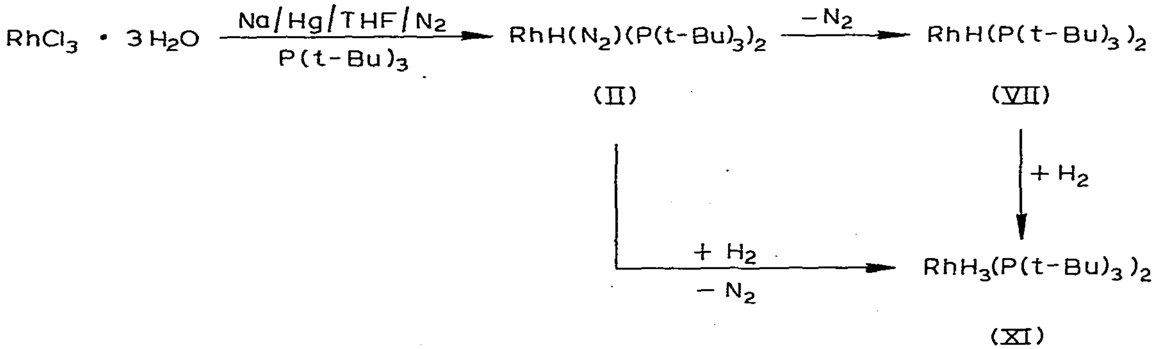
| | IR ($cm^{-1}$) [a] | | $^1H$ NMR [b] | | | |
|---|---|---|---|---|---|---|
| | ν(Rh—H) | ν(N≡N) | δ(Rh—H) | J(H—Rh) (Hz) | J(H—P) (Hz) | Others |
| *trans*-$RhH(N_2)(PPh(t\text{-}Bu)_2)_2$ (I) | 1977 | 2155 | −13.0(dt) | 16.0 | 19.0 | t-Bu, δ 1.44(t), $^3J(H—P) + {}^5J(H—P)$ = 12.6 Hz |
| *trans*-$RhH(N_2)(P(t\text{-}Bu)_3)_2$ (II) | 2063 | 2145 | [c] | | | t-Bu, δ 1.47(t), $^3J(H—P) + {}^5J(H—P)$ = 10.0 Hz |
| *trans*-$RhH(N_2)(P(c\text{-}C_6H_{11})_3)_2$ (III) | 1950<br>(1953) | 2130<br>(2125) | −13.0(dt) | 18.8 | 20.2 | c-$C_6H_{11}$, δ 1.8(b) |
| *trans*-$RhH(N_2)(P(i\text{-}Pr)_3)_2$ (IV) | (1962) | (2140) | −13.2(dt) | 17.6 | 20.0 | $CH_3$, δ 1.30(q), $^3J(H—P) + {}^5J(H—P)$ = 12.8 Hz, J(H—H) = 6.4 Hz; CH, δ 2.2(m) |
| $[RhH(P(c\text{-}C_6H_{11})_3)_2]_2(N_2)$ (V) | 1953 | | | | | |
| $[RhH(P(i\text{-}Pr)_3)_2]_2(N_2)$ (VI) | 1927 | | | | | |

[a] Measured in Nujol mull. The value obtained in n-hexane solution is shown in the parentheses. [b] Measured in toluene-$d_8$ at 25°C. [c] Owing to the rapid equilibrium II ⇌ VII + $N_2$ no hydride signal was observed even at −70°C.

plexes, and a T-shaped structure has been found for $[Rh(PPh_3)_3]^+$ [8].

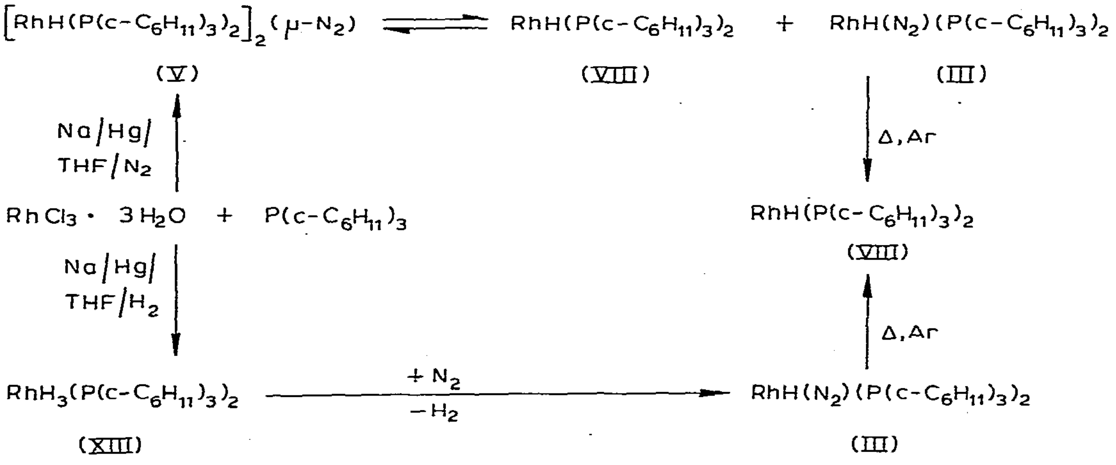
Facile loss of $N_2$ from the hydridodinitrogen complex II is an interesting and significant difference from stable $N_2$ coordination in the analogous hydridodinitrogen complex I. Although the phosphine ligands $PPh(t\text{-}Bu)_2$ in I and $P(t\text{-}Bu)_3$ in II have similar steric requirements, $P(t\text{-}Bu)_3$ is more basic. This strong basicity stabilizes the 14-electron, 3-coordinate complex VII relative to the hypothetical complex $RhH(PPh(t\text{-}Bu)_2)_2$. The steric bulk of the phosphine substituents precludes the stable coordination of a third phosphine ligand to form $RhHL_3$. We summarize the reactions of the hydrido complexes with $P(t\text{-}Bu)_3$ in Scheme 1. Both II and VII will oxidatively add $H_2$ to form the trihydrido complex $RhH_3(P(t\text{-}Bu)_3)_2$ (XII), as in the analogous reaction of I with $H_2$.

SCHEME 1



*Complexes with tricyclohexylphosphine, $P(c\text{-}C_6H_{11})_3$.* The dinitrogen complex, *trans*-$RhH(N_2)(P(c\text{-}C_6H_{11})_3)_2$ (III), could not be obtained by the direct reduction of $RhCl_3 \cdot 3\ H_2O$ in the presence of $P(c\text{-}C_6H_{11})_3$ under an atmosphere of $N_2$. Compound III was obtained instead from the reaction of $RhH_3(P(c\text{-}C_6H_{11})_3)_2$ (XIII) with $N_2$ in hexane (see Scheme 2). Complex XIII was pre-

SCHEME 2



pared by the Na/Hg reduction of $RhCl_3 \cdot 3\ H_2O$ in the presence of the phosphine under a hydrogen atmosphere. When the reduction is carried out under $N_2$ the complex initially obtained is $[RhH(P(c\text{-}C_6H_{11})_3)_2]_2(\mu\text{-}N_2)$ (V) (vide intra). The dinitrogen ligand is more firmly bound in III than in the $P(t\text{-}Bu)_3$ complex II, as the solid compound III does not lose dinitrogen at room temperature in vacuo. However, when the complex is dissolved in benzene there is dissociation of the coordinated dinitrogen ligand, even under one atmosphere of $N_2$. Two hydride signals are observed in the $^1H$ NMR spectrum of the solution, a double triplet at $\delta$ −13.0 ($J$(H—P) 20.2, $J$(H—Rh) 18.8 Hz) and a double triplet at $\delta$ −14.9 ($J$(H—P) 22.7, $J$(H—Rh) 18.5 Hz) with a relative intensity of ca. 2:3. The latter signal is assigned to $RhH(P(c\text{-}C_6H_{11})_3)_2$ (VIII) on the basis of the IR and $^1H$ NMR spectra of an authentic sample; the former signal is assigned to III. The observation of two hydride signals from III and VIII suggests the equilibrium III $\rightleftharpoons$ VIII + $N_2$ is not as rapid as that observed in the analogous $P(t\text{-}Bu)_3$ system.

