bond angle is 177.0° thus the configuration is slightly nonlinear as was shown for $K_2Pt(CN)_4{\cdot}3H_2O$[30] and for KCP(Br) and KCP(Cl).[9-14] The strong ligand repulsion is shown by the staggering of the TCP units juxtaposed along the chain. TCP(1) and TCP(3) are not exactly eclipsed perhaps because of the hydrogen bonding water molecules and the unit cell packing.

Conclusions

Although the formula $K_{1.75}Pt(CN)_4{\cdot}1.5H_2O$ appears to be nonstoichiometric, the unit cell is made up of tetrameric units of $K_7[Pt(CN)_4]_4{\cdot}6H_2O$ stoichiometry where the Pt has a formal oxidation state of +2.25. The distorted Pt chain has two crystallographically inequivalent but nearly equal Pt–Pt distances which suggests that the valence electrons on Pt are delocalized over the Pt chain. The Pt chain distortion is due to the asymmetric distribution of attractive forces exerted by the K^+ ions on TCP(2). The H_2O molecules form multiple hydrogen bonds which may contribute to conformation staggering of the TCP(1) and TCP(3) units along the Pt chain. Since the unit cell contains an uneven number of electrons, the possibility of a metallic state is suggested.

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Registry No. $K_{1.75}Pt(CN)_4{\cdot}1.5H_2O$, 59831-03-7.

Supplementary Material Available: Listing of scaled (×0.5) structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Hydrido(dinitrogen)bis[phenyl(di-*tert*-butyl)phosphine]rhodium(I)

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The structure of hydrido(dinitrogen)bis[phenyl(di-*tert*-butyl)phosphine]rhodium(I), $RhH(N_2)[P(C_6H_5)(C_4H_9)_2]_2$, has been determined crystallographically. The complex possesses a typical four-coordinate planar geometry about Rh with a slight bending of the phosphine groups toward the hydrido ligand (P–Rh–P = 168.12 (3)°). A linear H–Rh–N–N arrangement is required by the crystallographically imposed twofold axis. The compound crystallizes in space group C_{2h}^6-$C2/c$ of the monoclinic system with four formula units in a cell of dimensions a = 22.187 (2) Å, b = 8.340 (1) Å, c = 15.979 (2) Å, and β = 93.108 (6)°. Important distances are Rh–P = 2.297 (1) Å, Rh–H = 1.66 (5) Å, Rh–N = 1.970 (4) Å, and N–N = 1.074 (7) Å. The structural data were refined by full-matrix least-squares methods to a conventional R index of 0.034 based on those 2760 reflections having $F_o^2 > 3\sigma(F_o^2)$.

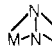
Introduction

Dinitrogen complexes of transition metals have held considerable interest since their discovery in 1965.[2] Several of these compounds, most notably those containing Mo or W, have been found to be intriguing starting materials for the conversion of molecular nitrogen to ammonia.[3-8] However, at this time somewhat rigorous conditions must be maintained for the laboratory reduction. Additionally, the nature of the involvement of transition metals in the nitrogen fixation process, i.e., oxidation state, mode of N_2 coordination, etc., still remains unclear.

Structurally dinitrogen has been found to bond to transition metals in three ways: terminally "end-on" (**1**), bridging

$M{-}N{\equiv}N$ **1**

$M{-}N{\equiv}N{-}M$ **2**



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"end-on" (**2**), and bridging "side-on" (**3**).[9,10] The N–N distance in the first two types (1.10–1.12 Å) is only slightly longer than that of free dinitrogen (1.0976 Å) with the exceptions of $ReCl[P(CH_3)_2(C_6H_5)]_4$–$N_2$–$MoCl_4(OCH_3)$[11] and $MoCl_4\{N_2ReCl[P(CH_3)_2(C_6H_5)]_4\}_2$[12] in which the N–N distances (1.21 and 1.28 (5) Å, respectively) approximate that of a double bond. Unlike the isoelectronic CO which is a more strongly coordinating ligand,[13] no bridging by way of one nitrogen in the N_2 fragment has yet been observed.

