Side-on bonded Dinitrogen and Dioxygen Complexes of Rhodium(I). Synthesis and Crystal Structures of *trans*-Chloro(dinitrogen)-, Chloro-(dioxygen)-, and Chloro(ethylene)-bis(tri-isopropylphosphine)rhodium(I)

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The complexes $[RhCl(N_2)(PPr^i_3)_2]$ (1), $[RhCl(O_2)(PPr^i_3)_2]$ (2), $[RhCl(C_2H_4)(PPr^i_3)_2]$ (3), and $[RhCl(CO)(PPr^i_3)_2]$ (4) have been prepared. The crystal structures of (1)—(3) have been determined by a three-dimensional *X*-ray study from diffractometer data (Mo-K_α radiation). Crystals of the three complexes are monoclinic, space group $P2_1/c$, with the following unit-cell dimensions: (1), a = 8.156(1), b = 8.935(2), c = 16.695(5) Å, β = 93.5(1)°, Z = 2; (2), a = 8.184(3), b = 9.001(4), c = 16.401(7) Å, β = 93.1(1)°, Z = 2; (3), a = 16.316(3), b = 9.164(2), c = 16.544(3) Å, β = 93.8(1)°, Z = 4. The structures have been solved by Patterson and Fourier methods and refined by full-matrix least squares to R 0.048 (1), 0.039 (2), and 0.022 (3) for 1 603, 1 327, and 4 586 independent observations respectively. The three complexes show similar molecular structures: the rhodium atom displays square-planar co-ordination with the two phosphines in *trans* positions and the N_2, O_2, and C_2H_4 ligands bonded side-on to the metal atom. The molecules of (1) and (2) lie on crystallographic centres of symmetry with a consequent disordered disposition of the chlorine atoms and N_2 or O_2 ligands. Short N–N [0.83(2) Å] and O–O [1.03(1) Å], and long Rh–N [2.51(1), 2.55(1) Å] and Rh–O [2.28(1), 2.28(1) Å] bond distances are observed, which are scarcely significant because of the disorder. Infrared spectra are in accord with weak Rh–N_2 and Rh–O_2 interactions, on the basis of the relatively high values of the N–N and O–O stretching frequencies. The ^1H n.m.r. spectrum of C_2H_4 in (3) shows that the ethylene co-ordination is similar to that of other square-planar rhodium complexes. The C–C [1.319(4) Å] and Rh–C [2.116(2), 2.128(2) Å] distances are also close to those observed in other square-planar complexes. The three complexes represent the first case of a homogeneous series containing the three ligands N_2, O_2, and C_2H_4 and the first example of four-co-ordinate complexes containing 'side-on' dinitrogen and dioxygen.

DINITROGEN metal complexes of the 'end-on' and bridging 'end-on' types have been reported;[1] only recently, some binuclear complexes with dinitrogen 'side-on' bonded bridges have been isolated.[2] For the dioxygen ligand, both 'side-on' and 'end-on' complexes have been reported.[3] The former type has only been found in the five-co-ordinate complexes $[IrX(CO)L_2(O_2)]$,[4a-c] $[M(Ph_2PCH_2CH_2PPh_2)_2(O_2)]^+$ (M = Rh or Ir),[4d-g] and $[M(PMe_2Ph)_4(O_2)]^+$ (M = Rh or Ir),[4d,f,g] and in the three-co-ordinate $[Pt(PPh_3)_2(O_2)]$·Solvent.[5]

In an unsuccessful attempt to synthesize trialkylphosphine derivatives $[RhCl(PR_3)_3]$, to our knowledge so far not isolated, we obtained the complex $[RhCl(N_2)(PPr^i_3)_2]$. The derivatives of O_2, C_2H_4, and CO also could be easily isolated and characterized. While this work was in progress, the preparation of complexes $[RhCl(X_2)\{P(C_6H_{11})_3\}_2]$ (X_2 = N_2, O_2, or C_2H_4) was reported.[6] In this paper we report the results of an *X*-ray investigation of the crystal structure of the complexes $[RhCl(N_2)(PPr^i_3)_2]$, $[RhCl(O_2)(PPr^i_3)_2]$, and $[RhCl(C_2H_4)(PPr^i_3)_2]$; the chemical and spectral properties of the complexes are also described.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 225 grating spectrophotometer, ^1H n.m.r. on a Varian HA 100, e.s.r. on a Varian 4502, and visible on a Hitachi spectrophotometer.

Preparation of $[RhCl(N_2)(PPr^i_3)_2]$. (1).—*Method* (*a*). The complex $[\{RhCl(C_8H_{14})_2\}_2]$ (1.0 g) in benzene (100 cm^3) was added to PPr^i_3 (2.0 cm^3) and heated under reflux for 1 h under a N_2 atmosphere. From the cool solution, benzene was distilled under reduced pressure (10 cm^3) and N_2 was readmitted. Yellow crystals were formed on standing overnight, yield 0.75 g (Found: C, 44.4; H, 9.0; Cl, 7.8; N, 5.3. $C_{18}H_{42}ClN_2P_2Rh$ requires C, 44.4; H, 8.7; Cl, 7.3; N, 5.8%).

Method (*b*). The complex $[\{RhCl(C_8H_{14})_2\}_2]$ (0.5 g) in pentane (100 cm^3) was treated with PPr^i_3 (2.0 cm^3). The suspension was stirred at room temperature under argon and a brown solution was obtained after a few minutes. Violet crystals precipitated soon after, and were discarded by filtration after 30 min. Nitrogen was then bubbled through the filtered solution, and the crystals which precipitated overnight were collected by filtration and dried *in vacuo* at room temperature, yield 0.1 g.

The following complexes were prepared by method (*b*): $[RhCl(O_2)(PPr^i_3)_2]$ (2), oxygen bubbled instead of nitrogen, with the immediate formation of a blue precipitate which was filtered off and washed with acetone, yield 0.25 g (Found: C, 44.6; H, 8.9; Cl, 7.6. $C_{18}H_{42}ClO_2P_2Rh$ requires C, 44.0; H, 8.6; Cl, 7.2%); $[RhCl(C_2H_4)(PPr^i_3)_2]$, (3), using an ethylene atmosphere, orange crystals precipitating from the resulting clear yellow solution after a few minutes, yield 0.30 g (Found: C, 49.8; H, 9.6; Cl, 7.4. $C_{20}H_{46}ClP_2Rh$ requires C, 49.3; H, 9.5; Cl, 7.3%).