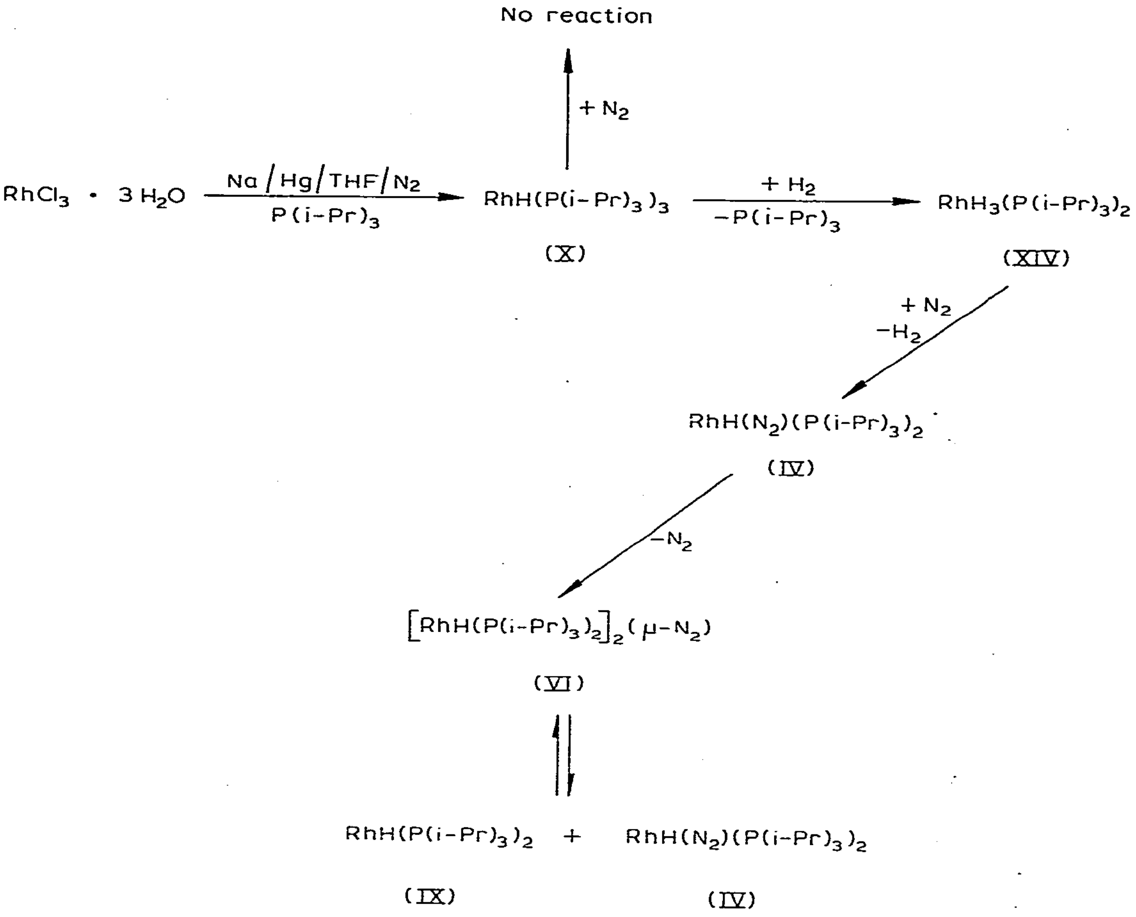
The product obtained from the direct reduction of $RhCl_3 \cdot 3\ H_2O$ with Na/Hg in the presence of $P(c\text{-}C_6H_{11})_3$ and $N_2$ is the binuclear $\mu$-dinitrogen compound $[RhH(P(c\text{-}C_6H_{11})_3)_2]_2(\mu\text{-}N_2)$ (V). This same complex V is also obtained upon recrystallizing III from aromatic hydrocarbons. The IR spectrum of the solid compound shows no N—N stretching mode, consistent with a linearly bridging dinitrogen ligand. The IR spectrum of a benzene solution of V, however, shows $\nu(N\equiv N)$ at 2125 $cm^{-1}$ and $\nu$(Rh—H) at 1953 $cm^{-1}$, identical with those of III (see Table 1). The hydride $^1H$ NMR signal is also indistinguishable from that of III. These spectroscopic data suggest to us that there is an almost complete dissociation of V into III and VIII (see Scheme 2) and reassociation is not sufficiently rapid to broaden the hydride $^1H$ NMR signal (contrast the behavior of II in solution). An analogous dissociation has been found for the related complex $[Ni(P(c\text{-}C_6H_{11})_3)_2]_2(\mu\text{-}N_2)$ [13]. We conclude that our isolation of V is mainly a result of its being the least soluble of the different species involved. Heating a benzene solution of the dinitrogen-containing compounds III or V under argon at 60—70° C affords VIII from complete loss of dinitrogen (see Scheme 2).

*Complexes with triisopropylphosphine, $P(i\text{-}Pr)_3$.* The reduction of $RhCl_3 \cdot 3\ H_2O$ with Na/Hg in the presence of the less bulky phosphine $P(i\text{-}Pr)_3$ affords a trisphosphine complex $RhH(P(i\text{-}Pr)_3)_3$ (X), rather than the expected hydridodinitrogen complex. The IR spectrum of X shows a Rh—H stretching frequency of 1975 $cm^{-1}$ and the hydride signal in the NMR spectrum is observed at $\delta$ −10.9 as a complex multiplet ($AB_2MX$ spin system). Except for the coupling between the hydride and the rhodium nuclei ($J$(H—Rh) 16.5 Hz) the $^1H$ NMR signal is very similar to the hydride signal of $[NiH(PEt_3)_3]^+$ [23]. The hydride $^1H$ NMR signal of X shows a temperature dependence in the temperature range −40 to +50° C which remains the same in the presence of an excess of free $P(i\text{-}Pr)_3$. This we interpret in terms of an intramolecular site exchange of the phosphine ligands, perhaps through a quasitetrahedral intermediate or transition state [7,23—26]. The $^{31}P$ NMR spectrum shows only a sharp doublet in the temperature range −40 to +40° C ($J$(P—Rh) 157 Hz) with some broadening at −80° C, also consistent with a rapid rearrangement process which does not entail ligand dissociation [7,26]. This contrasts with the very facile ligand dissociation observed for the complex $Pt(P(i\text{-}Pr)_3)_3$ ($K_{diss} = 0.04\ M$ at 20°C in hexane) [27].

The hydridotrisphosphine complex X does not react directly with dinitrogen. In contrast to the bulkier phosphine ligands $P(t\text{-}Bu)_3$, $PPh(t\text{-}Bu)_2$, and $P(c\text{-}C_6H_{11})_3$, apparently $P(i\text{-}Pr)_3$ is sufficiently small to permit formation of a stable hydridotrisphosphine complex and can replace the dinitrogen ligand if any of the hydridodinitrogen complex $RhH(N_2)(P(i\text{-}Pr)_3)_2$ (IV) were momentarily present.