In the majority of the complexes made thus far, the N_2 fragment remains essentially chemically inert.[13-20] However, in many cases the dinitrogen is labile,[16,21-23] opening up the possibility of utilizing these complexes as precursors to coordinatively unsaturated species which are of use in the field of homogeneous catalysis.[16] It is this area in which the title compound, the only known stable dinitrogen complex of rhodium(I), has potentially powerful applications.

Experimental Section

The title compound was prepared from the reduction of $RhCl_3 \cdot 3H_2O$ (0.24 g, 1 mmol) by 1% sodium amalgam (30 g) in the presence of $P(C_6H_5)(C_4H_9)_2$ using tetrahydrofuran as solvent. The reaction mixture was stirred under an N_2 atmosphere for 15 h at ambient temperature. After filtration the brown solution was concentrated to yield a brown crystalline solid. Recrystallization from hot *n*-hexane gave the final product as yellow air-sensitive prisms (0.23 g, 40%), mp 83–86°. Anal. Calcd for $C_{28}H_{47}N_2P_2Rh$: C, 58.60; H, 8.05; N, 4.86. Found: C, 58.25; H, 8.04; N, 4.68. ν(NN) 2155 cm^{-1}, ν(RhH) 1977 cm^{-1}.

Crystallographic Data. Since the compound is air sensitive even in the solid phase, crystals were mounted in glass capillaries in a drybox under an atmosphere of N_2. Preliminary film data showed the crystals to belong to the monoclinic system with extinctions hkl ($h + k$ odd), $h0l$, (h odd, l odd), and $0k0$ (k odd) indicative of the space groups C_s^4-Cc (noncentrosymmetric) and C_{2h}^6-$C2/c$ (centrosymmetric). The centrosymmetric space group was chosen initially and proved to be correct on the basis of the following results: (1) the successful refinement of the structure with reasonable positional and thermal parameters, (2) the clear location on a difference Fourier synthesis of all 23 organic hydrogen atoms in the asymmetric unit, and (3) the equivalence in intensities of 197 related pairs of reflections that would be nonequivalent in Cc owing to the effects of anomalous dispersion. The cell dimensions (see Table I) were obtained through a least-squares refinement of the setting angles of 15 hand-centered reflections in the range $46.3 \le 2\theta(\text{Cu } K\alpha_1) \le 53.8°$.

Data collection was achieved using a Picker four-circle diffractometer equipped with a scintillation counter and pulse height analyzer tuned to accept 90% of the Cu Kα peak. Background counts were measured at the beginning and end of each scan with the counter and crystal held stationary. Attenuators were automatically inserted if the intensity of the diffracted beam exceeded approximately 7000 counts/s. Six standard reflections were measured every 100 reflections out to $2\theta = 124°$. Beyond this point three standards were measured every 100 reflections. The stability of the intensities of the standards indicated no crystal decomposition throughout the data collection.

The intensities of 716 reflections (all reflections for $\pm h,\pm k,\pm l$ obeying the condition $h + k$ even) were measured out to $2\theta = 43°$ using Cu Kα radiation. All subsequent data (3276 reflections) were restricted to $\pm h,+k,-l$. A value of p[24] of 0.04 was used in the calculation of $\sigma(F_o^2)$. Only those 2760 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in succeeding calculations. After correction of the data for absorption[25] the R index for averaging the intensities of 197 symmetry-related reflections nonequivalent in Cc was 1.6%.

