The Structure of *trans*-Chloro(dinitrogen)bis(tri-isopropylphosphine)-rhodium(I): An *X*-Ray Study of the Structure in the Solid State and a Nuclear Magnetic Resonance Study of the Structure in Solution

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The crystal structure of [RhCl(N_2)(PPr$^i_3$)$_2$] has been redetermined at −160 °C. In contrast to the results of a previous structure determination, we conclude that a scattering model in which the N_2 ligand is end-on (η^1) co-ordinated is fully consistent with the data. Such end-on co-ordination is confirmed in solution at +30 °C from the ^{31}P and ^{15}N n.m.r. spectra of a $^{15}N_2$ labelled sample. The material crystallizes in the space group $P2_1/c(C^5_{2h})$ of the monoclinic system in a cell of dimensions a = 8.062(2), b = 8.883(2), c = 16.431(4) Å, β = 92.45(1)°, Z = 2; the final R and R' are 0.024 and 0.031, respectively, based on the full-matrix refinement of 124 variables and 3 597 observations. The ^{31}P n.m.r. spectrum of the $^{15}N_2$-labelled complex shows a doublet of doublets, J_{P-Rh} 122.3 and $J_{P-^{15}N}$ 4.25 Hz, and proves the N_2 co-ordination to be η^1 in solution. The ^{15}N n.m.r. spectrum of the labelled complex is also consistent with η^1-co-ordination: $J_{^{15}N(1)-Rh}$ 28, $J_{^{15}N(1)-^{15}N(2)}$ 4, $J_{^{15}N(1)-P}$ 4, $J_{^{15}N(2)-Rh}$ 4 Hz; $\delta_{N(1)}$ 269 and $\delta_{N(2)}$ 302 p.p.m. (downfield from external $^{15}NH_4^+$).

IN a recent publication [1] the crystal structure of the title compound [RhCl(N_2)(PPr$^i_3$)$_2$] (Pr^i = isopropyl) was reported, in which the dinitrogen ligand was claimed to be co-ordinated to the rhodium atom in a ' side-on ' (η^2) fashion. As was noted by the authors,[1] such co-ordination is unprecedented for non-bridging dinitrogen, and is in fact inconsistent with the observed N≡N i.r. stretching frequency of 2 100 cm^{-1}, typical of ' end-on ' bonded (η^1) dinitrogen. In view of the overwhelming structural evidence accumulated to date that both non-bridging [2-9] and bridging [9-16] dinitrogen molecules show a strong preference to adopt η^1-co-ordination to transition metals,[17] we suspected the proposal of η^2-co-ordination to be incorrect. On the basis of an analysis of *X*-ray diffraction data obtained at −160 °C, and of n.m.r. data obtained on the $^{15}N_2$-labelled species, we conclude that both in the solid state and in solution the N_2 ligand in [RhCl(N_2)(PPr$^i_3$)$_2$] is co-ordinated in an end-on (η^1) fashion.

EXPERIMENTAL

Single crystals of [RhCl(N_2)(PPr$^i_3$)$_2$] were prepared from [{RhCl(C_8H_{14})$_2$}$_2$] and PPr$^i_3$ in benzene under N_2, as in the earlier work.[1] The $^{15}N_2$-labelled complex was prepared using 99% $^{15}N_2$ obtained from Stohler Isotope Chemicals. Infrared spectra, recorded on a Perkin-Elmer 283 spectrometer, have strong, sharp N≡N stretching frequencies at 2 100 ($^{14}N_2$), 2 065 ($^{14}N^{15}N$), and 2 035 ($^{15}N_2$) cm^{-1}; the 2 065 band is unsplit at a resolution of 2 cm^{-1} (Nujol mull and hexane solution).[18] Proton-decoupled ^{31}P n.m.r. spectra were recorded on a Varian CFT-20 spectrometer at 32.199 MHz, locked on the aromatic deuterium signal of [$^2H_8$]toluene used as the solvent. The ^{15}N n.m.r. spectrum was recorded at room temperature on a Varian FT-80A spectrometer operating with a synthesizer frequency of 5.808 MHz.