Complex IV can be obtained in solution by the route used for the preparation of III (Scheme 3). Treatment of a hexane solution of $RhH_3P(i\text{-}Pr)_3)_2$ (XIV), itself obtained from the reaction of X with $H_2$, with $N_2$ affords a dinitrogen compound, as deduced from the intense absorption in the IR spectrum at 2140 $cm^{-1}$ which we ascribe to $\nu(N{\equiv}N)$. Two Rh—H bands are present in the IR spectrum (1962, 1930 $cm^{-1}$) and thus we infer the existence of two hydride species in the solution. This is confirmed by the $^1H$ NMR spectrum, which shows two hydride signals at $\delta$ —13.2 (dt, $J$(H—P) 20.0, $J$(H—Rh) 17.6 Hz) and $\delta$ —14.5

SCHEME 3



(dt, $J$(H—P) 21.0, $J$(H—Rh) 17.2 Hz) in approximately a 1:3 ratio. After the solution is purged with argon its IR spectrum shows only one Rh—H stretching band (1930 cm$^{-1}$) and no N≡N stretching band, and its $^1$H NMR spectrum shows only the higher-field signal ($\delta$ −14.5). Our interpretation of these results is that the initial reaction product with dinitrogen is the hydridodinitrogen complex RhH(N$_2$)(P(i-Pr)$_3$)$_2$ (IV) which readily loses N$_2$ to form several new hydrido complexes, one of which has been found by an X-ray structure determination to be the dinitrogen-bridged compound [RhH(P(i-Pr)$_3$)$_2$]$_2$($\mu$-N$_2$) (VI). The facile dissociation of N$_2$ has prevented isolation of IV in pure solid form, and attempts to obtain it by recrystallization from pentane under N$_2$ have resulted instead in the isolation of VI. Elemental analyses of samples of VI (recrystallized from pentane under argon) indicated partial or complete loss of dinitrogen, and the complex VI was originally formulated as a dimer of RhH(P(i-Pr)$_3$)$_2$ (IX). The IR spectrum of a solid sample of VI shows $\nu$(Rh—H) at 1927 cm$^{-1}$ but no $\nu$(N≡N), consistent with the $D_2$ symmetrical structure found in the X-ray study. However, the IR spectrum of a hexane solution of VI, which had been prepared under argon, shows $\nu$(N≡N) at 2140 cm$^{-1}$ and $\nu$(Rh—H) at 1962 cm$^{-1}$ and 1930 cm$^{-1}$. These results strongly suggest a dissociation of VI into IV and RhH(P(i-Pr)$_3$)$_2$ (IX). The $^1$H NMR spectrum of VI (in toluene-$d_8$ under Ar) also indicates the presence of IV (hydride signal at $\delta$ −13.2, dt), as well as a much stronger hydride signal at $\delta$ −14.5. After N$_2$ was bubbled through the solution, the relative concentration of IV increased, as indicated by an enhancement of the signal at $\delta$ −13.2 relative to the signal at $\delta$ −14.5. We do not know whether the $^1$H NMR signal at $\delta$ −14.5 (double triplet, $J$(H—Rh) 17.2, $J$(H—P) 21.0 Hz) is from undissociated dimer VI or the nitrogen-free complex IX, or a fortuitous overlapping of signals from both.

When attempts were made to recrystallize the dinitrogen-bridged compound VI under an argon atmosphere, a new yellow-orange complex was obtained. Elemental analyses of this compound indicate it to be free of nitrogen, and we presently formulate it as RhH(P(i-Pr)$_3$)$_2$ (IX). Molecular weight measurements of IX in benzene suggest it to be dimeric (found: 835; calculated for a dimer: 848 g/mole). Spectra of complex IX in solution show several of the same features as seen for spectra of the dinitrogen-bridged dimer VI (IR: $\nu$(Rh—H) 1930 cm$^{-1}$; $^1$H NMR: $\delta$ −14.5, dt). The hydride signal in the $^1$H NMR spectrum of IX is inconsistent with a possible hydrido-bridged dimeric structure, and the structure of IX is still under investigation.

*Description of the structure of [RhH(P(i-Pr)$_3$)$_2$]$_2$($\mu$-N$_2$) (VI).* This structure determination was undertaken on what was believed to be the nitrogen-free complex IX or the dimer of IX. Instead the structure determination revealed for the first time the existence of compound VI, the dinitrogen-bridged species. The compound crystallizes in the triclinic space group $C_i^1$-$P\bar{1}$ with two molecules in the unit cell. A view of the complex is shown in Fig. 1. Each dimeric molecule consists of two planar HRhP$_2$ centers coupled by a dinitrogen molecule, with a dihedral angle between the planes of 55.2°. Average deviations from the local coordination planes are 0.014 Å. The H—Rh—N—N—Rh—H linkage is essentially linear and the dimeric complex has an overall point group symmetry very close to $D_2$ (222). Bond distances and angles around the two rhodium centers are insignificantly different (see Table 2). The unit cell pack-

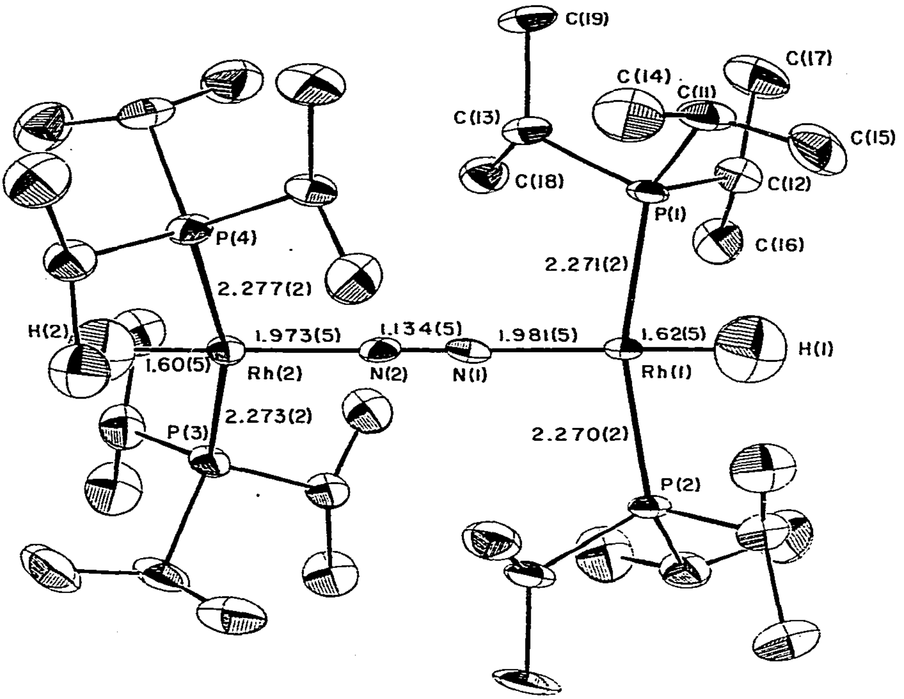


Fig. 1. A drawing of a molecule of $[RhH(P(i\text{-}Pr)_3)_2]_2(\mu\text{-}N_2)$. Thermal ellipsoids are drawn at the 50% probability level here and in Fig. 2. Selected interatomic distances are given. The carbon atoms of the isopropyl groups on P(1) are labeled to illustrate the numbering scheme.

ing is shown in Fig. 2. It appears to be determined by Van der Waals' and steric interactions among the hydrogen atoms of the isopropyl groups. The shortest intermolecular H···H contact is 2.44 Å. Inspection of a space-filling model suggests that there could be severe steric crowding among isopropyl groups of the two dimer halves. This is considerably relieved by bending the phosphine ligands away from the bridging dinitrogen group towards the terminal hydride ligands (average P—Rh—P angle, 163.3(1)°) and by decreasing the dihedral angle between coordination planes from 90°. Even in sterically-unencumbered planar $d^8$ monomeric complexes, however, there is a pronounced tendency for *trans*-phosphine ligands to bend towards a mutually *cis*-hydrido ligand [7,10,28—30]. The dihedral angle of 55.2° is very likely established by optimal inter- and intra-molecular packing of the isopropyl groups. Electronic effects alone would probably favor a dihedral angle of 90°, but the potential surface for twisting about the Rh—N—N—Rh bond is likely to be very soft *.

The $Rh—P(i\text{-}Pr)_3$ bond distances (ave. 2.273(3) Å) are shorter than values of 2.348(1) [32] and 2.31(1) Å [33] found previously in low-temperature structural determinations. The Rh—P bond length in $RhH(N_2)(PPh(t\text{-}Bu)_2)_2$ [10] is 2.297(1) Å. Planar rhodium(I)—phosphine compounds in which the P—Rh—P angle of nominally *trans*-phosphine ligands is considerably less than 180° (ave. 163.3(1)° in the present compound, VI; 168.12(3)° in $RhH(N_2)(PPh(t\text{-}Bu)_2)_2$, I

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* The overall MO argument resembles that presented by Hoffmann et al. [31].