X-Ray Analysis.—The crystals selected for *X*-ray analysis were sealed in thin-walled glass capillaries under an inert atmosphere; they were prismatic in shape with the dimensions 0.20 × 0.18 × 0.38 (1), 0.15 × 0.10 × 0.45 (2), and

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[1] See, for example, A. D. Allen, R. O. Harris, B. R. Loescher, J. R. Stevens, and R. N. Whiteley, *Chem. Rev.*, 1973, **73**, 11; D. Sellmann, *Angew. Chem. Internat. Edn.*, 1974, **13**, 639.

[2] K. Jonas, D. J. Brauer, C. Krüger, P. J. Roberts, and Y. H. Tsay, *J. Amer. Chem. Soc.*, 1976, **98**, 74 and refs. therein.

[3] See, for example, J. S. Valentine, *Chem. Rev.*, 1973, **73**, 235.

[4] (*a*) J. A. Ibers and S. J. LaPlaca, *J. Amer. Chem. Soc.*, 1965, **87**, 2581; (*b*) J. A. McGinnety, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 2243; (*c*) *Science*, 1967, **155**, 709; (*d*) J. A. McGinnety, N. C. Paune, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1969, **91**, 6301; (*e*) M. J. Nolte, E. Singleton, and M. Laing, *J. Amer. Chem. Soc.*, 1975, **97**, 6396; (*f*) M. J. Nolte and E. Singleton, *Acta Cryst.*, 1976, **B32**, 1410; (*g*) M. Laing, M. J. Nolte, and E. Singleton, *J.C.S. Chem. Comm.*, 1975, 660.

[5] C. D. Cook, P.-T. Cheng, and S. C. Nyburg, *J. Amer. Chem. Soc.*, 1969, **91**, 2123; T. Kashiwagi, N. Yasuoka, N. Kasai, M. Kakudo, S. Takahashi, and N. Hagihara, *Chem. Comm.*, 1969, 743; P.-T. Cheng, C. D. Cook, S. C. Nyburg, and K. Y. Wan, *Canad. J. Chem.*, 1971, **49**, 3772.

[6] H. L. M. van Gaal, F. G. Moers, and J. J. Steggerda, *J. Organometallic Chem.*, 1974, **65**, C43.

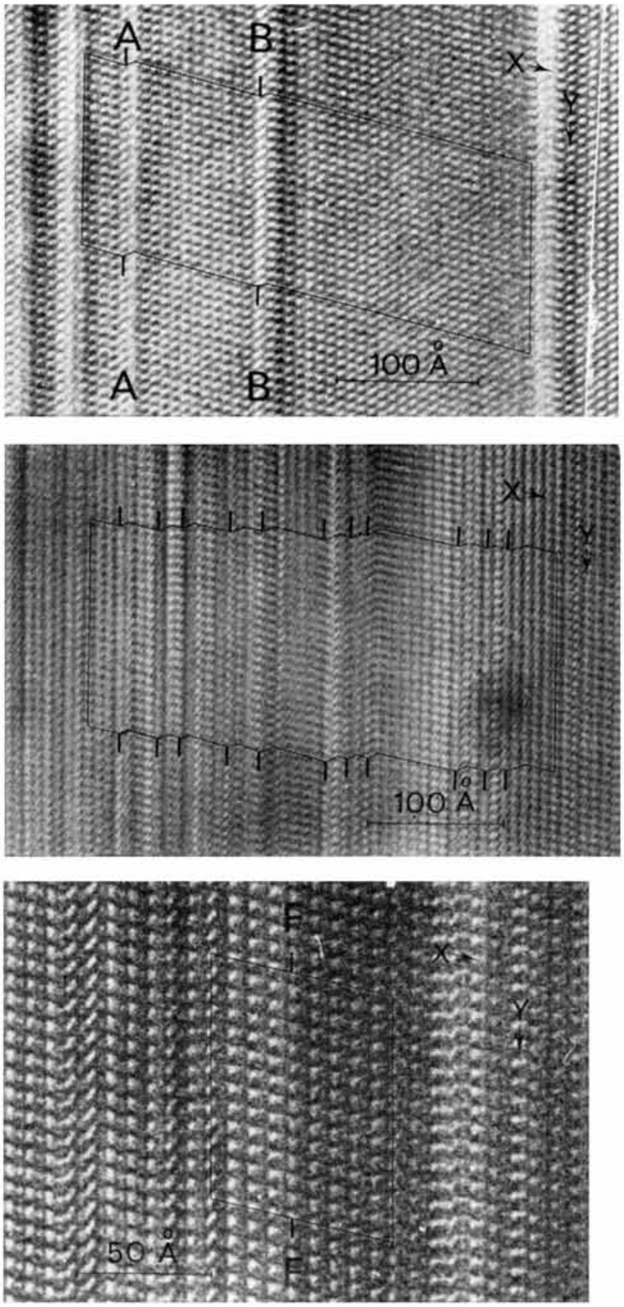

FIGURE 2 (*a*) Stacking faults in a largely triclinic wollastonite from Finland. (*b*) Numerous faults in a severely disordered wollastonite from California. *X*-Ray investigations were unable to characterise this sample as either mono- or tri-clinic. (*c*) A pronounced change of contrast with no apparent faulting in the sample from Finland

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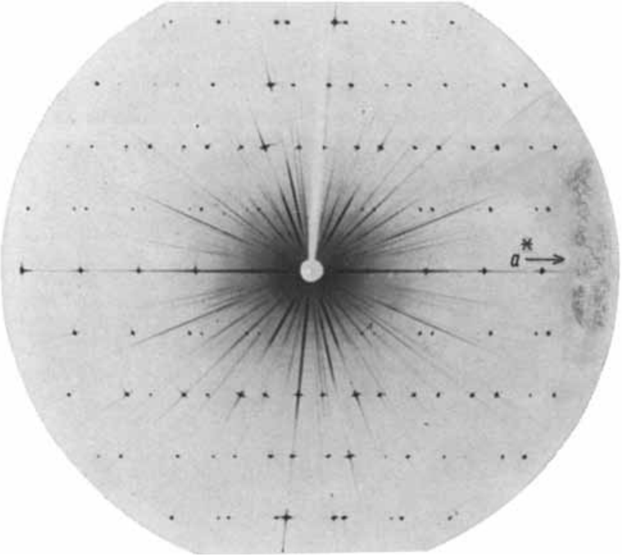

FIGURE 3 X-Ray precession photograph of a single crystal of the Californian sample. The reciprocal lattice level recorded is the $(h0l)$ section