Structure Refinement. The rhodium and phosphorus atoms were located readily from a sharpened, origin-removed Patterson synthesis. Full-matrix least-squares refinements and difference Fourier syntheses assuming the centrosymmetric space group $C2/c$ were used to locate all remaining atoms with the exception of the hydrido ligand. The phenyl group was treated throughout the refinement as a planar rigid body with uniform C–C distances of 1.392 Å and individual isotropic thermal parameters for each carbon atom. Even though all organic hydrogen atoms were located on a difference Fourier synthesis, their positions were idealized, and they were included as fixed contributions in the final anisotropic refinements; the C–H distance was assumed to be 0.95 Å with normal C–C–H bond angles. The isotropic thermal parameter of a hydrogen atom was assumed to be 1.0 $Å^2$ larger than that of the carbon atom to which it is attached. After application of an extinction correction, the hydrido ligand was located at 75% of its calculated electron density (0.51 e/$Å^3$) and was refined isotropically. The final agreement indices are $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.034$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.050$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and w is taken as $4F_o^2/\sigma^2(F_o^2)$. The quantity minimized during refinements was $\sum w(|F_o| - |F_c|)^2$. Atomic scattering factors were taken from Cromer and Waber's tabulation.[26] Anomalous dispersion terms for Rh and P were included in F_c.[27]

Table I. Summary of Crystal Data and Intensity Collection

Compd	$RhH(N_2)[P(C_6H_5)(C_4H_9)_2]_2$
Formula	$C_{28}H_{47}N_2P_2Rh$
Formula wt	576.55
a	22.187 (2) Å
b	8.340 (1) Å
c	15.979 (2) Å
β	93.108 (6)°
V	2952.5 $Å^3$
Z	4
Density	1.296 g/cm^3 (calcd)
Space group	C_{2h}^6-$C2/c$ (monoclinic)
Crystal dimensions	0.43 × 0.25 × 0.17 mm
Crystal shape	Wedge-shaped prism with well-formed {100}, $(00\bar{1})$, and {111} faces
Crystal vol	0.011 mm^3
Temp	23 °C
Radiation	Cu Kα_1 (λ 1.540 56 Å) prefiltered with 1 mil of Ni foil
μ(Cu Kα)	59.34 cm^{-1}
Transmission factors	0.248–0.474
Receiving aperture	2.3 mm wide × 2.3 mm high; 30 cm from crystal
Takeoff angle	3.0°
Scan speed	2.0° in 2θ/min
Scan range	0.9° below Kα_1 to 1.0° above Kα_2
Background counts	10 s
2θ limits	2.0–160.0°
Final no. of variables	112
Unique data used, $F_o^2 > 3\sigma(F_o^2)$	2760
Error in observation of unit wt	2.01 electrons

A final difference Fourier synthesis of residual electron density revealed as the highest features ripples near the phenyl carbon atoms (0.5–0.1 e/$Å^3$). The average carbon electron density was 3.4 e/$Å^3$. All but three unobserved reflections obey the relationship $|F_o^2 - F_c^2| < 3\sigma(F_o^2)$.

The final positional and thermal parameters of all atoms and groups appear in Tables II–IV. Root-mean-square amplitudes of vibration are listed in Table V. The observed and calculated structure amplitudes for the data used are available as supplementary material.

Results and Discussion

The complex $RhH(N_2)[P(C_6H_5)(C_4H_9)_2]_2$ (I) is obtained in a fairly straightforward manner by the sodium amalgam reduction of $RhCl_3 \cdot 3H_2O$ in the presence of the phosphine. The reaction is carried out at room temperature in THF under a dinitrogen atmosphere. Infrared measurements show stretching frequencies assignable to ν(RhH) 1977 cm^{-1} and ν(NN) 2155 cm^{-1}. It is interesting that using $P(C_6H_{11})_3$ in the above scheme generates only the N_2-bridged dimer $\{RhH[P(C_6H_{11})_3]_2\}_2N_2$. The $P(C_6H_{11})_3$ analogue of I can be prepared thus far only from the reaction of N_2 with $RhH_3[P(C_6H_{11})_3]_2$, but the dinitrogen is easily lost in solution even under an N_2 atmosphere. This is somewhat surprising since the $P(C_6H_{11})_3$ analogue of I has ν(NN) 2130 cm^{-1}, implying slightly stronger coordination of the N_2 to the central metal.