TABLE 2

SELECTED BOND DISTANCES (Å) AND ANGLES (deg) FOR $[RhH(P(i\text{-}Pr)_3)_2]_2(\mu\text{-}N_2)$ (VI)

| | | | | | |
|---|---|---|---|---|---|
| Rh(1)—P(1) | 2.271(2) | C(21)—C(24) | 1.514(9) | C(11)—P(1)—C(12) | 103.5(3) |
| Rh(1)—P(2) | 2.270(2) | C(21)—C(25) | 1.512(9) | C(11)—P(1)—C(13) | 103.7(3) |
| Rh(2)—P(3) | 2.273(2) | C(22)—C(26) | 1.529(8) | C(12)—P(1)—C(13) | 108.8(3) |
| Rh(2)—P(4) | 2.277(2) | C(22)—C(27) | 1.532(8) | C(21)—P(2)—C(22) | 103.8(3) |
| Rh—P(ave) | 2.273(3) [a] | C(23)—C(28) | 1.525(8) | C(21)—P(2)—C(23) | 102.9(3) |
| | | C(23)—C(29) | 1.535(7) | C(22)—P(2)—C(23) | 109.5(3) |
| | | C(31)—C(34) | 1.502(10) | C(31)—P(3)—C(32) | 103.0(3) |
| Rh(1)—N(1) | 1.981(5) | C(31)—C(35) | 1.529(9) | C(31)—P(3)—C(33) | 104.3(3) |
| Rh(2)—N(2) | 1.973(5) | C(32)—C(36) | 1.521(8) | C(32)—P(3)—C(33) | 108.8(3) |
| Rh—N(ave) | 1.977(6) | C(32)—C(37) | 1.543(7) | C(41)—P(4)—C(42) | 103.0(3) |
| | | C(33)—C(38) | 1.514(9) | C(41)—P(4)—C(43) | 103.3(3) |
| | | C(33)—C(39) | 1.534(8) | C(42)—P(4)—C(43) | 109.7(3) |
| Rh(1)—H(1) | 1.62(5) | C(41)—C(44) | 1.517(9) | | |
| Rh(2)—H(2) | 1.60(5) | C(41)—C(45) | 1.517(9) | C(11)—P(1)—Rh(1) | 113.5(2) |
| Rh—H(ave) | 1.61(4) | C(42)—C(46) | 1.524(6) | C(12)—P(1)—Rh(1) | 112.9(2) |
| | | C(42)—C(47) | 1.529(8) | C(13)—P(1)—Rh(1) | 113.6(2) |
| | | C(43)—C(48) | 1.522(8) | C(21)—P(2)—Rh(1) | 114.0(2) |
| | | C(43)—C(49) | 1.543(7) | C(22)—P(2)—Rh(1) | 112.5(2) |
| N(1)—N(2) | 1.134(5) | C—C(ave) [a] | 1.525(12) | C(23)—P(2)—Rh(1) | 113.3(2) |
| | | | | C(31)—P(3)—Rh(2) | 113.7(2) |
| | | | | C(32)—P(3)—Rh(2) | 113.6(2) |
| P(1)—C(11) | 1.854(6) | P(1)—Rh(1)—P(2) | 163.32(6) | C(33)—P(3)—Rh(2) | 112.6(2) |
| P(1)—C(12) | 1.845(6) | P(3)—Rh(2)—P(4) | 163.18(6) | C(41)—P(4)—Rh(2) | 113.9(2) |
| P(1)—C(13) | 1.850(6) | P—Rh—P(ave) | 163.3(1) | C(42)—P(4)—Rh(2) | 113.3(2) |
| P(2)—C(21) | 1.858(5) | | | C(43)—P(4)—Rh(2) | 112.8(2) |
| P(2)—C(22) | 1.843(6) | | | | |
| P(2)—C(23) | 1.847(6) | P(1)—Rh(1)—H(1) | 83(2) | | |
| P(3)—C(31) | 1.847(6) | P(2)—Rh(1)—H(1) | 81(2) | | |
| P(3)—C(32) | 1.848(6) | P(3)—Rh(2)—H(2) | 81(2) | | |
| P(3)—C(33) | 1.845(6) | P(4)—Rh(2)—H(2) | 83(2) | | |
| P(4)—C(41) | 1.834(5) | | | | |
| P(4)—C(42) | 1.844(5) | P(1)—Rh(1)—N(1) | 98.5(1) | | |
| P(4)—C(43) | 1.857(6) | P(2)—Rh(1)—N(1) | 98.2(1) | | |
| P—C(ave) | 1.848(7) | P(3)—Rh(2)—N(2) | 98.4(1) | | |
| | | P(4)—Rh(2)—N(2) | 98.4(1) | | |
| | | H(1)—Rh(1)—N(1) | 177(2) | | |
| C(11)—C(14) | 1.528(9) | H(2)—Rh(2)—N(2) | 178(2) | | |
| C(11)—C(15) | 1.500(8) | | | | |
| C(12)—C(16) | 1.526(8) | Rh(1)—N(1)—N(2) | 179.3(3) | | |
| C(12)—C(17) | 1.518(8) | Rh(2)—N(2)—N(1) | 179.3(3) | | |
| C(13)—C(18) | 1.522(8) | | | | |
| C(13)—C(19) | 1.540(7) | | | | |

[a] The value in parentheses for an average value is the standard deviation of a single observation and is the larger of that estimated from the average standard deviation of the individual observations or on the assumption that the values averaged are from the same population.

[10]) may have atypically short Rh—P bond lengths as a result of a slight diminution of the mutual *trans*-influence of the phosphines. The P—C and C—C bond lengths in VI are normal (averages 1.848(7), 1.525(12) Å, respectively). The Rh—N distances (average, 1.977(6) Å) are longer than those found in related rhodium(I) complexes with terminally-bound dinitrogen ligands (1.885(4) Å in $RhCl(N_2)(P(i\text{-}Pr)_3)_2$ * [32]; 1.970(4) Å in $RhH(N_2)$-

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* The structure of $RhCl(N_2)(P(i\text{-}Pr)_3)_2$, originally claimed to have a side-bonded dinitrogen ligand [34] with a Rh—N separation of 2.54(2) Å, has been redetermined. The dinitrogen ligand is actually terminally bonded [32].

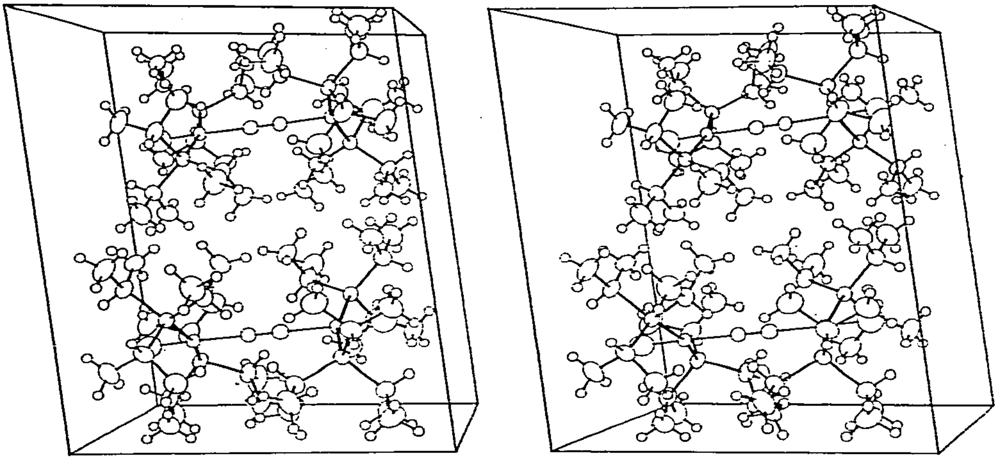

Fig. 2. Stereoscopic view of the unit cell contents of $[RhH(P(i\text{-}Pr)_3)_2]_2(\mu\text{-}N_2)$. Alkyl hydrogens atoms are included with an artificial isotropic B of 1.0 Å$^2$. The crystallographic *a* axis runs from left to right and the *b* axis from bottom to top. The point (0, 0, 0) is at the center of each drawing.