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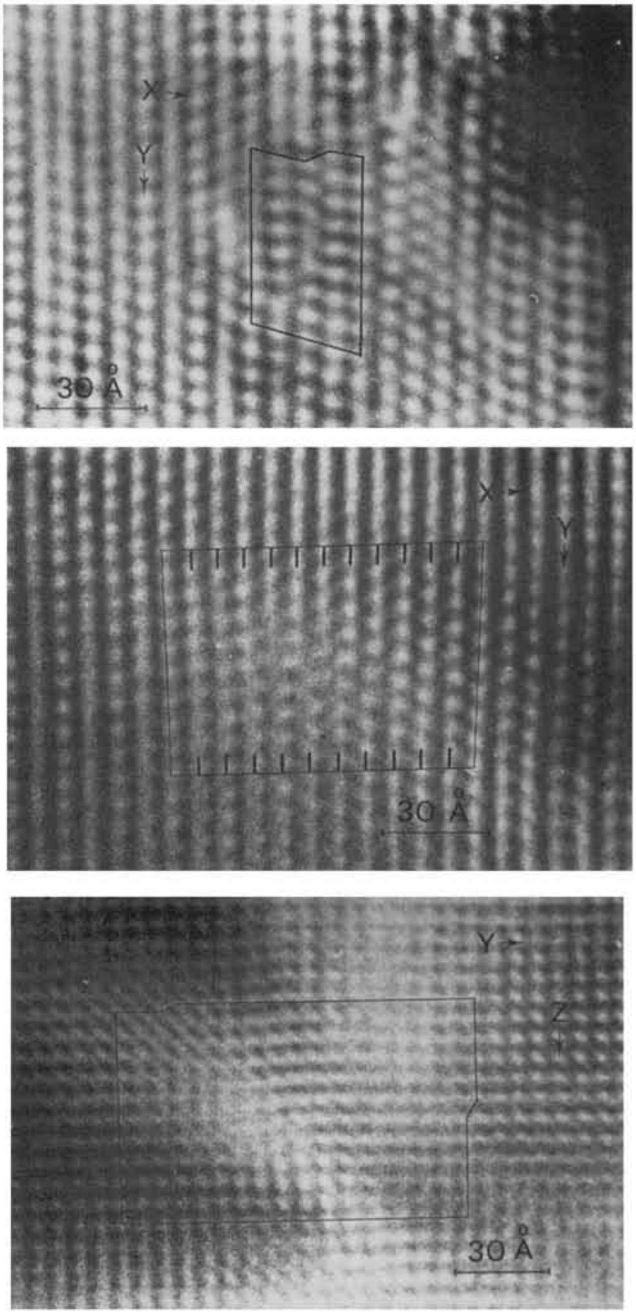

FIGURE 4 (*a*) (100)[010] dislocation observed in a sample of wollastonite from Devon. (*b*) (010)$\frac{1}{2}$[100] dislocation noted in a monoclinic specimen of wollastonite from Tanzania. (*c*) A distinctive type of fault observed in a specimen of synthetic wollastonite. In this case the lattice image is of the (0*kl*) type

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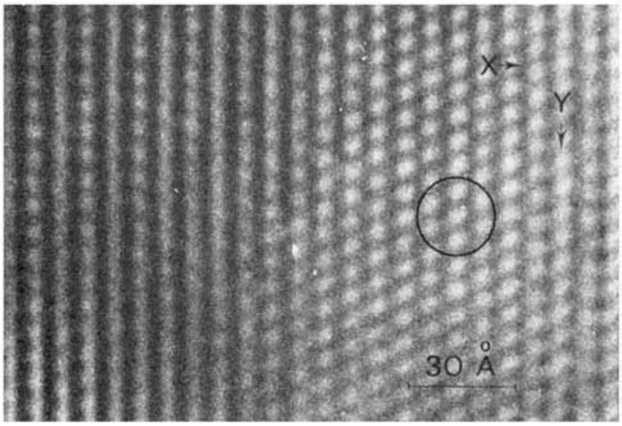

FIGURE 5 An apparent 0.5*b* displacement occurring in a near perfect monoclinic wollastonite from Tanzania

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0.60 × 0.40 × 0.42 mm (3). For all the complexes, Weissenberg photographs showed monoclinic symmetry with systematic absences consistent with space group $P2_1/c$. Unit-cell calibrations were carried out by a least-squares fit of the angular parameters of 25 reflections, carefully measured on the diffractometer.

Crystal data. (1), $C_{18}H_{42}ClN_2P_2Rh$, $M = 486.9$, Monoclinic, $a = 8.156(1)$, $b = 8.935(2)$, $c = 16.695(5)$ Å, $\beta = 93.5(1)°$, $U = 1\,214.4$ Å^3, $Z = 2$, $D_c = 1.331$ g cm^{-3}. Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 10.1$ cm^{-1}. Space group $P2_1/c$. (2), $C_{18}H_{42}ClO_2P_2Rh$, $M = 490.9$, Monoclinic, $a = 8.184(3)$, $b = 9.001(4)$, $c = 16.401(7)$ Å, $\beta = 93.1(1)°$, $U = 1\,206.3$ Å^3, $Z = 2$, $D_c = 1.351$ g cm^{-3}. Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 10.2$ cm^{-1}. Space group $P2_1/c$. (3), $C_{20}H_{46}ClP_2Rh$, $M = 486.9$, Monoclinic, $a = 16.316(3)$, $b = 9.164(2)$, $c = 16.544(3)$ Å, $\beta = 93.8(1)°$, $U = 2\,468.4$ Å^3, $Z = 4$, $D_c = 1.310$ g cm^{-3}. Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 9.9$ cm^{-1}. Space group $P2_1/c$.

Intensities were measured for $2\theta < 26°$ [(1) and (2)] and $2\theta < 28°$ [(3)] by a Siemens AED diffractometer, following the θ—2θ scan method and 'five-points' technique;[7] zirconium-filtered Mo-K_α radiation was used. The crystals were mounted with the a axis parallel to the ϕ axis of the diffractometer. A total of 2 364 (1), 2 337 (2), and 5 928 (3) reflections were collected, of which 1 603, 1 327, and 4 586 respectively, having $I > 3\sigma(I)$, were used in the structure determinations. Because of the large size of the crystal used, absorption corrections were applied for (3) according to the method of Busing and Levy;[8] no correction was necessary for (1) and (2).