The crystal structure of I consists of the packing of four discrete molecules per unit cell (Figure 1). A perspective view of the molecule, perpendicular to the coordination plane, together with the labeling scheme is shown in Figure 2. There are no significant intermolecular interactions in the unit cell, the shortest nonbonded contact being 2.43 Å between H2C(3) and H3C(8). The coordination geometry about the Rh atom is a distorted square plane with the phosphine ligands bent

Table II. Positional and Thermal Parameters for the Nongroup Atoms of $RhH(N_2)[P(C_6H_5)(C_4H_9)_2]_2$

ATOM	X^A	Y	Z	B11^B OR B,A^2	B22	B33	B12	B13	B23
RH	0	0.07293(3)	1/4	11.71(7)	97.4(5)	39.91(18)	0	-5.67(6)	0
P	0.097113(26)	0.04441(8)	0.30548(4)	10.73(12)	92.3(8)	30.4(3)	-1.06(22)	-1.91(14)	2.5(3)
N(1)	0	0.3091(5)	1/4	20.5(9)	117.(6)	111.(4)	0	-25.0(15)	0
N(2)	0	0.4378(6)	1/4	39.2(20)	108.(8)	250.(11)	0	-51.(4)	0
C(1)	0.15145(14)	0.0685(4)	0.21897(21)	16.3(6)	166.(5)	33.5(13)	-2.3(12)	2.6(7)	9.8(19)
C(2)	0.14944(17)	0.2445(5)	0.19222(25)	22.7(8)	196.(6)	51.6(18)	-7.3(17)	3.4(9)	40.7(27)
C(3)	0.12542(21)	-0.0316(6)	0.14437(25)	30.7(10)	261.(8)	32.3(16)	-10.5(24)	2.9(10)	-9.8(29)
C(4)	0.21725(15)	0.0184(5)	0.23706(25)	16.5(6)	219.(6)	50.9(18)	5.2(17)	8.4(9)	1.9(28)
C(5)	0.11439(12)	-0.1470(3)	0.36602(19)	14.5(5)	97.(3)	36.2(12)	0.5(10)	-1.8(6)	8.6(16)
C(6)	0.06335(15)	-0.1657(4)	0.42661(23)	20.6(7)	158.(5)	46.4(16)	-6.5(15)	2.9(8)	28.4(23)
C(7)	0.11302(16)	-0.2923(4)	0.30754(24)	24.6(8)	104.(4)	52.7(17)	1.4(14)	-6.6(9)	-3.9(20)
C(8)	0.17439(14)	-0.1443(4)	0.41860(22)	17.3(6)	141.(5)	44.4(15)	4.7(13)	-5.9(8)	12.8(21)
H	0	-0.126(7)	1/4	6.6(13)					

^{A}ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. ^{B}THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: EXP[-(B11H^2+B22K^2+B33L^2+2B12HK+2B13HL+2B23KL)]. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X 10^4.

Table III. Derived Parameters for the Rigid-Group Atoms of $RhH(N_2)[P(C_6H_5)(C_4H_9)_2]_2$

ATOM	X	Y	Z	B,A^2	ATOM	X	Y	Z	B,A^2
C(11)	0.11681(8)	0.19854(22)	0.38681(11)	3.04(4)	C(14)	0.13688(10)	0.41744(26)	0.51688(13)	4.89(7)
C(12)	0.06912(6)	0.24767(26)	0.43377(13)	3.79(5)	C(15)	0.18456(7)	0.36831(27)	0.46992(14)	4.57(6)
C(13)	0.07916(9)	0.35712(27)	0.49880(13)	4.80(7)	C(16)	0.17453(7)	0.25886(25)	0.40488(13)	3.81(5)

RIGID GROUP PARAMETERS

GROUP	X$_C$^{A}	Y$_C$	Z$_C$	DELTA^B	EPSILON	ETA
PH	0.12684(6)	0.30799(17)	0.45184(9)	-1.5309(13)	2.8949(12)	2.2769(14)

^{A}X$_C$, Y$_C$, AND Z$_C$ ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. ^{B}THE RIGID GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETA(RADIANS) HAVE BEEN DEFINED PREVIOUSLY: S.J. LA PLACA AND J.A. IBERS, ACTA CRYSTALLOGR., 18, 511(1965).