$(PPh(t\text{-}Bu)_2)_2$ [10]) but the latter distances are rendered unreliable by known or suspected disorder. We have noted [33] a trend in Rh—H distances in terminally-bound hydrido complexes which is maintained in this structure: $Rh^{I}$—H distances found by X-ray methods tend to be around 1.6 Å in length, while $Rh^{III}$—H distances may be somewhat shorter. In the present complex the average $Rh^{I}$—H distance is 1.61(4) Å. The N—N separation (1.134(5) Å) is slightly longer than the shortest value reported for linearly-bridging dinitrogen complexes [13,35—41] (values range from 1.12 [13,36] to 1.28 Å [39]) and may be indicative of minimal π-delocalization in the Rh—N—N—Rh chain relative to the other analogous dimeric compounds. However, there may still be some slight long-range delocalization of *d*-electrons of one Rh center into the nominally-empty *p*-orbital of the other Rh center *, which could enhance the stability of the dimeric complex VI relative to the terminally-bonded dinitrogen complex IV.

Upon close examination of the unit-cell diagram, Fig. 2, it can be seen that an isostructural analogue of VI with $P(t\text{-}Bu)_3$ replacing $P(i\text{-}Pr)_3$ could not exist. Each dimer has an intramolecular H···H contact of about 2.52 Å between the hydrogen atoms on atoms C(13) and C(42), and a similar contact between the hydrogen atoms on atoms C(23) and C(32). In a hypothetical isostructural $P(t\text{-}Bu)_3$ complex, the present sites of hydrogen atoms on atoms C(13), C(23), C(32), and C(43) would be occupied by carbon atoms of methyl groups, and impossible interatomic contacts would result. By rearranging the packing of the phosphine substituents and optimizing the interplanar dihedral angle it might be possible to accommodate the bulk of the t-butyl groups in such a dimeric complex. However, our studies strongly suggest that such a dimeric complex is not formed in the reactions involving $P(t\text{-}Bu)_3$. Tricyclohexylphosphine has been found to have very comfortable intramolecular packing of the

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* This is referred to as the "push-pull" effect in a somewhat similar Ti complex; see ref. 39.

cyclohexyl substituents in a related complex [13]. We suspect that favorable intramolecular packing, while not necessarily the dominant driving force for dimer formation, is definitely a determining factor in permitting the dimerization.

## Experimental

$^1$H NMR spectra were recorded on JEOL 4H-100 or JEOL C-60HL spectrometers. IR spectra were measured on a Hitachi Model 295 spectrometer. All reactions and physical measurements were carried out under dinitrogen or argon atmospheres. The following compounds were prepared by literature methods: $P(t\text{-}Bu)_3$ [42], $P(c\text{-}C_6H_{11})_3$ [43], $PPh(t\text{-}Bu)_2$ [44], $P(i\text{-}Pr)_3$ [45], $[RhCl(CH_2{=}CH_2)_2]_2$ [46], and $[RhCl(C_8H_{14})_2]_2$ [47]. Physical properties and analytical data are shown in Table 3. The spectral data of the trihydride complexes $RhH_3L_2$ are summarized in Table 4. Spectral data for the dinitrogen complexes are in Table 1.

*trans-RhH(N₂)(PPh(t-Bu)₂)₂ (I).* Preparation of I by reduction of the system $RhCl_3 \cdot 3\ H_2O/PPh(t\text{-}Bu)_2$ with Na/Hg has been reported [10]. Compound I was also prepared by two alternative methods: (a) Under a hydrogen atmosphere $AgClO_4$ (0.23 g, 1.1 mmol) was added to a yellow solution obtained from $[RhCl(CH_2{=}CH_2)_2]_2$ (0.20 g, 0.5 mmol) and $PPh(t\text{-}Bu)_2$ (0.45 g, 2.0 mmol) in THF (10 ml). The filtered dark brown solution was treated with 1 *N* aqueous NaOH (2 ml) and the mixture was stirred at room temperature for 2 h

TABLE 3

PHYSICAL AND ANALYTICAL DATA

| | Color | M.p. (°C) | Analysis (Found (calcd.) (%)) | | |
|---|---|---|---|---|---|
| | | | C | H | N |
| *trans*-$RhH(N_2)[PPh(t\text{-}Bu)_2]_2$ | yellow | 85 (dec) | 58.25 | 8.04 | 4.64 |
| (I) | | | (58.60) | (8.05) | (4.86) |
| *trans*-$RhH(N_2)[P(t\text{-}Bu)_3]_2$ | yellow | 0 (dec) | 54.18 | 10.39 | 4.18 |
| (II) | | | (53.72) | (10.33) | (5.22) |
| *trans*-$RhH(N_2)[P(c\text{-}C_6H_{11})_3]_2$ | orange yellow | 145 (dec) | 62.57 | 9.74 | 3.84 |
| (III) | | | (62.41) | (9.75) | (4.04) |
| $\{RhH[P(c\text{-}C_6H_{11})_3]_2\}_2(N_2)$ | orange yellow | 165 (dec) | 63.53 | 10.03 | 2.03 |
| (V) | | | (63.70) | (9.95) | (2.06) |
| $\{RhH[P(i\text{-}Pr)_3]_2\}_2(N_2)$ | orange | 105 (dec) | 48.81 | 9.83 | 3.15 |
| (VI) | | | (49.31) | (9.89) | (3.19) |
| $RhH[P(t\text{-}Bu)_3]_2$ [a] | dark brown | 160 (dec) | 56.68 | 10.71 | 0 |
| (VII) | | | (56.68) | (10.90) | |
| $RhH[P(i\text{-}Pr)_3]_2$ [b] | orange | 80 (dec) | 51.28 | 9.10 | 0 |
| (IX) | | | (50.94) | (10.21) | |
| *trans*-$RhH_3[PPh(t\text{-}Bu)_2]_2$ | yellow | 90 (dec) | 61.27 | 8.98 | |
| (XI) | | | (61.07) | (8.98) | |
| *trans*-$RhH_3[P(t\text{-}Bu)_3]_2$ | yellow | 20 (dec) | 56.33 | 10.89 | |
| (XII) | | | (56.46) | (11.25) | |
| *trans*-$RhH_3[P(c\text{-}C_6H_{11})_3]_2$ | yellow | 140 (dec) | 64.45 | 10.14 | |
| (XIII) | | | (64.84) | (10.43) | |
| *trans*-$RhH_3[P(i\text{-}Pr)_3]_2$ | yellow | 100 (dec) | 51.02 | 10.88 | |
| (XIV) | | | (50.70) | (10.64) | |

[a] Mol. wt. calcd.: 508, found: 491 (in benzene). [b] Mol. wt: calcd. for dimer; 848, found: 835 (in benzene).

TABLE 4

SPECTRAL DATA OF *trans*-$RhH_3L_2$

| | IR (cm$^{-1}$)[a] $\nu$(Rh—H) | $^1$H NMR[b] | |
|---|---|---|---|
| | | $\delta$(Rh—H) | Others |
| *trans*-$RhH_3[PPh(t\text{-}Bu)_2]_2$ (XI) | 1910, 1957 | —5.95(b)<br>(—5.77[c]) | t-Bu, $\delta$ 1.47(t), $^3J$(H—P) + $^5J$(H—P) = 12.8 Hz; Ph, $\delta$ 7.1(m) and 8.4(m) |
| *trans*-$RhH_3[P(t\text{-}Bu)_3]_2$ (XII) | 1980 | —7.75(b)<br>(—6.27[d] | t-Bu, $\delta$ 1.53(t), $^3J$(H—P) + $^5J$(H—P) = 10.5 Hz |
| *trans*-$RhH_3[P(c\text{-}C_6H_{11})_3]_2$ (XIII) | 2040 | —8.80(b) | c-$C_6H_{11}$, $\delta$ 1.8(bm) |
| *trans*-$RhH_3[P(i\text{-}Pr)_3]_2$ (XVI) | 2035 | —12.5(b) | $CH_3$, $\delta$ 1.34(q), $^3J$(H—P) + $^5J$(H—P) = 12.0 Hz, $J$(H—H) = 6.0 Hz, CH, $\delta$ 2.0(m) |

[a] Measured in Nujol mull prepared under argon. [b] Measured in toluene-$d_8$ at 25°C under argon. [c] At —20°C, dt, $J$(H—Rh) 19 Hz and $J$(H—P) 8 Hz. [d] At —60°C, dt, $J$(H—Rh) 20 Hz and $J$(H—P) 7 Hz.

under dinitrogen. The brown solid obtained by concentration in vacuo was recrystallized from n-hexane to give I as yellow crystals (0.30 g, 52%). (b) Complex I was obtained in 40% yield by treating a mixture of $[RhCl(CH_2{=}CH_2)_2]_2$ (0.195 g, 0.5 mmol) and $PPh(t\text{-}Bu)_2$ (0.45 g, 2.0 mmol) with a pentane solution (3 ml) of n-BuLi (1.2 mmol) at 0°C for 0.5 h.