Structure determination and refinement. The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares. The function minimized was $\Sigma w(F_o - F_c)^2$ with Cruickshank's weighting scheme.[9] The atomic scattering factors were from Cromer and Mann[10] for non-hydrogen atoms and from Stewart *et al.*[11] for hydrogen. The calculations included both $\Delta f'$ and $\Delta f''$ corrections for anomalous-dispersion effects on the rhodium, chlorine, and phosphorus atoms.[12]

Some of the hydrogen atoms were located from difference Fourier syntheses; the positions of those not clearly detectable from these maps were calculated according to the usual tetrahedral geometry. For all the complexes, the positional and isotropic thermal parameters of the hydrogen atoms were varied in additional cycles of the refinement. With the exception of ORTEP,[13] all the computer programs used were written by Immirzi.[14]

In (1) and (2), with two formula units per unit cell, the rhodium atom could be located unambiguously at the origin with $\bar{1}$ site symmetry; this was clearly confirmed by the Patterson map. Because of the disorder involving the positions of the chloride and N_2 or O_2 ligands, as required by the $\bar{1}$ crystallographic symmetry, the nitrogen and oxygen atoms were better located by difference-Fourier syntheses, after two cycles of isotropic least-squares refinement including the contribution of the chlorine atom. For both complexes, the ΔF map showed two independent peaks only, with electron densities of *ca.* 3 (1) and 4 eÅ^{-3} (2), in addition to Fourier ripple peaks around the metal atom; no other peaks greater than 1 eÅ^{-3} were detectable. The two peaks were equidistant from the rhodium-atom position [*ca.* 2.5 and 2.3 Å for (1) and (2) respectively], and were separated by *ca.* 1.0 Å in both complexes. The above features indicated unequivocally 'side-on' co-ordination of the N_2 and O_2 ligands.

The refinement, in which the Cl, N, or O atoms were left isotropic, converged to give final R factors of 0.048 and 0.039 for (1) and (2) respectively. Where an ordered disposition of Cl, N, or O was assumed in Pc or $P2_1$ space groups and the final atomic parameters, obtained by refining with $P2_1/c$, were used, R factors only slightly higher with respect to the disordered model were obtained for both complexes. Attempts were therefore made to refine with the acentric space groups Pc or $P2_1$, but inconsistent coefficients of the anisotropic thermal parameters of some carbon atoms were obtained. Moreover the N–N and O–O bond distances remained short (0.8—1.0 Å), as for the centrosymmetric case; values in the above range are quite unreliable and can be justified only if disorder is present. These facts further support the choice of both the $P2_1/c$ space group and of the disordered model as the correct one for (1) and (2). No ambiguity arose in the structure determination of (3), since the molecule is placed in a general x, y, z position; the final R factor was 0.022.

The final atomic parameters of non-hydrogen atoms are in Table 1. Anisotropic thermal parameters, atomic fractional co-ordinates, and isotropic thermal parameters of hydrogen atoms, and the observed and calculated structure factors, are deposited as Supplementary Publication No. 22080 SUP (40 pp.).*

RESULTS AND DISCUSSION

Preparation.—The methods of preparation are similar to that suggested by Wilkinson:[15] $[\{RhCl(C_8H_{14})_2\}_2]$ reacts with PPr^i_3 in a solution of benzene or pentane, and the addition of the gas X_2 causes the precipitation of $[RhCl(X_2)(PPr^i_3)_2]$ [$X_2 = N_2$ (1), O_2 (2), C_2H_4 (3), or CO (4)]. The use of benzene as solvent is suitable for the preparation of the dinitrogen complex, while pentane is convenient for all the complexes. In the case of the reaction in pentane, an extremely unstable, uncharacterized, violet compound precipitated first; for (1) and (2), it is convenient to admit the gas X_2 into the pentane solution only after filtration of this violet product.

Properties.—Complexes (1), (3), and (4) are fairly stable kinetically both in the solid state and in solution. The brilliant blue colour of (2) vanishes slowly in aromatic hydrocarbons, more rapidly in more polar solvents. This change in colour is related to the loss of the O_2 ligand from the co-ordination sphere and the partial oxidation of the phosphine ligand, as shown by the appearance of the P=O stretching band at 1 180 cm^{-1}. Qualitatively, the relative order of stability of the complexes is (1) < (2) <

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

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[8] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

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(3) < (4), *i.e.* C_2H_4 can replace N_2 or O_2 in the complex. The replacement of N_2 by O_2 is also possible but is complicated by the above side reactions. Finally, X_2 substitution in (1), (2), or (3) by CO is the best method of preparation of (4).

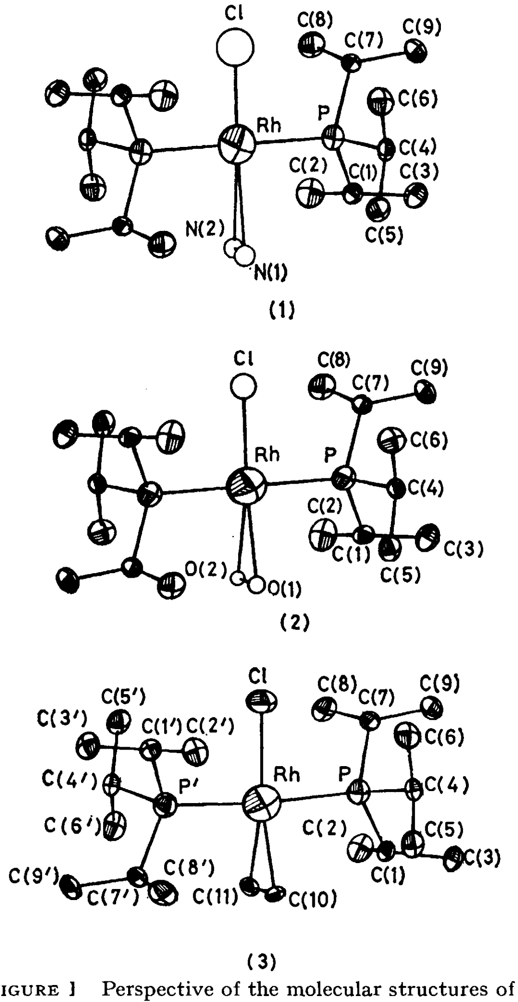
TABLE 1

Atomic fractional co-ordinates ($\times 10^4$) and isotropic thermal parameters ($\times 10^2$ Å^2) for non-hydrogen atoms. $\langle B\rangle$ = (1/3)trace **B** ($\times 10^2$) are reported as an indication of the magnitude of the thermal vibrations