Table IV. Idealized Positional Coordinates for Hydrogen Atoms

Atom	x	y	z	Atom	x	y	z
H1C(2)	0.165	0.310	0.238	H1C(7)	0.078	−0.289	0.271
H2C(2)	0.173	0.261	0.145	H2C(7)	0.148	−0.292	0.275
H3C(2)	0.109	0.276	0.179	H3C(7)	0.113	−0.389	0.340
H1C(3)	0.085	0.002	0.129	H1C(8)	0.180	−0.241	0.449
H2C(3)	0.150	−0.022	0.098	H2C(8)	0.207	−0.131	0.383
H3C(3)	0.124	−0.143	0.160	H3C(8)	0.175	−0.057	0.457
H1C(4)	0.219	−0.092	0.252	HC(12)	0.030	0.206	0.422
H2C(4)	0.240	0.034	0.188	HC(13)	0.046	0.391	0.531
H3C(4)	0.235	0.081	0.282	HC(14)	0.143	0.492	0.561
H1C(6)	0.065	−0.082	0.467	HC(15)	0.224	0.410	0.483
H2C(6)	0.025	−0.160	0.396	HC(16)	0.207	0.225	0.373
H3C(6)	0.066	−0.266	0.455				

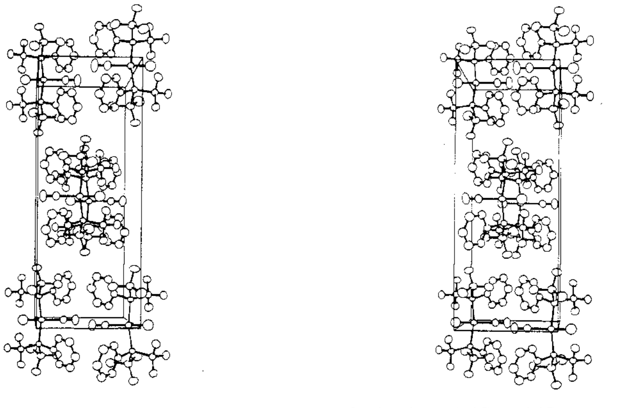

Figure 1. Stereoview of a unit cell of $RhH(N_2)[P(C_6H_5)(C_4H_9)_2]_2$. The vibrational ellipsoids are drawn at the 50% probability level, and the organic hydrogen atoms have been omitted. The x axis is vertical (positive direction to the bottom of the figure), the y axis is horizontal to the right, and the z axis is normal to the paper coming toward the reader.

Table V. Root-Mean-Square Amplitudes of Vibration (Å) for $RhH(N_2)[P(C_6H_5)(C_4H_9)_2]_2$

Atom	Min	Intermed	Max
Rh	0.1558 (5)	0.1852 (5)	0.2401 (5)
P	0.158 (1)	0.179 (1)	0.204 (1)
N(1)	0.178 (5)	0.203 (6)	0.409 (7)
N(2)	0.195 (7)	0.251 (7)	0.606 (13)
C(1)	0.193 (4)	0.209 (4)	0.247 (4)
C(2)	0.193 (4)	0.242 (4)	0.309 (5)
C(3)	0.202 (5)	0.268 (5)	0.312 (5)
C(4)	0.187 (4)	0.263 (5)	0.280 (4)
C(5)	0.175 (3)	0.189 (3)	0.226 (4)
C(6)	0.189 (4)	0.231 (4)	0.278 (4)
C(7)	0.191 (4)	0.223 (4)	0.285 (4)
C(8)	0.179 (4)	0.227 (4)	0.260 (4)