*trans-RhH(N$_2$)(P(t-Bu)$_3$)$_2$ (II).* A mixture of $RhCl_3 \cdot 3\ H_2O$ (0.49 g, 2.0 mmol) and $P(t\text{-}Bu)_3$ (1.22 g, 6.0 mmol) in THF (20 ml) was stirred at room temperature for 20 h. The brown solid residue obtained by concentration in vacuo was treated with 1% Na/Hg (30 g) in THF (20 ml) and stirred at room temperature for 20 h under an atmosphere of dinitrogen. Filtration of the dark brown solution and subsequent concentration gave a brown solid. Recrystallization from n-hexane at —20°C gave II as yellowish brown crystals (0.57 g, 53%).

*trans-RhH(N$_2$)(P(c-C$_6$H$_{11}$)$_3$)$_2$ (III).* The brown reaction mixture of $RhCl_3 \cdot 3\ H_2O$ (0.49 g, 2.0 mmol) and $P(c\text{-}C_6H_{11})_3$ (1.55 g, 5.5 mmol) obtained in a manner similar to that described above was treated with 1% Na/Hg (30 g) in THF (20 ml) under a hydrogen atmosphere for 20 h at room temperature. After filtration under $H_2$, the filtrate was concentrated in vacuo to give a brown solid. Recrystallization from n-hexane under a dinitrogen atmosphere gave III as yellow-orange crystals (0.52 g, 40%). Compound III dissolves in toluene under dinitrogen with evolution of $N_2$ to give V in 80% yield.

*[RhH(P(c-C$_6$H$_{11}$)$_3$)$_2$]$_2$($\mu$-N$_2$) (V).* The brown reaction mixture of $RhCl_3 \cdot 3\ H_2O$ (0.73 g, 3 mmol) and $P(c\text{-}C_6H_{11})_3$ (1.7 g, 6 mmol) obtained by a method similar to that described for II was treated with 1% Na/Hg (40 g) in THF (20 ml) under $N_2$ for 20 h. The yellow solid which separated was dissolved in toluene (20 ml) and the mixture was filtered. After concentration of the solution to 10 ml and cooling at —10°C yellow crystals of V separated (1.5 g, 73%). Recrystallization from toluene gave an analytically pure sample.

*[RhH(P(i-Pr)$_3$)$_2$]$_2$($\mu$-N$_2$) (VI) and "RhH(P(i-Pr)$_3$)$_2$" (IX).* Recrystallization of $RhH_3(P(i\text{-}Pr)_3)_2$ (XIV) (0.13 g, 0.3 mmol) from n-pentane (10 ml) under a dinitrogen atmosphere gave yellow crystals as the major product and a few dark brown crystals. Separation could only be effected by manual sorting. The yellow complex was recrystallized from n-pentane under argon to give orange crys-

tals (0.045 g, 34%), shown by an X-ray structure determination to be VI. Elemental analysis of samples obtained from separate preparations showed varying amounts of nitrogen (calculated for VI: 3.19%; found: 0 to 2.42%) and indicate the presence of IX. Analytically pure VI was obtained by recrystallizing the yellow solid from pentane under an atmosphere of $N_2$.

*$RhH(P(t\text{-}Bu)_3)_2$ (VII).* Compound II (0.16 g, 0.3 mmol) was dissolved in n-hexane (20 ml) with extensive evolution of $N_2$. The solution was concentrated in vacuo to a quarter of the original volume and kept at −20° C under an argon atmosphere to give VII as dark brown crystals (0.12 g, 70%).

*$RhH(P(c\text{-}C_6H_{11})_3)_2$ (VIII).* Compound V (0.26 g, 0.2 mmol) was dissolved in benzene (15 ml) and the solution was heated at 60–70° C for 3 h with a constant stream of argon bubbling through the solution. Concentration in vacuo gave a brown oily solid. Several attempts to obtain a crystalline sample have failed. Extreme sensitivity of the product toward air has prevented an accurate elemental analysis. Compound VIII was also obtained by heating a benzene solution of III under argon.

*$RhH(P(i\text{-}Pr)_3)_3$ (X).* THF (35 ml), $P(i\text{-}Pr)_3$ (1.0 ml, 5 mmol), and 1% Na/Hg (40 g) were added successively to the brown solid obtained from $RhCl_3 \cdot 3\ H_2O$ (0.98 g, 4 mmol) and $P(i\text{-}Pr)_3$ (1.6 ml, 8 mmol) in the manner employed for II. The mixture was stirred at room temperature for 20 h. The filtered reaction solution was dried in high vacuum ($10^{-3}$ mmHg) to remove excess $P(i\text{-}Pr)_3$. Recrystallization of the resulting dark brown solid residue from pentane containing free $P(i\text{-}Pr)_3$ (0.5 ml) gave X as yellow crystals (1.4 g, 60%).

*$RhH_3(PPh(t\text{-}Bu)_2)_2$ (XI).* Hydrogen was passed through a solution of I (0.34 g, 0.6 mmol) in pentane (50 ml) at room temperature. The concentrated mixture was kept under $H_2$ at −20° C to give yellow crystals of XI (0.26 g, 80%).

*$RhH_3(P(t\text{-}Bu)_3)_2$ (XII).* Reaction of II with $H_2$ under conditions similar to those employed above gave yellow crystals of XII in 20% yield. The compound $RhH_3[P(t\text{-}Bu)_3]_2$ was also obtained by treating VII with $H_2$.

*$RhH_3(P(c\text{-}C_6H_{11})_3)_2$ (XIII).* (a) The brown reaction mixture of $RhCl_3 \cdot 3\ H_2O$ (0.25 g, 1 mmol) and $P(c\text{-}C_6H_{11})_3$ (0.62 g, 2.2 mmol) (obtained by a similar procedure to that employed for the preparation of III) was stirred with 1% Na/Hg (20 g) under a hydrogen atmosphere for 20 h. The filtered mixture was concentrated in vacuo. The yellow solid residue was recrystallized from n-hexane under $H_2$ to give pale yellow crystals of XIII (0.38 g, 53%). The crystals were dried under a $H_2$ stream. (b) Hydrogen was passed through a suspension of V (0.2 g, 0.15 mmol) in n-pentane (10 ml) at room temperature for 0.5 h to give a clear yellow solution. On standing at −20° C $RhH_3(P(c\text{-}C_6H_{11})_3)_2$ (0.09 g, 45%) precipitated from the solution.

*$RhH_3(P(i\text{-}Pr)_3)_2$ (XIV).* Hydrogen was bubbled through a solution of $RhH(P(i\text{-}Pr)_3)_3$, X (0.23 g, 0.4 mmol) in n-pentane (10 ml) at room temperature. The solution was concentrated to 5 ml and kept at −40° C under $H_2$ to give dark yellow crystals. Recrystallization from n-pentane gave an analytically pure sample of XIV (0.13 g, 76%).

### *X-ray data collection*

Single crystals of VI, $[RhH(P(i\text{-}Pr)_3)_2]_2(\mu\text{-}N_2)$, were obtained by recrystallization of VI from a pentane solution under argon. Owing to the extreme sensitivity of the compound to oxygen, the crystals were handled under an argon atmosphere. It was only during the actual data collection process that any exposure to nitrogen occurred, at which time the temperature was sufficiently low (—85° C) to preclude any possible reaction. The same crystal was used both for preliminary photographic measurements and for the data collection. The Weissenberg and precession photographs of this crystal encapsulated under Ar in a capillary showed no apparent symmetry other than the trivial center of symmetry and no systematic absences. A Delaunay reduction of the derived cell constants revealed no hidden symmetry. The centrosymmetric space group $C_i^1$-$P\bar{1}$ was assumed, and is confirmed by the eventual successful refinement. The room temperature cell constants lead to a density of 1.25 g/cm$^3$ calculated for two $Rh_2P_4C_{36}H_{86}N_2$ units in the cell, in good agreement with the observed density, 1.26(1) g/cm$^3$ (measured by flotation in aqueous $ZnCl_2$).