	x	*y*	*z*	$\langle B\rangle$
(*a*) [RhCl(N_2)(PPr^i_3)$_2$]				
Rh	0	0	0	283
C(1)	568(8)	604(7)	−1 749(3)	444
C(3)	−3 290(9)	1 532(10)	−2 448(4)	651
C(5)	1 336(9)	1 408(9)	−1 975(4)	601
C(7)	−2 421(7)	3 153(6)	−536(3)	420
C(9)	−3 041(11)	4 395(9)	−1 113(5)	677
P	−1 256(2)	1 594(1)	−973(1)	292
C(2)	−3 885(11)	−348(10)	−1 373(6)	778
C(4)	293(7)	2 529(6)	−1 559(3)	403
C(6)	1 378(9)	3 560(9)	−1 014(5)	650
C(8)	−3 752(11)	2 601(10)	−26(5)	752
				B
Cl	39(9)	1 869(7)	908(4)	652(14)
N(1)	407(16)	−1 967(15)	−1 078(8)	443(28)
N(2)	−520(15)	−2 171(14)	−936(7)	385(25)
(*b*) [RhCl(O_2)(PPr^i_3)$_2$]				
				$\langle B\rangle$
Rh	0	0	0	245
C(1)	−2 602(7)	677(7)	−1 762(3)	412
C(3)	−3 244(10)	1 622(11)	−2 475(4)	715
C(5)	1 282(8)	1 442(9)	−2 028(4)	596
C(7)	−2 379(7)	3 186(7)	−521(4)	426
C(9)	−2 950(11)	4 438(8)	−1 085(5)	678
P	−1 266(2)	1 634(1)	−979(1)	265
C(2)	−3 950(9)	−219(11)	−1 386(5)	770
C(4)	282(7)	2 564(6)	−1 569(3)	363
C(6)	1 355(9)	3 571(9)	−1 033(5)	653
C(8)	−3 732(9)	2 651(10)	13(5)	707
				B
Cl	133(5)	1 887(4)	966(2)	284(5)
O(1)	452(10)	−1 660(8)	−1 011(4)	274(17)
O(2)	−637(9)	−2 020(8)	−788(4)	200(14)
(*c*) [RhCl(C_2H_4)(PPr^i_3)$_2$]				$\langle B\rangle$
Rh	2 514(1)	−107(1)	−60(1)	245
P	1 861(1)	1 548(1)	−987(1)	259
C(1)	1 257(1)	734(2)	−1 867(1)	369
C(3)	1 103(2)	1 687(3)	−2 628(1)	515
C(5)	3 211(2)	1 887(3)	−1 940(2)	537
C(7)	1 196(1)	2 883(2)	−490(1)	392
C(9)	777(2)	4 055(3)	−1 032(2)	588
C(2′)	4 511(2)	305(3)	1 238(2)	577
C(4′)	2 398(1)	−2 354(2)	1 645(1)	365
C(6′)	1 744(2)	−3 273(3)	1 189(2)	592
C(8′)	4 502(2)	−2 894(3)	260(2)	658
C(10)	2 813(2)	−1 496(3)	−1 019(1)	491
Cl	2 588(1)	1 819(1)	893(1)	449
P′	3 154(1)	−1 603(1)	959(1)	257
C(2)	437(2)	113(4)	−1 629(2)	630
C(4)	2 601(1)	2 747(2)	−1 482(1)	359
C(6)	3 053(2)	3 788(3)	−879(2)	577
C(8)	580(2)	2 154(4)	44(2)	578
C(1′)	3 877(1)	−601(2)	1 671(1)	372
C(3′)	4 285(2)	−1 477(3)	2 375(2)	555
C(5′)	1 997(2)	−1 173(3)	2 128(2)	584
C(7′)	3 686(1)	−3 263(2)	606(1)	377
C(9′)	3 793(2)	−4 555(3)	1 203(2)	547
C(11)	2 128(2)	−1 988(2)	−736(1)	471

The four complexes are essentially diamagnetic. Measurements of the magnetic susceptibility of (1)—(3) at different temperatures (77 K to room temperature) reveal a weak temperature-independent magnetic moment. This could be related to the presence of rhodium(II) impurities, possibly [$RhCl_2(PPr^i_3)_2$], in accord with the weak e.s.r. spectrum exhibited by these three complexes [more intense in (1) and (2) than in (3) at 77 K (g_1 3.78, g_2 1.57, and g_3 1.26)].

Description of the Structures.—Complexes (1) and (2) are isomorphous, as clearly indicated by their crystal data; two molecules are contained in the unit cell, each one lying on a crystallographic centre of symmetry. Because the molecules do not intrinsically possess $\bar{1}$ symmetry, this is obtained in the crystals by a disordered disposition of the chlorine atoms and N_2 or O_2 molecules. Complex (3) crystallizes in the same space group; however, the *a* axis is doubled, so that four molecules with ordered disposition of the ligands are present in the unit cell.



(1)

(2)

(3)

FIGURE 1 Perspective of the molecular structures of complexes (1)—(3)

In all the three complexes the rhodium atom displays square-planar co-ordination, with the two phosphine ligands in *trans* positions (Figure 1). The two X atoms or groups of the X_2 molecule [X = N, O, and CH_2 in (1), (2), and (3) respectively] are equidistant from the rhodium atom and the X–X bond is perpendicular to the co-ordination plane of the metal. Slight departures are observed from the ideal symmetrical co-ordination of the X_2 ligands; in particular, the angle between the RhX_2 plane and the co-ordination plane deviates from 90° (see Table 2), probably to relieve intramolecular contacts between the X atoms of the X_2 ligand and the C(1) and C(7′) atoms of the phosphines.

Intramolecular interactions should also be responsible for the deviation from the ideal square-planar co-ordination in (3), where the phosphine ligands are pushed towards the chlorine atom [P–Rh–Cl and P′–Rh–Cl 87.4(1) and 87.5(1)° respectively]. Similar distortion from the square plane has been found in $[IrCl(C_2H_4)(PPh_3)_2]$.[16] Complexes (1) and (2) lack similar distortions because the intramolecular N ··· C and O ··· C contacts (minimum values 3.2—3.3 Å) are less critical than the C ··· C (minimum values of 3.37 Å must be considered quite short).

TABLE 2

Least-squares planes in the form $Ax + By + Cz - D = 0$ (*x*, *y*, and *z* are the crystallographic fractional co-ordinates) and deviations (Å) of the atoms from these planes in square brackets

(*a*) Complex (1)

Plane (1): Rh, Cl, P, P′

$$-7.492x - 2.529y + 5.528z = 0$$

[N(1) 0.403, N(2) −0.421]

Plane (2): Rh, N(1), N(2)

$$-2.942x - 5.548y + 11.232z = 0$$

(*b*) Complex (2)

Plane (1): Rh, Cl, P, P′

$$-7.504x - 2.393y + 5.708z = 0$$

[O(1) 0.519, O(2) −0.512]

Plane (2): Rh, O(1), O(2)

$$3.864x - 5.265y + 10.372z = 0$$

(*c*) Complex (3)

Plane (1): Rh, Cl, P, P′

$$-14.936x - 2.373y + 6.080z + 3.754 = 0$$

[Rh −0.012, Cl −0.001, P 0.007, P′ 0.007, C(10) 0.712, C(11) −0.600]

Plane (2): Rh, C(10), C(11)

$$8.026x - 5.311y + 10.194z - 2.013 = 0$$

Plane (3): C(10), C(11), H(1)–C(10), H(2)–C(10), H(1)–C(11), H(2)–C(11)

$$0.348x + 6.760y + 11.118z + 2.157 = 0$$

[Rh 2.106, C(10) 0.111, C(11) 0.069, H(1)–C(10) −0.026, H(2)–C(10) −0.078, H(1)–C(11) −0.065, H(2)–C(11) −0.010]