Collection and Reduction of X-*Ray Data*.—Although crystals of [RhCl(N_2)(PPr$^i_3$)$_2$] appear to be stable in air for at least an hour, they were handled in an inert atmosphere (Ar or N_2) throughout this study. Preliminary photographs at room temperature showed the crystals to be monoclinic and confirmed the unit cell and space group obtained previously.[1] Systematic absences ($0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$) are consistent with the space group $P2_1/c$ (C^5_{2h}) and two [RhCl(N_2)(PPr$^i_3$)$_2$] molecules are present in the unit cell. As noted previously,[1] a crystallographic inversion centre is thus imposed on the individual molecules with resultant disorder of the Cl and N_2 ligands. Neither photographs nor a diffractometer search revealed any evidence of doubling along the a axis. For data collection a second crystal, a hexagonal prism measuring 0.14 × 0.35 (av.) × 0.90 mm, was mounted on a Picker diffractometer. The crystal was bathed in a cold stream of dry N_2 gas (T *ca.* −160 °C).[19] At this temperature the cell constants were obtained from 16 hand-centred reflections [20] for 2θ in the range 30—35°. A total of 4 684 reflections was measured in the range $3.5 \leqslant 2\theta \leqslant 64.5°$ using Mo-K_α radiation. Of these, 3 597 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. Six strong reflections were chosen as standards and were remeasured every 100 reflections throughout the data collection; they showed no significant intensity fluctuations.

Crystal Data.—$C_{18}H_{42}ClN_2P_2Rh$, $M = 486.85$, $T = -160$ °C, $a = 8.062(2)$, $b = 8.883(2)$, $c = 16.431(4)$ Å, $\beta = 92.45(1)°$, $U = 1176$ Å^3, $D_c = 1.375$ g cm^{-3}, $Z = 2$, $D_m = 1.33(1)$ g cm^{-3} (20 °C), space group $P2_2/c$ ($C^5_{2}h$). Crystal dimensions 0.14 × 0.35 × 0.90 mm, crystal shape, distorted hexagonal prism with pseudo-C_6 axis [100]; remaining faces of forms {001}, {011}, and {01$\bar{1}$}, crystal volume 0.046 mm^3. Mo-K_α radiation [$\lambda(K_{\alpha1}) = 0.709\,3$ Å] from a graphite monochromator, linear absorption coefficient 9.67 cm^{-1}, transmission factors 0.704—0.880; take-off angle 2.5°, receiving aperture 5 × 6.5 mm, 30 cm from crystal, scan speed 2° min^{-1}, scan range 0.9° below $K_{\alpha1}$ peak to 0.9° above $K_{\alpha2}$, background counts of 10 s with re-scan option, 2θ limits 3.5—64.5°, final number of variables, 124.

Solution and Refinement.—For refinement, each reflection was given a weight $w = 4F_o^2/\sigma^2(F_o^2)$, where the standard deviation $\sigma(F_o^2)$ was estimated from counting statistics and a value of p of 0.03.[20] The data were corrected for absorption effects.[21] Scattering factors for non-hydrogen atoms were from the tabulation of Cromer and Waber,[22] and the values of Stewart *et al.*[23] were used for hydrogen atoms. Anomalous dispersion terms [24] were included in F_c for Rh, Cl, and P. The function minimized during refinement was $Q = \Sigma w(|F_o| - |F_c|)^2$; R' is defined as $(Q/\Sigma wF_o^2)^{\frac{1}{2}}$ and R is defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$.

The published positional parameters were used initially.[1]

Two cycles of isotropic refinement with the Cl and N atoms omitted gave an R of 0.184. A subsequent difference-Fourier map revealed a large, essentially featureless ellipsoidal region of high electron density at the site of the disordered Cl/N$_2$ ligand.