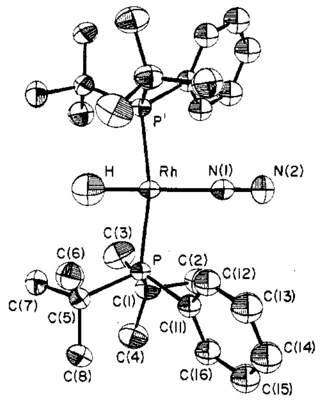

Figure 2. Perspective view of $RhH(N_2)[P(C_6H_5)(C_4H_9)_2]_2$ showing the labeling scheme. Organic hydrogen atoms have been omitted. The vibrational ellipsoids are drawn at the 50% probability level.

Table VI. Selected Distances (Å) and Angles (deg) in $RhH(N_2)[P(C_6H_5)(C_4H_9)_2]_2$

	Bond Distances		
Rh–P	2.297 (1)	C(1)–C(2)	1.528 (4)
Rh–H	1.66 (5)	C(1)–C(3)	1.542 (5)
Rh–N(1)	1.970 (4)	C(1)–C(4)	1.531 (5)
N(1)–N(2)	1.074 (7)	C(5)–C(6)	1.537 (4)
P–C(1)	1.894 (3)	C(5)–C(7)	1.528 (4)
P–C(5)	1.895 (3)	C(5)–C(8)	1.535 (4)
P–C(11)	1.863 (2)	Av C–C	1.534 (6)
	Nonbonded Distances		
Rh–H1C(3)	2.85	H–H1C(7)	2.21
Rh–HC(12)	3.00	H3C(3)–H2C(7)	2.25
P–H	2.69	H1C(4)–H2C(8)	2.14
N(1)–H3C(2)	2.75	H3C(4)–HC(16)	2.02
N(1)–HC(12)	2.92		
	Bond Angles		
P–Rh–N(1)	95.94 (2)	P–C(1)–C(3)	106.29 (24)
P–Rh–H	84.06 (2)	P–C(1)–C(4)	118.13 (25)
P–Rh–P′	168.12 (3)	P–C(5)–C(6)	105.75 (20)
Rh–P–C(1)	109.16 (10)	P–C(5)–C(7)	110.97 (21)
Rh–P–C(5)	116.34 (8)	P–C(5)–C(8)	114.35 (20)
Rh–P–C(11)	112.17 (6)	C(2)–C(1)–C(3)	107.45 (30)
C(1)–P–C(5)	110.05 (13)	C(2)–C(1)–C(4)	109.14 (29)
C(1)–P–C(11)	107.55 (12)	C(3)–C(1)–C(4)	108.15 (31)
C(5)–P–C(11)	101.07 (11)	C(6)–C(5)–C(7)	108.31 (25)
P–C(11)–C(12)	115.02 (14)	C(6)–C(5)–C(8)	107.66 (26)
P–C(11)–C(16)	124.93 (15)	C(7)–C(5)–C(8)	109.52 (24)
P–C(1)–C(2)	107.21 (23)	Av C–C–C	108.37 (81)
	Torsion Angles		
C(11)–P–P′–C(11)′	78.72 (14)	C(11)–P–P′–C(5)′	−166.16 (12)
C(11)–P–P′–C(1)′	−44.16 (12)		

toward the hydrido ligand. There are no close interactions between Rh and H atoms from the phosphine groups; the Rh atom is strictly four-coordinate. The large cone angle of the phosphine precludes formation of the tris(phosphine) species, and to our knowledge I is the only example of a four-coordinate hydrido complex of rhodium(I).