(*d*) Angles (°) between planes

	Complex		
Plane	(1)	(2)	(3)
(1)—(2)	87.9	94.6	95.7
(1)—(3)			90.1

The hydrogen atoms of the ethylene molecule in (3)

TABLE 3

Bond distances (Å) and angles (°) for $[RhCl(N_2)(PPr^i{}_3)_2]$ (1), $[RhCl(O_2)(PPr^i{}_3)_2]$ (2), and $[RhCl(C_2H_4)(PPr^i{}_3)_2]$ (3)

	(1)	(2)	(3)
Rh–P	2.348(1)	2.373(1)	2.361(1)
Rh–P′			2.363(1)
Rh–Cl	2.254(6)	2.321(3)	2.365(1)
Rh–N(1)	2.55(1)		
Rh–N(2)	2.51(1)		
Rh–O(1)		2.28(1)	
Rh–O(2)		2.28(1)	
Rh–C(10)			2.116(2)
Rh–C(11)			2.128(2)
P–C(1)	1.854(6)	1.853(6)	1.860(2)
P–C(4)	1.844(6)	1.838(6)	1.862(2)
P–C(7)	1.860(6)	1.850(6)	1.862(2)
C(1)–C(2)	1.534(11)	1.524(10)	1.529(4)
C(1)–C(3)	1.520(10)	1.516(10)	1.539(3)
C(4)–C(5)	1.510(9)	1.525(9)	1.512(3)
C(4)–C(6)	1.536(10)	1.510(10)	1.534(3)
C(7)–C(8)	1.503(10)	1.527(10)	1.534(4)
C(7)–C(9)	1.535(10)	1.515(10)	1.531(4)
Cl–Rh–P	90.2(1)	90.2(1)	87.4(1)
Cl–Rh–P′	89.8(1)	89.8(1)	87.5(1)
P–Rh–P′			174.9(1)
Rh–P–C(1)	113.8(2)	113.6(2)	116.4(1)
Rh–P–C(4)	110.9(1)	110.5(2)	112.8(1)
Rh–P–C(7)	113.3(2)	113.6(2)	112.7(1)
C(1)–P–C(4)	103.3(1)	104.1(1)	102.6(1)
C(4)–P–C(7)	104.6(1)	103.8(1)	102.7(1)
C(1)–P–C(7)	110.2(1)	110.3(2)	108.4(1)
P–C(1)–C(2)	111.5(3)	112.2(3)	112.0(1)
P–C(1)–C(3)	117.1(3)	116.1(3)	117.5(1)
P–C(4)–C(5)	111.5(3)	111.3(3)	112.3(1)
P–C(4)–C(6)	110.3(3)	111.2(3)	112.3(1)
P–C(7)–C(8)	112.3(3)	112.6(3)	113.0(1)
P–C(7)–C(9)	116.9(3)	117.1(3)	116.9(1)
C(2)–C(1)–C(3)	111.6(3)	112.4(3)	108.8(1)
C(5)–C(4)–C(6)	110.4(3)	112.0(3)	110.2(1)
C(8)–C(7)–C(9)	111.8(3)	112.1(3)	110.0(1)
C(10)–C(11)–H(1)–C(11)			128(2)
C(10)–C(11)–H(2)–C(11)			124(2)
H(1)–C(10)–C(10)–H(2)–C(10)			111(1)
N(1)–N(2)	0.83(2)		
O(1)–O(2)		1.03(1)	
C(10)–C(11)			1.319(4)
C(10)–H(1)–C(10)			0.95(2)
C(10)–H(2)–C(10)			0.92(3)
C(11)–H(1)–C(11)			0.94(3)
C(11)–H(2)–C(11)			0.91(3)
P′–C(1′)			1.855(2)
P′–C(4′)			1.862(2)
P′–C(7′)			1.864(2)
C(1′)–C(2′)			1.539(4)
C(1′)–C(3′)			1.531(4)
C(4′)–C(5′)			1.519(3)
C(4′)–C(6′)			1.520(3)
C(7′)–C(8′)			1.526(4)
C(7′)–C(9′)			1.544(4)
P–Rh–CX_2*	90.3	89.1	92.7
P′–Rh–CX_2	89.7	90.9	92.4
Rh–P′–C(1′)			113.5(1)
Rh–P′–C(4′)			111.7(1)
Rh–P′–C(7′)			116.3(1)
C(1′)–P′–C(4′)			102.4(1)
C(4′)–P′–C(7′)			103.2(1)
C(1′)–P′–C(7′)			108.2(1)
P′–C(1′)–C(2′)			113.0(1)
P′–C(1′)–C(3′)			116.8(1)
P′–C(4′)–C(5′)			112.5(1)
P′–C(4′)–C(6′)			111.9(1)
P′–C(7′)–C(8′)			112.0(1)
P′–C(7′)–C(9′)			117.4(1)
C(2′)–C(1′)–C(3′)			111.4(1)
C(5′)–C(4′)–C(6′)			110.1(1)
C(8′)–C(7′)–C(9′)			110.2(1)
C(11)–C(10)–H(1)–C(10)			124(2)
C(11)–C(10)–H(2)–C(10)			120(2)
H(1)–C(11)–C(11)–H(2)–C(11)			107(1)

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[16] R. J. Restivo, G. Ferguson, T. L. Kelly, and C. V Senoff, *J. Organometallic Chem.*, 1975, **90**, 101.

* CX_2 is the midpoint of the X–X bond, *i.e.* N–N in (1), O–O in (2), and C–C in (3).

are bent out of the plane of the double bond away from the metal atom (see Table 2); the same effect has been observed in $[IrCl(C_2H_4)(PPh_3)_2]$ [16] and Zeise's salt.[17]

Significantly different values of the Rh–P distance [from 2.348(1) in (1) to 2.373(1) Å in (2)] are observed in the three complexes (see Table 3); it is probable that both *cis* effects and steric factors [the influence of the size of ethylene is evident from the distortion of the square co-ordination in (3)] are contributing to these bond distances. The Rh–C distances in (3) [2.116(2) and 2.128(2) Å] are slightly shorter than the corresponding mean [2.167(2) Å] reported [18] for $[Rh(C_5H_5)(C_2F_4)(C_2H_4)]$ and comparable with the values [2.112(8) and 2.123(8)] found for the Ir–C bond in $[IrCl(C_2H_4)(PPh_3)_2]$.[16]