Initially, we placed the Cl and N atoms in the positions reported previously.[1] Refinement of this isotropic model was not successful. In successive cycles the thermal parameter of one of the N atoms increased to 7.2 Å^2 while that of the other decreased to 0.7 Å^2 and the N–N separation approached 0.75 Å. Difference-Fourier maps displayed large peaks (*ca.* 3.5 e Å^{-3}) at the expected sites of the N atoms of an end-on bonded dinitrogen ligand. Consequently we abandoned the refinement of a side-on bonded (η^2) model in favour of an end-on bonded (η^1) model for the dinitrogen ligand. We placed the Cl atom 2.36 Å from the rhodium atom and an end-on bonded N$_2$ ligand *trans* to the Cl atom, with Rh–N 1.97 and N–N 1.08 Å. Two cycles of isotropic least-squares refinement converged to R = 0.068. A difference-Fourier map at this stage revealed the positions of the hydrogen atoms on the isopropyl carbon atoms. These hydrogen atoms were placed in idealized positions (C–H 0.95 Å, tetrahedral angles) and each was given an isotropic parameter 1.0 Å^2 greater than that of the carbon atom to which it is attached. During all subsequent cycles of refinement the hydrogen atoms were kept fixed at these locations. In the final refinement of 124 variables, all non-hydrogen atoms were allowed to vibrate anisotropically. This refinement converged to values of R and R' of 0.024 and 0.031, respectively, and to an error in an observation of unit weight of 1.34 e. Except for some ripples in the immediate vicinity of the rhodium atom, there are no peaks on the final difference-Fourier map of height greater than 0.5 e Å^{-3}. An analysis of $\Sigma w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, setting angles, and Miller indices reveals no unexpected trends. Table 1 lists the final values of the positional and thermal parameters; the structure-factor table is deposited as Supplementary Publication No. SUP 22577 (14 pp.).*

TABLE 1

Positional and thermal parameters for the atoms of [RhCl(N$_2$)(PPr$^i{}_3$)$_2$] with estimated standard deviations in parentheses

Atom	x	y	z	U_{11} *	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	0	0	0	14.007(72)	13.385(68)	12.681(68)	0.981(54)	−1.270(47)	0.796(52)
Cl	−0.022 83(25)	−0.197 20(14)	−0.095 687(86)	53.44(72)	12.50(80)	20.59(79)	7.81(65)	−18.62(59)	−9.75(41)
P	−0.124 633(44)	0.164 096(40)	−0.096 543(22)	11.62(14)	15.35(14)	14.22(15)	0.61(12)	−0.27(11)	1.90(13)
N(1)	0.006 50(71)	0.155 64(51)	0.078 07(31)	36.6(20)	18.9(25)	27.5(26)	5.2(19)	−12.3(18)	7.2(16)
N(2)	0.013 96(84)	0.236 79(58)	0.116 46(33)	52.7(27)	25.9(28)	32.6(30)	0.7(23)	−20.8(23)	2.8(18)
C(1)	−0.266 52(19)	0.068 13(18)	−0.171 495(94)	18.65(66)	23.36(72)	21.48(67)	−3.19(54)	−5.51(53)	1.11(55)
C(2)	−0.403 17(27)	−0.018 76(25)	−0.129 37(14)	32.10(95)	54.9(14)	38.7(11)	−25.39(94)	−4.17(80)	1.04(89)
C(3)	−0.340 37(25)	0.163 56(22)	−0.241 16(11)	34.98(95)	35.02(88)	29.99(85)	0.11(80)	−16.85(74)	2.02(74)
C(4)	0.032 53(18)	0.253 66(16)	−0.159 827(87)	14.60(59)	19.30(60)	17.47(60)	0.36(47)	2.50(47)	2.00(49)
C(5)	0.134 03(22)	0.134 31(20)	−0.202 57(11)	24.71(79)	29.91(84)	32.87(86)	3.90(65)	12.73(66)	−0.59(68)
C(6)	0.147 37(22)	0.355 88(21)	−0.109 02(11)	24.13(79)	35.77(92)	32.23(85)	−13.19(69)	4.13(66)	−3.36(72)
C(7)	−0.231 44(18)	0.325 35(17)	−0.050 137(89)	17.44(62)	20.73(64)	19.57(63)	4.40(54)	3.60(49)	1.05(53)
C(8)	−0.365 59(24)	0.276 53(23)	0.006 94(12)	27.68(85)	38.80(96)	36.58(94)	7.32(72)	16.48(74)	4.04(81)
C(9)	−0.295 26(25)	0.450 63(21)	−0.107 13(11)	37.94(99)	25.97(76)	29.05(85)	15.16(72)	4.91(74)	4.05(67)

* The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. The quantities given are the thermal coefficients in units of Å multiplied by 10^3.