For data collection the crystal was removed from the capillary and was mounted on a Picker diffractometer directly in a stream of cold nitrogen gas * at an estimated temperature of —85° C; this temperature never varied by more than ±5° during the course of the data collection. We chose this temperature since crystals shattered at —150° C, apparently because of a sluggish phase transition commencing at ca. —100° C. Data collection and reduction were carried out as described previously [49]. A total of 9116 reflections (8852 unique in $P\bar{1}$) were collected in the range $4.0 \leqslant 2\,\theta(\text{Mo-}K_{\alpha1}) \leqslant 51.6°$. Six reflections were chosen as standards and were remeasured every 100 reflections during the data collection; their intensities showed no significant fluctuation or deterioration. The data were corrected for absorption effects **. Information regarding the data collection is summarized in Table 5.

### *Solution and refinement of the structure*

Scattering factors for nonhydrogen atoms are those used previously [51]. The scattering factors for hydrogen atoms are from Stewart, Davidson, and Simpson [52]. Anomalous dispersion terms [51] for the rhodium and phosphorus atoms were included in $F_c$.

Positions of the rhodium and phosphorus atoms consistent with space group $P\bar{1}$ were deduced from a Patterson map, and the remaining nonhydrogen atoms were located by Fourier methods. After several cycles of refinement in which the carbon atoms were refined isotropically and the rhodium, phosphorus, and nitrogen atoms were refined anisotropically, the positions of most of the hydrogen atoms of the isopropyl groups and the two hydrido ligands were clear from a difference Fourier map. The isopropyl hydrogen atoms were placed in idealized locations (C—H distance 0.95 Å, tetrahedral angles), each given an iso-

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* The design of the apparatus is from J.C. Huffman [48].

** Computer programs used in the data reduction and refinement include AGNOST, the Northwestern absorption program, modified versions of Zalkin's FORDAP Fourier summation program, Busing's and Levy's ORFFE error function program, and Johnson's ORTEP plotting program. NUCLS, our full-matrix least-squares program, in its nongroup form closely resembles the Busing-Levy ORFLS program. The diffractometer was run under the disk-oriented Vanderbilt system [50]. Final calculations were carried out by remote hook-up to the CDC 7600 computer at Lawrence Berkeley Laboratory. The same programs were employed.

TABLE 5

SUMMARY OF CRYSTAL DATA AND INTENSITY COLLECTION FOR $[RhH(P(i\text{-}Pr)_3)_2]_2(\mu\text{-}N_2)$, VI

| | |
|---|---|
| Compound | $[RhH(P(i\text{-}Pr)_3)_2]_2(\mu\text{-}N_2)$ |
| Formula | $C_{36}H_{86}N_2P_4Rh_2$ |
| Temperature | —85°C |
| Formula weight | 876.81 amu |
| $a$ | 12.703(16) Å |
| $b$ | 16.455(16) Å |
| $c$ | 11.389(8) Å |
| $\alpha$ | 90.25(9)° |
| $\beta$ | 103.87(3)° |
| $\gamma$ | 97.58(3)° |
| $V$ | 2289 $Å^3$ |
| $Z$ | 2 |
| Density (calc) | 1.272 $g/cm^3$ (—85°C), 1.25 $g/cm^3$ (25°C) |
| Density (obs) | 1.26(1) $g/cm^3$ (25°C) |
| Space group | $C_i^1\text{-}P\bar{1}$ |
| Crystal shape and dimensions [a] | Irregular hexagonal plate, faces of forms $\{100\}$ (0.46), $\{01\bar{1}\}$ (0.38), $\{011\}$ (0.46), $\{010\}$ (0.29) and $\{\bar{1}11\}$ (0.60) |
| Crystal volume | 0.0551 $mm^3$ |
| Radiation | Mo-$K_\alpha$ ($\lambda$(Mo-$K_{\alpha 1}$) 0.709300 Å) |
| Linear absorption coefficient | 8.71 $cm^{-1}$ |
| Transmission factors | 0.664 to 0.797 |
| Takeoff angle | 3.2° |
| Scan speed | 2° in $2\theta$/min |
| Scan range | 1.2° below $K_{\alpha_1}$ peak to 1.15° above $K_{\alpha_2}$ peak |
| $2\theta$ limits | 4.0 to 51.6° |
| Background collection | 10 sec for $2\theta$ less than 46.9°,<br>20 sec for $2\theta$ greater than 46.9°,<br>all with rescan option |
| Final number of variables | 405 |
| Unique data used in final refinement [b] | 8852 |
| Unique data, $F_0^2 > 3\sigma(F_0^2)$ | 6124 |
| $R$ (on $F_0{}^2$, all data) | 0.098 |
| $R_w$ (on $F_0{}^2$, all data) | 0.122 |
| $R$ (on $F_0$ for $F_0^2 > 3\sigma(F_0^2)$) | 0.051 |
| $R_w$ (on $F_0$ for $F_0^2 > 3\sigma(F_0^2)$) | 0.060 |
| Error in observation of unit weight | 1.64 electrons |

[a] The perpendicular distance between the indicated face and its Friedel mate is given in parentheses (in mm). [b] This includes reflections with $F_0{}^2 < 0$.

tropic thermal parameter $B$ 1.0 $Å^2$ greater than that of its attached carbon atom, and held fixed during all subsequent refinement. A table of positional and thermal parameters for these hydrogen atoms is available *. The hydrido hydrogen atoms were fixed at 1.60 Å from the respective rhodium atoms until the final refinement cycle, during which their positional and isotropic thermal parameters were refined.