TABLE 4

Characteristic i.r. bands

Complex	Band (cm^{-1})	Assignment
$[RhCl(N_2)(PPr^i_3)_2]$	2 100m	$\nu(N\equiv N)$
	495m	
	470m	
$[RhCl(O_2)(PPr^i_3)_2]$	990m	$\nu(O=O)$
$[RhCl(C_2H_4)(PPr^i_3)_2]$	1 510w	$\nu(C=C)$
	1 200m	$\rho(CH_2)$
	955m	$\rho(CH_2)$
$[RhCl(CO)(PPr^i_3)_2]$	1 940s	$\nu(C\equiv O)$
	580m	

The C–C bond distance [1.319(4) Å] in (3) is the shortest reported for co-ordinated ethylene and can be compared to that found in the free molecule [1.337(5) Å] [19] and in $[Rh(C_5H_5)(C_2F_4)(C_2H_4)]$; [18] short values of the C–C distance have been reported for other square-planar complexes, *i.e.* $[IrCl(C_2H_4)(PPh_3)_2]$ [1.375(10) Å] [16] and Zeise's salt [1.375(4) Å].[17] On the other hand, higher values have been found in five-co-ordinate complexes: the average values of 1.43 and 1.45 Å have been observed in $[Ir\{C_3H_6PPr^i_2\}(PPr^i_3)(C_2H_4)_2]$ and $[Ir(C_6H_4PPh_2)(PPh_3)(C_2H_4)_2]$ respectively.[20]

The disorder present in the crystals of (1) and (2) certainly affected the refinement of the positional parameters of the chloride and O_2 or N_2 ligands. In fact, the N–N and O–O bond distances found [0.83(2) and 1.03(1) Å] are certainly unreliable, being less than the corresponding ones for the free molecules [1.10 and 1.21 Å respectively].[19] As a consequence, any comparison with O–O bond distances observed in 'side-on' oxygen adducts (usually [4] 1.3—1.5 Å), and the N–N bond distances in 'end-on' (1.074 Å [21]) or bridging 'side-on' complexes (1.34—1.36 Å [2]) is not significant. Also the Rh–Cl and Rh–X bond distances found in (1) and (2) cannot be used for comparison purposes, being correlated with the disorder. However, since the Cl and X atoms appear in a composite electron-density peak, it seems reasonable to assume that the true Rh–N and Rh–O bond distances lie, at least approximately, between the minimum and the maximum values observed for the Rh–Cl or Rh–X distances. If so, the true Rh–N in (1) and Rh–O in (2) would be in the ranges 2.25—2.55 and 2.28—2.32 Å respectively. Such Rh–N bond distances are longer than the value [1.970(4) Å] observed in the 'end-on' dinitrogen complex $[RhH(N_2)(PBu_2Ph)_2]$.[21] A similar conclusion can be made for the Rh–O distance which, in 'side-on' oxygen adducts, is usually found in the range 2.0—2.1 Å.[4]

The crystal structures of the three complexes show no unusually short intermolecular non-bonded distances: all the contacts between non-hydrogen atoms are greater than 3.7 Å.

Infrared and Magnetic-resonance Spectra.—Selected i.r. bands for the new complexes are in Table 4. The O–O stretching vibration is at higher frequencies than reported [3] for the five- and three-co-ordinate 'side-on' O_2 complexes (800—900 cm^{-1}). Although this frequency cannot be regarded as an absolute measure of the O–O bond strength, its meaningfully high value in (2) supports the hypothesis of a rather strong O–O bond in this complex. The N≡N stretching frequency in (1) cannot be directly compared with that of the other N_2 complexes, because the geometries are different; however, from calculations of Yatsimirskii and Kraglyak,[22] the ν(N≡N) stretching frequency of 'side-on' bonded N_2 is expected to be lower than the 'end-on' value. The value of 2 100 cm^{-1} found in (1), very close to that reported for 'end-on' N_2 complexes,[1] is therefore higher than predicted. Thus, the ligand-stretching frequencies are higher than expected for both complexes (1) and (2), for this type of geometry, suggesting rather weak Rh–N_2 and Rh–O_2 interactions.

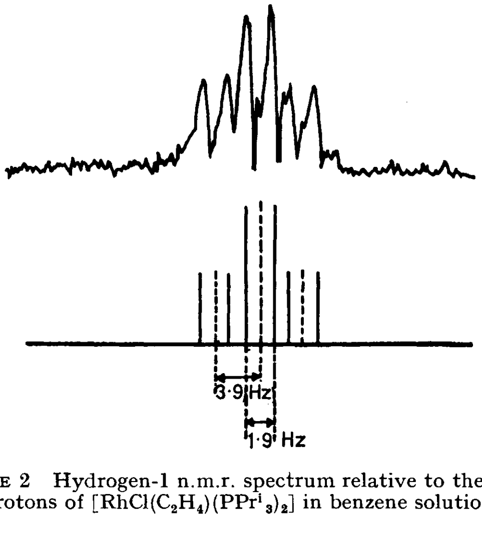

FIGURE 2 Hydrogen-1 n.m.r. spectrum relative to the C_2H_4 protons of $[RhCl(C_2H_4)(PPr^i_3)_2]$ in benzene solution

The frequency of the C=C stretching lies close to that

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TABLE 5

Hydrogen-1 n.m.r parameters [a,b]

Complex	Chemical shift (τ)	Relative area	Assignment	Coupling constants (Hz)	Solvent
$[RhCl(N_2)(PPr^i_3)_2]$	8.69 (q)	6	CH_3	$J(CH-CH_3)$ 6.3	$CDCl_3$
	7.55 (m)	1	CH	$J(P-CH_3)$ 6.3	
				$J(P-CH)$ 3.1	
$[RhCl(C_2H_4)(PPr^i_3)_2]$	8.72 (q)	18	CH_3	$J(CH-CH_3)$ 6.3	$CDCl_3$ [c]
	7.70 (m) [d]	3	CH	$J(P-CH_3)$ 6.3	
	7.51 [e]	2	C_2H_4	$J(P-CH)$ 3.1	
				$J(P-C_2H_4)$ 3.9	
				$J(Rh-C_2H_4)$ 1.9	
$[RhCl(C_2H_4)(PPr^i_3)_2]$	8.66 (q)	18	CH_3	$J(CH-CH_3)$ 6.5	C_6D_6
	7.57 (m)	3	CH	$J(P-CH_3)$ 6.5	
	7.30 [e]	2	C_2H_4	$J(P-CH)$ 3.4	
				$J(P-C_2H_4)$ 3.9	
				$J(Rh-C_2H_4)$ 1.9	

[a] q = Quadruplet, m = multiplet; data referred to 25 °C. [b] No data are given for the oxygen complex, because the solution is unstable. [c] Recorded at 70 °C. [d] Not well resolved. [e] Triplet of doublets.

found for other ethylene complexes.[23] It should be noted that no strong bands are found in the range 400—500 cm^{-1}, where the metal–ethylene vibration is commonly observed in platinum, palladium, and rhodium complexes.[23-25] It is possible that this vibration is too weak to be detectable in the presence of the phosphine absorption at *ca.* 450 cm^{-1}, or is masked by the intense phosphine band at 525 cm^{-1}.