RESULTS AND DISCUSSION

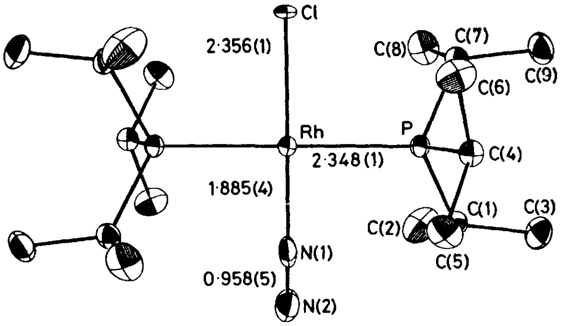

FIGURE 1 A drawing of the molecule with selected bond lengths. Thermal ellipsoids are drawn at the 50% probability level

Crystallographic Results.—In contrast to the earlier proposed side-on co-ordination of the dinitrogen ligand in this complex,[1] our data are totally consistent with end-on co-ordination. The satisfyingly low values of the agreement indices (R = 0.024 and R' = 0.031) suggest that no other scattering model exists for this structure which will yield substantially better agreement with experiment. On the other hand, in disorder problems of this type, there is no way in which a ' unique ' solution can be derived. Undoubtedly more elaborate models can be contrived that will give equally good agreement with experiment and which will lead to some changes in the derived metrical parameters. The need for a more elaborate model is apparent from the results obtained here. Figure 1 shows a view of the molecule, together with some bond distances; Table 2 presents a more extensive tabulation of distances and angles. It is apparent from these data that the N–N separation of 0.958(5) Å is atypical, values of 1.10—1.12 Å being expected for the N–N distance in η^1-co-ordinated dinitrogen.[8] On the other hand, the Rh–Cl, Rh–P, P–C, and C–C distances are all within normal ranges. Figure 2 displays a different view of the molecule and emphasizes certain features of the thermal ellipsoids of

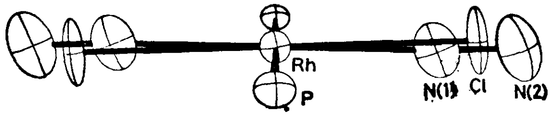

FIGURE 2 A drawing of the inner co-ordination sphere, showing the disorder and the large anisotropy of the Cl and N$_2$ ligands. Thermal ellipsoids are drawn at the 50% probability level. The view is approximately along the P–Rh–P′ axis

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

TABLE 2

Selected bond distances (Å) and angles (°) for $[RhCl(N_2)(PPr^i_3)_2]$

Rh–P	2.348(1)	P–C(1)–C(2)	111.5(1)
Rh–Cl	2.356(1)	P–C(1)–C(3)	117.0(1)
Rh–N(1)	1.885(4)	P–C(4)–C(5)	110.6(1)
Rh–N(2)	2.843(4)	P–C(4)–C(6)	111.3(1)
N(1)–N(2)	0.958(5)	P–C(7)–C(8)	112.8(1)
P–C(1)	1.852(2)	P–C(7)–C(9)	117.4(1)
P–C(4)	1.853(2)	P–C–C (av.)	113(3)
P–C(7)	1.852(2)	C(1)–P–C(4)	104.02(7)
P–C (av.)	1.852(2) [a]	C(1)–P–C(7)	110.17(7)
C(1)–C(2)	1.534(3)	C(4)–P–C(7)	103.89(7)
C(1)–C(3)	1.525(2)	C–P–C (av.)	106(3)
C(4)–C(5)	1.529(2)	C(2)–C(1)–C(3)	110.7(2)
C(4)–C(6)	1.521(2)	C(5)–C(4)–C(6)	109.9(1)
C(7)–C(8)	1.525(2)	C(8)–C(7)–C(9)	110.8(1)
C(7)–C(9)	1.529(2)	C–C–C (av.)	110.4(5)
C–C (av.)	1.527(5)		
P–Rh–Cl	89.53(4) [b]		
P–Rh–N(1)	90.2(2)		
Cl–Rh–N(1)	176.9(2)		
Rh–N(1)–N(2)	177.3(8)		
Rh–P–C(1)	113.43(5)		
Rh–P–C(4)	111.26(5)		
Rh–P–C(7)	113.27(5)		
Rh–P–C (av.)	112.7(12)		

