Nitrosyl Complexes of Rhenium. Part 2.[1] Crystal and Molecular Structure of Dihydridonitrosyltris(triphenylphosphine)rhenium(I)–Benzene(2/1)

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The crystal and molecular structure of the title compound has been determined by Patterson and Fourier methods from three-dimensional X-ray data collected by diffractometer. Crystals are orthorhombic, space group $Pca2_1$, with cell constants a = 25.069(6), b = 18.737(4), and c = 20.644(5) Å. The structure has been refined by least-squares methods to R 0.048 for 2 938 independent reflections. The two crystallographically independent molecules in the asymmetric unit are very similar and exhibit markedly distorted octahedral geometry, with one phosphine ligand, the NO group, and the two hydrido-ligands (mutually *cis*) in equatorial positions, with the other two phosphine ligands axial, largely bent toward the hydrido H atoms. The three Re–P distances are 2.370(7), 2.439(7), and 2.403(8) Å in the first molecule and 2.401(6), 2.498(8), and 2.386(8) Å in the second. The nitrosyl groups are linked linearly to the metal atoms, as NO$^+$ ligands, with Re–N 1.77(2) and 1.73(2) and N–O 1.25(3) and 1.24(3) Å in the two molecules. The largest deviation from ideal geometry is shown by the axial P–Re–P angles [143.4(3) and 143.0(3)°].

WE are currently studying the stereochemistry of some mononitrosyl complexes of rhenium obtained from the pentahalogenonitrosyl species $[ReX_5(NO)]^{2-}$. The structures of the anions $[ReBr_4(NCMe)(NO)]^-$ and $[ReBr_4(NO)(HOEt)]^-$ have already been reported.[1] A derivative recently obtained is the diamagnetic complex $[ReH_2(NO)_2(PPh_3)_3]$,[2] the second example of a hydrido-nitrosyl complex of rhenium to be reported, the first being $[ReH(NO)_2(PPh_3)_2]$.[3] The i.r. spectrum of the complex exhibits two bands (1 950 and 1 800 cm^{-1}) assigned to the Re–H stretching modes, indicating a *cis* configuration for the two hydrido-ligands; it also shows a rather low ν(NO) frequency at 1 640 cm^{-1}.[2] Since the ligand arrangement in this type of complex is very often highly distorted from ideal geometry, owing to the low steric hindrance of the hydrogen ligands, and since this steric factor could have some effect on metal–nitrosyl interaction, we have undertaken an X-ray single-crystal analysis in order to ascertain its stereochemistry and to establish the nature of the Re–NO bond.

EXPERIMENTAL

Crystal Data.—$C_{57}H_{50}NOP_3Re$, M = 1 044.2, Orthorhombic, a = 25.069(6), b = 18.737(4), c = 20.644(5) Å, U = 9 696.9 Å^3, D_m = 1.41(2) (by flotation), Z = 8, D_c = 1.431, $F(000)$ = 4 216. Space group $Pca2_1$ (no. 29) or $Pcam$ (non-standard setting of $Pbcm$, no. 57), from systematic absences. Mo-K_α radiation, λ = 0.7107 Å; μ(Mo-K_α) = 27.9 cm^{-1}.

Intensity Measurements.—The crystal used for data collection was an elongated prism 0.06 × 0.07 × 0.27 mm. Intensity measurements were made on a Philips PW 1100 automatic diffractometer, by the θ–2θ scan method, and with graphite-monochromatized radiation, scan range 1.2°, scan speed 0.04° s^{-1}, with background counts of 15 s taken on each side of the scan. The total number of reflections, collected within $2\theta \leqslant 46°$, was 6 977. Three standard reflections, measured at regular intervals, showed no evidence of crystal decay. Integrated intensities were corrected for Lorentz and polarization factors. Transmission factors, calculated by the Busing and Levy method [4] for a sample of reflections, were in the range 0.70—0.74, so no absorption correction was applied. A final set of 2 938 independent non-zero reflections, having $\sigma(I)/I \leqslant 0.26$, were used in the solution and refinement of the structure.

Determination and Refinement of the Structure.—The structure solution was based on a three-dimensional Patterson map, which showed the positions of the rhenium atoms. We first assumed the centrosymmetric space group $Pcam$, which would require the presence of one molecule in the asymmetric unit. After a preliminary refinement of the rhenium atom a successive difference-Fourier map showed most of the remaining non-hydrogen atoms. While rather broad peaks were observed for one phosphorus atom and the NO group atoms, all the other atoms clearly showed double images. We therefore then undertook refinement in the non-centrosymmetric space group $Pca2_1$, with two crystallographically independent $[ReH_2(NO)(PPh_3)_3]$ molecules. Refinements were carried out by block-matrix least squares, with the phenyl rings constrained to rigid-body motion (D_{6h} symmetry, assuming C–C 1.392 Å). Anisotropic temperature factors were used for the Re and P atoms; an average isotropic thermal factor was assigned to each phenyl ring. During these refinements small oscillations were observed for some positional parameters of P(2), N(1), and O(1) atoms in the first molecule and, correspondingly, of P(5), N(2), and O(2) atoms in the second one, indicating some correlation between the parameters of these pairs of atoms. After several cycles of refinement a difference-Fourier synthesis revealed the presence of a solvent benzene molecule, which was refined rigidly with D_{6h} symmetry. All the non-hydrido-hydrogen atoms were located in fixed ideal positions (C–H 1.08 Å) and their contributions introduced into the structure-factor calculations. At this stage anomalous scattering was also taken into account (for rhenium and phosphorus) and refinements were made in order to establish the correct structure enantiomorph. The final values of the agreement indices R and R' were 0.048 and 0.059 $\{R' = [\Sigma w(|F_o| - k|F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$. Weights were assigned according to the formula $w = 1/(A + B|F_o| + C|F_o|^2)$ where, in the final stages of refinements, A was

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215.4, B — 1.83, and C 6 × 10^{-3}, in order to obtain a constant distribution of the weighted mean quadratic errors as a function of $\sin\theta/\lambda$ and F_o. Atomic scattering factors were taken from ref. 5 for non-hydrogen atoms, and from ref. 6 for hydrogen. Corrections for both the real and imaginary parts of the anomalous scattering were taken from ref. 7.