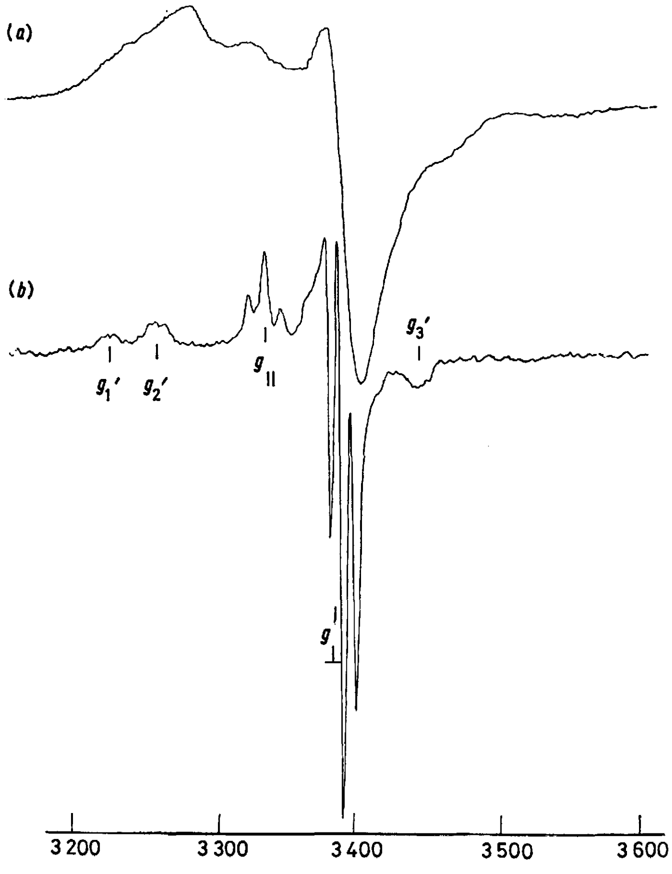

FIGURE 3 E.s.r. spectra of $[RhCl(O_2)(PPr^i_3)_2]$ central part: (*a*) powder, (*b*) toluene glass at 77 K

N.m.r. data for the new complexes are in Table 5. The observed quartet for the CH_3 group protons should be interpreted as a doublet of triplets, with $J(CH-CH_3) = J(P-CH_3)$: the triplets arise from the virtual coupling with two equivalent P atoms. This suggests that the two phosphine groups lie in the *trans* position, as confirmed by the crystal-structure determination. The C_2H_4 multiplet is interpretable as a triplet of doublets (Figure 2), arising from proton coupling with the equivalent P atoms and with the Rh nucleus. Varying the temperature causes a slight change in the chemical shift in all the spectra. In addition, the ethylene spectrum is well resolved in C_6D_6 but not in $CDCl_3$: in the latter solvent, this portion of the spectrum may be resolved by increasing the temperature to 60 °C. These data relative to the ethylene ligand, being very similar to those for other square-planar rhodium complexes,[26] both in chemical shift and $J(Rh-H)$ coupling constants, suggest a similar ethylene co-ordination in these complexes.

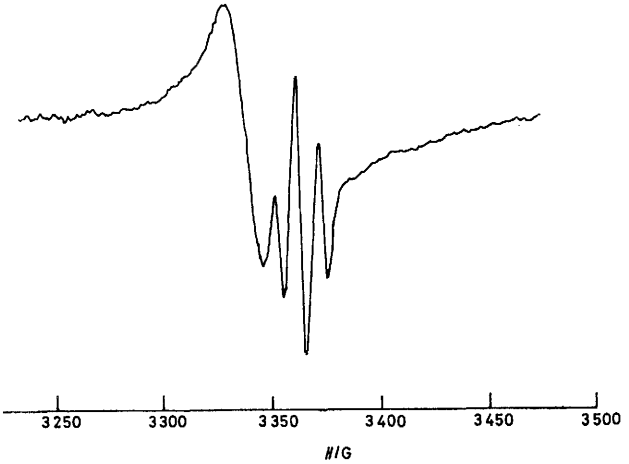

FIGURE 4 E.s.r. spectrum of $[RhCl(O_2)(PPr^i_3)_2]$ in toluene solution at room temperature

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Although essentially diamagnetic, the oxygen complex presents a weak unresolved e.s.r. signal in the range g 1.9—2.1 [Figure 3(*a*)]. In toluene glass this signal is resolved into two components: one ($g_{\parallel}$ 2.04, $g_{\perp}$ 2.00) is very similar to the spectra reported for the $[O_2]^{-\cdot}$ ion in cobalt(II) complexes;[27] the second component (g_1' 2.09, g_2' 2.07, g_3' 1.96) is indicative of a rhodium(II) species [Figure 3(*b*)]. These two components can also be found at room temperature ($g_{iso.}$ 2.02, $g_{iso.}'$ 2.03) (Figure 4). Spectra of this kind have been assigned to hyperoxorhodium(II) species.[28] The signal related to the hyperoxide ion shows a hyperfine structure of ^{31}P ($A_{\parallel}$ 13.10 × 10^{-4}, $A_{\perp}$ 8.87 × 10^{-4}, $A_{iso.}$ 10.49 × 10^{-4} cm^{-1}), indicating a weak $Rh^{II}-O_2^{\cdot}$ interaction.[29] The presence of rhodium hyperoxide as an impurity is also confirmed by the absorption band at 590 nm in the visible spectrum,[30] observed as the reflectance spectrum of the pure solid. Possibly, this corresponds to an impurity which derives from the initial stage of decomposition of the oxygen complex.

Conclusions.—' Side-on ' co-ordination has been well established for complexes (1)—(3) which represent the first example of a homogeneous series containing the three ligands N_2, O_2, and C_2H_4. Complex (1) represents the first structure determination of a ' side-on ' mononuclear dinitrogen complex, and (2) is the first example of four-co-ordinate ' side-on ' dioxygen complex. The ' side-on ' co-ordination of ethylene in (3) is similar to that usually found in other ethylene complexes.[16,31] The disorder present in the crystals of (1) and (2) does not allow the determination of the true N–N and O–O bond distances. However, rather strong N–N and O–O bonds, and consequently weak $Rh-N_2$ and $Rh-O_2$ interactions, can be inferred from i.r. considerations. This is consistent with the relatively long Rh–N and Rh–O bond distances observed.

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