[a] The value in parentheses 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. [b] These angles are based on the atomic positions of Table 1. Angles between symmetry-related atoms can be found by inspection.

atoms Cl, N(1), and N(2). These atoms display rather large thermal vibrations for a molecule at −160 °C. All these unusual features suggest that the simple anisotropic model is insufficient. It is interesting that the Cl atom displays a root-mean-square displacement of 0.26 Å normal to the co-ordination plane (Figure 2). At the extremes of this motion is where the nitrogen atoms were placed in the earlier determination.[1] Clearly the earlier isotropic model for the motion of the chlorine atom was completely inadequate, particularly for room-temperature data.

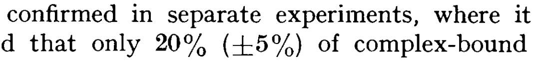
Spectroscopic Studies.—Owing to the slightly equivocal nature of the *X*-ray results on $[RhCl(N_2)(PPr^i_3)_2]$ in the solid state it seemed especially important to establish the nature of the bonding of the dinitrogen ligand in solution. The existence of the end-bonded (η^1) geometry in solution is confirmed by ^{31}P n.m.r. measurements of the ^{15}N-labelled complex. The spectrum of the unlabelled complex, $[RhCl(^{14}N_2)(PPr^i_3)_2]$, in $[^2H_8]$toluene at +30 °C shows the expected doublet [Figure 3(*a*)], J_{P-Rh} 122.5 Hz, centred at 41.8 p.p.m. downfield from 85% aqueous H_3PO_4. The spectrum of the labelled complex, $[RhCl(^{15}N_2)(PPr^i_3)_2]$ (99% ^{15}N), shows a doublet of doublets [Figure 3(b)], J_{P-Rh} 122.3 and $J_{P-^{15}N}$ 4.25 Hz. Had the dinitrogen molecule been co-ordinated in a side-bonded (η^2) fashion, each phosphorus nucleus would have been equally coupled to *two* equivalent ^{15}N nuclei ($I = 1/2$) and the resulting spectrum would have been a doublet of *triplets*. This same pattern would also be expected for a rapid $\eta^1 \rightleftharpoons \eta^2$ equilibrium. In the observed spectrum, however, the doublet of doublets demands that each phosphorus nucleus be coupled significantly to only *one* ^{15}N nucleus, a result consistent with static end-on (η^1) co-ordination. The ^{31}P n.m.r. spectrum does not provide information as to ***which*** nitrogen nucleus is most strongly coupled to the phosphorus nuclei, but this is unimportant for the structural assignment.

It is somewhat surprising that the $^{15}N-^{31}P$ coupling can be observed at +30 °C. We had feared there could be loss of coupling owing to intermolecular $^{15}N_2$ exchange, permitted by an equilibrium dissociation of dinitrogen [equation (1)]. Another possible exchange process is an