The P–Rh–P′ angle of 168.12 (3)° (see Table VI) displays the reduced steric requirements of the hydride. This distortion has also been observed in $PtHCl[P(C_2H_5)(C_6H_5)_2]_2$,[30] $PtHBr[P(C_2H_5)_3]_2$,[31] and $MHCl[P(C_3H_7)_3]_2$ (M = Ni, Pd).[32] The H–Rh–N(1)–N(2) fragment lies on the crystallographically imposed twofold axis and therefore is strictly linear in the absence of disorder. The Rh–H distance of 1.66 (5) Å falls well within the range of 1.5–1.7 Å typically found for second-row transition metal hydrides.[32] Although the Rh–P distance (2.297 (1) Å) is somewhat short in comparison with other Rh(I) compounds where the phosphines are mutually trans (2.31–2.33 Å), the phosphine is more basic than in the other known structures.

The P–C(alkyl) distance of 1.894 (3) Å is, as expected, longer than the P–C(aryl) distance of 1.863 (2) Å. The phenyl ring is somewhat displaced toward the metal atom as evidenced by the P–C(11)–C(16) and P–C(11)–C(12) angles (124.9 (2) and 115.0 (1)°). This bending has been observed previously in $M[P(C_6H_5)(C_4H_9)_2]_2$ (M = Pd, Pt)[29,33] where the distortion was ascribed to metal–ortho hydrogen interaction. In the present case, it appears that the phenyl bending arises from steric interaction between H3C(4) and HC(16), whose nonbonded distance is 2.02 Å resulting in the "pushing" of the phenyl group toward the Rh atom. The closest Rh···H nonbonding interaction is 2.85 Å (Rh–H1C(3)), which is long in comparison with the close contact of 2.59 Å observed in $RuCl_2[P(C_6H_5)_3]_3$.[34] The P–C–C bond angles within the *tert*-butyl group show the wide variations that have been similarly observed elsewhere.[29] The C(11)–P–P′–C(11)′ torsion angle of 78.72 (14)° reflects only a small deviation from a totally staggered conformation of the phosphine substituents.

The compression of the Rh–N bond (1.970 (4) Å) in comparison with apparent single-bond values[35–37] is indicative of some π back-bonding from the metal to the appropriate antibonding orbitals of the N_2. This distance could perhaps be even shorter if it were not for the fact that the N_2 is located opposite to a strong trans director, the hydride. Similarly, if the Rh–N_2 linkage is disordered to deviate significantly from linearity, the lack of maximum orbital overlap would also contribute to a weaker Rh–N bond. For comparison, the Rh–C bond distances in some four-coordinate square-planar carbonyl complexes of Rh(I) are in the range 1.72–1.83 Å.[37–41] In the trigonal-bipyramidal complex $RhH(CO)[P(C_6H_5)_3]_3$, the average Rh–C distance is 1.829 (28) Å.[42]

The N(1)–N(2) distance (1.074 (7) Å) is shorter than that in molecular nitrogen (1.0976 Å); this is unreasonable on chemical and spectroscopic grounds (see Table VII). There is large anisotropic thermal motion of both nitrogen atoms (see Table V and Figures 2 and 3). If one assumes that atom N(2) rides on atom N(1), then the N(1)–N(2) distance, adjusted for such a librational effect, is 1.18 Å. This is clearly an overadjustment. It is possible that the thermal ellipsoids are a manifestation of slight disorder of one or both N atoms off the twofold axis, a situation that was described earlier for the NO group in $IrCl_2(NO)[P(C_6H_5)_3]_2$.[43] As discussed there,

Table VII. Structural Data for Some Dinitrogen Compounds[a]