After the hydrogen atoms had been located and their contributions to $F_c$

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### TABLE 6

### POSITIONAL AND THERMAL PARAMETERS (X$10^4$) FOR THE ATOMS OF [RhH(P($i$-Pr)$_3$)$_2$]$_2$($\mu$-N$_2$)

| Atom | $x$ | $y$ | $z$ | $B_{11}$ [b] or $B$(Å$^2$) | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| RH(1) | -0.297832(30) | 0.230349(24) | -0.302465(31) | 33.52(29) | 23.44(17) | 15.73(28) | 2.47(17) | 6.25(22) | 4.41(16) |
| RH(2) | 0.298682(30) | 0.271656(24) | -0.194619(32) | 33.38(29) | 24.16(17) | 17.75(29) | 4.64(17) | 6.28(22) | -6.25(16) |
| P(1) | -0.23511(11) | 0.289935(80) | -0.48462(10) | 40.97(90) | 24.53(52) | 16.52(87) | 0.31(54) | 4.24(71) | 4.32(53) |
| P(2) | -0.23441(11) | 0.164722(84) | -0.13492(11) | 41.26(91) | 29.71(57) | 20.04(91) | 7.47(57) | 13.04(73) | 8.18(56) |
| P(3) | 0.23695(11) | 0.338711(87) | -0.01255(11) | 43.19(94) | 32.42(60) | 16.69(90) | 10.14(59) | 3.38(73) | -9.23(58) |
| P(4) | 0.23488(11) | 0.214485(81) | -0.36317(11) | 43.36(93) | 25.64(53) | 22.53(93) | 3.13(55) | 13.42(74) | -6.68(55) |
| N(1) | -0.04566(38) | 0.24559(24) | -0.25993(32) | 47.3(34) | 23.0(18) | 14.1(30) | 4.7(18) | 5.1(24) | -0.2(18) |
| N(2) | 0.04718(37) | 0.25471(24) | -0.23656(32) | 40.9(33) | 23.0(18) | 15.6(30) | 3.5(17) | 12.5(24) | -3.1(18) |
| C(11) | -0.28742(49) | 0.21541(34) | -0.61493(43) | 75.0(49) | 30.0(24) | 22.4(38) | -2.6(27) | 8.3(34) | -3.7(24) |
| C(12) | -0.33970(45) | 0.35496(34) | -0.50545(48) | 53.0(41) | 28.7(24) | 45.1(44) | 6.9(24) | 5.4(34) | 3.4(25) |
| C(13) | -0.10872(45) | 0.34557(34) | -0.51560(45) | 57.1(41) | 34.6(24) | 33.7(41) | 1.8(25) | 18.0(33) | 12.4(25) |
| C(14) | -0.20375(59) | 0.15674(46) | -0.61516(58) | 103.3(64) | 39.6(30) | 67.0(58) | 9.6(34) | 21.1(49) | -20.7(33) |
| C(15) | -0.39584(53) | 0.16717(39) | -0.61362(56) | 76.7(52) | 38.5(28) | 57.8(55) | -6.5(30) | -13.4(42) | -9.5(31) |
| C(16) | -0.32490(50) | 0.41617(37) | -0.39431(58) | 62.4(47) | 35.8(27) | 76.1(61) | 10.8(28) | 16.4(43) | -2.8(32) |
| C(17) | -0.36182(60) | 0.40763(43) | -0.62063(58) | 101.1(64) | 48.6(34) | 61.3(57) | 27.6(37) | -2.0(48) | 21.1(35) |
| C(18) | -0.06473(49) | 0.41784(36) | -0.42560(52) | 60.3(46) | 33.4(25) | 55.6(52) | -8.3(26) | 11.8(39) | 8.3(28) |
| C(19) | -0.10976(53) | 0.37078(42) | -0.64593(50) | 79.9(54) | 60.2(35) | 40.3(46) | -5.6(34) | 28.2(40) | 21.0(32) |
| C(21) | -0.27979(47) | 0.22921(37) | -0.02723(46) | 62.6(45) | 46.8(29) | 33.0(42) | 16.9(29) | 18.4(35) | -2.2(28) |
| C(22) | -0.34325(48) | 0.07609(35) | -0.17106(51) | 59.3(45) | 33.6(25) | 49.9(50) | 4.5(26) | 21.3(38) | 11.1(28) |
| C(23) | -0.10844(46) | 0.13193(37) | -0.04066(45) | 56.0(42) | 45.6(27) | 28.1(40) | 16.6(27) | 11.0(33) | 18.0(26) |
| C(24) | -0.39153(54) | 0.25379(43) | -0.08136(61) | 69.3(51) | 60.6(35) | 82.5(65) | 22.9(34) | 37.1(48) | -10.6(38) |
| C(25) | -0.19627(60) | 0.30493(45) | 0.00913(61) | 85.3(60) | 51.4(35) | 77.8(62) | 13.1(36) | 17.9(49) | -26.4(37) |
| C(26) | -0.33347(56) | 0.02174(39) | -0.27411(58) | 68.2(57) | 30.1(28) | 70.7(59) | -0.9(31) | 23.7(47) | -1.2(32) |
| C(27) | -0.36402(60) | 0.02374(45) | -0.06586(65) | 92.0(62) | 54.3(36) | 88.5(69) | 2.0(37) | 41.2(53) | 28.1(40) |
| C(28) | -0.56823(51) | 0.06771(39) | -0.10976(53) | 69.6(50) | 46.5(30) | 56.1(51) | 26.0(31) | 16.1(41) | 22.1(31) |
| C(29) | -0.10553(58) | 0.10660(47) | 0.08951(47) | 100.5(63) | 79.3(41) | 27.4(40) | 35.7(41) | 14.9(40) | 32.5(33) |
| C(31) | 0.28604(52) | 0.27578(40) | 0.11805(46) | 79.6(52) | 52.7(32) | 23.5(39) | 28.2(33) | 2.0(35) | 4.9(28) |
| C(32) | 0.11143(44) | 0.37036(35) | 0.01772(44) | 49.8(40) | 42.1(25) | 26.2(39) | 10.6(25) | 9.9(32) | -14.5(25) |
| C(33) | 0.34261(47) | 0.42940(37) | 0.00063(52) | 52.6(43) | 39.5(26) | 54.6(51) | 5.0(26) | 5.0(37) | -19.1(29) |
| C(34) | 0.25445(44) | 0.20944(47) | 0.11478(59) | 114.0(69) | 49.0(37) | 67.1(57) | 19.9(41) | 19.4(50) | 26.3(37) |
| C(35) | 0.39872(50) | 0.25198(47) | 0.11951(61) | 89.3(60) | 70.4(39) | 66.7(61) | 40.5(39) | -4.5(48) | 17.9(39) |
| C(36) | 0.06786(50) | 0.43394(39) | -0.07247(54) | 66.4(48) | 44.7(29) | 59.5(55) | 21.4(30) | 12.0(41) | -15.2(32) |
| C(37) | 0.11123(55) | 0.39651(45) | 0.14791(50) | 86.4(57) | 77.3(38) | 36.8(45) | 23.5(37) | 23.4(41) | -27.6(33) |
| C(38) | 0.32936(57) | 0.40254(39) | -0.10273(61) | 86.6(57) | 34.7(28) | 80.7(65) | -3.8(31) | 22.6(49) | -10.5(34) |
| C(39) | 0.36404(57) | 0.48253(43) | 0.12317(62) | 84.4(57) | 53.0(33) | 77.5(66) | -2.1(34) | 12.1(49) | -39.0(38) |
| C(41) | 0.28215(49) | 0.28284(34) | -0.46772(46) | 68.4(49) | 31.2(24) | 38.0(42) | -1.9(27) | 27.7(37) | 3.1(25) |
| C(42) | 0.10838(43) | 0.15351(34) | -0.45869(42) | 53.5(38) | 36.2(24) | 18.4(37) | 2.2(24) | 7.1(30) | -10.9(23) |
| C(43) | 0.34314(45) | 0.14255(34) | -0.32783(46) | 57.6(42) | 34.8(24) | 40.2(42) | 15.5(25) | 16.8(34) | -9.1(25) |
| C(44) | 0.20016(58) | 0.34250(42) | -0.50709(59) | 87.1(59) | 43.9(32) | 76.7(60) | 10.3(34) | 31.4(48) | 24.1(35) |
| C(45) | 0.39351(55) | 0.33980(41) | -0.41149(64) | 69.9(53) | 43.2(31) | 92.3(70) | -7.2(32) | 33.3(50) | 10.9(37) |
| C(46) | 0.10491(54) | 0.12650(42) | -0.58957(48) | 88.6(56) | 59.4(33) | 27.2(42) | -6.1(34) | 11.3(38) | -27.7(30) |
| C(47) | 0.06506(48) | 0.08141(36) | -0.39133(53) | 60.6(46) | 34.6(25) | 57.0(52) | -9.6(27) | 15.5(39) | -17.7(28) |
| C(48) | 0.33081(54) | 0.08698(37) | -0.22410(59) | 73.2(53) | 32.7(26) | 76.0(52) | 14.6(29) | 20.2(46) | 2.0(32) |
| C(49) | 0.36105(56) | 0.09283(41) | -0.43492(59) | 90.4(56) | 53.7(33) | 71.9(61) | 28.9(34) | 35.3(48) | -16.5(35) |
| H(1) | -0.3464(41) | 0.2131(39) | -0.3380(47) | 7.0(11) | | | | | |
| H(2) | 0.3395(41) | 0.2689(30) | -0.1603(47) | 6.1(11) | | | | | |

[a] Estimated standard deviations in the least significant figure are given in parentheses. [b] The form of the anisotropic thermal ellipsoid is: $\mathrm{Exp}[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

had been included, all nonhydrogen atoms were refined anisotropically. In the final cycle of anisotropic refinement, the function minimized was $\Sigma w(F_0^2 - F_c^2)^2$ and all unique data were used, including reflections for which $F_0^2 \leqslant 0$. The final agreement indices, computed on $F_0$ for those reflections with $F_0^2 \geqslant 3\sigma(F_0^2)$, are $R = 0.051$, $R_w = 0.060$. Table 5 lists other agreement indices. A final difference Fourier map revealed no peaks above 1 $e/\text{Å}^3$ except for ripples (1.5(2) $e/\text{Å}^3$) within 1 Å of the rhodium centers. The final positional and thermal parameters for the nonhydrogen atoms and the hydrido ligands are listed in Table 6. A listing of 10 $|F_0|$ vs. $|F_c|$ is available (see footnote on p. 198).

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