$$[RhCl(^{15}N_2)P_2] \rightleftharpoons [RhClP_2] + {}^{15}N_2 \qquad (1)$$

$$P = \text{phosphine}$$

intramolecular $\eta^1 \rightleftharpoons \eta^2$ equilibrium, effectively a rotation of the end-bonded dinitrogen ligand through a side-bonded intermediate [equation (2)].[25] However, neither exchange process occurs sufficiently rapidly, even at +30 °C, to broaden the ^{31}P resonances or to average the $^{15}N-^{31}P$ coupling. Further evidence that intermolecular exchange is slow comes from the ^{31}P n.m.r. spectrum of a mixture of $[RhCl(^{14}N_2)(PPr^i_3)_2]$–$[RhCl(^{15}N_2)(PPr^i_3)_2]$ (*ca.* 1 : 3) under an atmosphere of $^{14}N_2$. The observed pattern is a superposition of the peaks of the separate compounds, without noticeable broadening. Slow exchange of free $^{14}N_2$ for bound $^{15}N_2$ was confirmed in separate experiments, where it was found that only 20% (±5%) of complex-bound $^{15}N_2$ was exchanged for $^{14}N_2$ in toluene solution after 36 h under 1 atm $^{14}N_2$ at room temperature. Exchange of other ligands (*e.g.* CO) for bound N_2 is virtually immediate, both in this [1] and closely related complexes.[26,27]



(2)

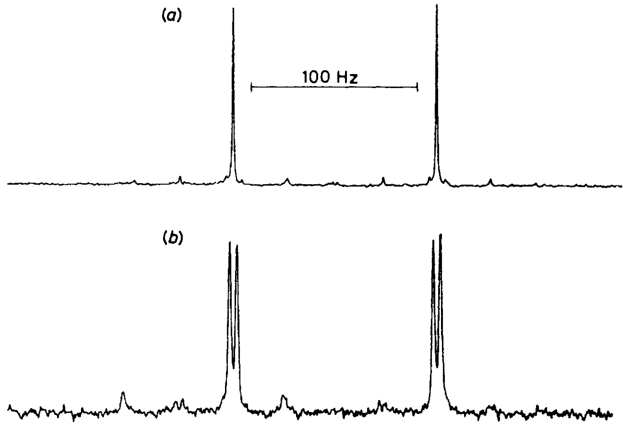


FIGURE 3 ^{31}P n.m.r. spectra of (*a*) $[RhCl(^{14}N_2)(PPr^i_3)_2]$; (*b*) $[RhCl(^{15}N_2)(PPr^i_3)_2]$. Both spectra were measured at +30 °C in $[^2H_8]$toluene, and the centre of the peaks is 41.8 p.p.m. downfield from 85% H_3PO_4

Owing to long relaxation times for the ^{15}N nuclei, a satisfactory ^{15}N n.m.r. spectrum of $[RhCl(^{15}N_2)(PPr^i_3)_2]$ could be obtained only after adding $[Cr(acac)_3]$ (acac =

acetylacetonate) to a toluene solution of the dinitrogen complex. At room temperature the signal from the distal ^{15}N nucleus, N(2) in Figures 1 and 2, is a triplet, 302 p.p.m. downfield from $^{15}NH_4^+$, $J_{^{15}N(1)-^{15}N(2)}$ 4 and $J_{^{15}N(2)-Rh}$ 4 Hz. The signal from the proximal ^{15}N nucleus [N(1)] is a distorted double quartet, 269 p.p.m. downfield from $^{15}NH_4^+$, $J_{^{15}N(1)-Rh}$ 28, $J_{^{15}N(1)-^{15}N(2)}$ 4 and $J_{^{15}N(1)-P}$ 4 Hz.[28] These results are fully consistent with static η^1-coordination and show that the phosphorus nuclei are measurably coupled only with $^{15}N(1)$, the proximal (rhodium-bonded) nitrogen atom.

Conclusions.—The N_2 ligand in $[RhCl(N_2)(PPr^i_3)_2]$ is co-ordinated in an end-on (η^1) fashion in solution, even at +30 °C as indicated by the ^{31}P and ^{15}N n.m.r. spectra of the ^{15}N-labelled complex. Such a co-ordination is consistent with the *X*-ray measurements on a single crystal at −160 °C. Thus there would appear to be no basis for the earlier claim [1] that the N_2 ligand is side-on (η^2) co-ordinated in this complex. To date, then, there are no substantiated examples of such a co-ordination in isolable mononuclear transition metal–dinitrogen complexes.

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