Compd	M–N, Å	N–N, Å	M–N–N, deg	ν(NN), cm⁻¹
N_2		1.0976		2330
$RhH(N_2)[P(C_6H_5)(C_4H_9)_2]_2$[b]	1.970 (4)	1.074 (7)	Linear	2155
$[Rh(NH_3)_5(N_2)]Cl_2$[c]	2.10 (1)	1.12 (8)	Linear	2105[d]
$[Ru(N_3)(N_2)(en)_2]PF_6$[e]	1.894 (9)	1.11 (1)	179.3 (9)	2103
$[(H_3N)_5RuN_2Ru(NH_3)_5](BF_4)_4$[f]	1.928 (6)	1.12 (2)	178.3 (5)	2100
$CoH(N_2)[P(C_6H_5)_3]_3$[g]	1.83 (1), 1.78 (1)	1.12 (1) 1.10 (1)	178 (2), 178 (1)	2088[h]
$\{Ni[P(C_6H_{11})_3]_2\}_2N_2$[i]	1.77, 1.79	1.12	178.2, 178.3	(2028, monomer)
$[Os(NH_3)_5(N_2)]Cl_2$[j]	1.84 (1)	1.12 (2)	178.3 (13)	2025, 2010
$Mo(N_2)_2[(C_6H_5)_2PC_2H_4P(C_6H_5)_2]_2$[k]	2.01 (1)	1.10 (2)	171.8 (11)	2020, 1970[l]
$ReCl(N_2)[P(C_6H_5)(CH_3)_2]_4$[m]	1.97 (2)	1.06 (3)	177 (1)	1922
$MoCl_4\{N_2ReCl[P(C_6H_5)(CH_3)_2]_4\}_2$[n]	1.75 (4) (Re) 1.99 (4) (Mo)	1.28 (5)	Linear	1800
$[(CH_3)_2(C_6H_5)P]_4ClReN_2MoCl_4(OCH_3)$[o]	1.79 (Re) 1.89 (Mo)	1.21	Linear	1660

[a] Absence of standard deviations occurs only where these values are omitted in the original reference. Abbreviation: en, $H_2NCH_2CH_2NH_2$. [b] This work. [c] F. Bottomley and S. C. Nyburg, *Chem. Commun.*, 897 (1966); F. Bottomley and S. C. Nyburg, *Acta Crystallogr., Sect. B*, 24, 1289 (1968). [d] A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Am. Chem. Soc.*, 89, 5595 (1967). [e] B. R. Davis and J. A. Ibers, *Inorg. Chem.*, 9, 2768 (1970). [f] I. M. Treitel, M. T. Flood, R. E. Marsh, and H. B. Gray, *J. Am. Chem. Soc.*, 91, 6512 (1969). [g] B. R. Davis, N. C. Payne, and J. A. Ibers, *ibid.*, **91**, 1240 (1969); B. R. Davis, N. C. Payne, and J. A. Ibers, *Inorg. Chem.*, 8, 2719 (1969). [h] Reference 16. [i] P. W. Jolly, K. Jonas, C. Krüger, and Y.-H. Tsay, *J. Organomet. Chem.*, **33**, 109 (1971). [j] J. E. Fergusson, J. L. Love, and W. T. Robinson, *Inorg. Chem.*, **11**, 1662 (1972). [k] T. Uchida, Y. Uchida, M. Hidai, and T. Kodama, *Bull. Chem. Soc. Jpn.*, **44**, 2883 (1971). [l] Reference 19. [m] B. R. Davis and J. A. Ibers, *Inorg. Chem.*, **10**, 578 (1971). [n] Reference 12. [o] Reference 11.

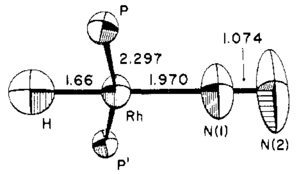

Figure 3. View of the coordination sphere of $RhH(N_2)[P(C_6H_5)(C_4H_9)_2]_2$ with bond distances. The vibrational ellipsoids are drawn at the 50% probability level. Note the large motion of the N_2 fragment.

it is not possible on the basis of the x-ray diffraction experiment alone to separate the ordered model from a manifold of disordered models. But since typical N–N distances are found in the range 1.10–1.12 Å (Table VII) and do not correlate with variations in ν(NN), it is clear that spectroscopic measurements are far more sensitive than are diffraction measurements to small variations in the N–N bond strength (and perhaps bond length).

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Supplementary Material Available: Listing of structure amplitudes (20 pages). Ordering information is given on any current masthead page.

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