TABLE 1

Positional and thermal parameters of non-group atoms *

Atom	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Re(1)	−10 819(4)	−4 094(6)	0	100(1)	1(6)	3(5)	213(2)	−35(8)	156(2)
Re(2)	38 312(4)	−45 362(6)	−16 696(6)	99(1)	−10(6)	0(5)	217(3)	1(9)	146(2)
P(1)	−238(2)	−227(4)	−490(3)	12(1)	1(3)	−1(2)	22(2)	−6(3)	12(1)
P(2)	−1 656(2)	−433(4)	−953(3)	13(1)	7(4)	−6(2)	14(2)	−10(5)	18(1)
P(3)	−1 645(3)	−22(4)	873(3)	12(1)	0(3)	−3(2)	24(2)	6(4)	15(1)
P(4)	4 769(2)	−4 739(3)	−1 531(3)	8(1)	0(2)	4(2)	12(2)	5(3)	14(1)
P(5)	3 542(2)	−4 350(3)	−524(4)	11(1)	−8(2)	0(2)	15(2)	3(3)	18(1)
P(6)	3 043(3)	−5 026(4)	−2 141(3)	10(1)	0(3)	−6(2)	27(2)	−7(4)	17(2)
				B					
N(1)	−1 132(9)	−1 346(12)	77(12)	4.1(4)					
O(1)	−1 196(7)	−2 006(11)	90(11)	5.3(4)					
N(2)	3 779(8)	−3 619(11)	−1 754(11)	3.3(4)					
O(2)	3 713(7)	−2 966(11)	−1 825(10)	4.6(5)					

* Estimated standard deviation in the last significant figure is given in parentheses here and in succeeding Tables. The Re parameters × 10^5; others except for the isotropic B factors (Å^2), × 10^4. Anisotropic temperature factors are given by $\exp -(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})$.

The final difference-Fourier synthesis, apart from the regions surrounding the two rhenium atoms, which will be examined later, showed some residual peaks, not >0.6 eÅ^{-3}, close to phenyl carbon atoms, and deriving very probably from the assumption of an average thermal factor for all the atoms of a ring.

The Hydrido-hydrogen Atoms.—In the final part of the structural determination we attempted to locate the hydrido-hydrogen atoms by the method of La Placa and Ibers.[8] We compared four difference syntheses, computed at decreasing $\sin\theta/\lambda$, namely at 0.55, 0.45, 0.35, and 0.25, corresponding to 2 938 (all data), 2 230, 1 276, and 519 independent reflections. In the first map two peaks (0.66 and 0.71 eÅ^{-3}) were found around Re(1) near to the expected positions for the hydrido-ligands, with Re–H 1.57 Å in both cases and H–Re–H 100°. Around Re(2) a suitable peak (0.80 eÅ^{-3}) was observed, with Re–H 1.75 Å, but in the position expected for the other one only a very broad peak was found, probably deriving from the overlap with other residual peaks due to the heavy atom. In the second map also the fourth hydride peak became apparent. However, the presence of residual heavy-atom peaks, in different positions from map to map and overlapping with the hydride peaks, seemed to lower significantly the reliability of the analysis. In fact, the hydride atom positions seemed to change in the various maps, with variations in Re–H up to *ca*. 0.30 Å. Using the criterion of the maximum $\rho : \sigma(\rho)$ ratio, the best situation was the following: (*i*) the two peaks around Re(1) were found to lie in the Re(1),P(2),N(1) plane, with Re–H 1.57 and 1.41 Å, and a H–Re–H 91°; (*ii*) the two peaks around Re(2), lying in the Re(2),P(5),N(2) plane, both had Re–H 1.44 Å, and H–Re–H 89°. These results are rather unsatisfactory because of the too short Re–H distances, and give only a rough indication of the hydride atom positions.

We also made an indirect determination through potential-energy calculations. Energy maps were computed taking into account all the non-bonding intramolecular interactions of a hydrido-ligand by scanning a spherical surface centred at the rhenium atom, a procedure already adopted for $[ReH_3(Ph_2PC_2H_4PPh_2)_2]$ (ref. 9) and $[ReH_3(PPh_3)_2(Ph_2PC_2H_4PPh_2)]$.[10] Each interaction was computed as $V_i = a_i\exp(-b_ir_i) - c_ir_i^{-6}$, with a, b, and c taken from ref. 11 for H–P, and from ref. 12 for H–O, H–N, H–C, and H–H interactions. The Re–H distance was assigned values 1.70 and 1.60 Å, typical for this type of interaction. In both cases two very clear minima were found around each rhenium atom. These minima lay fairly well in the equatorial molecular planes Re(1),P(2),N(1) and Re(2),P(5),N(2) and formed H–Re(1)–H and H–Re(2)–H of 100 and 101° (Re–H 1.70 Å) and of 99 and 102° (Re–H 1.60 Å).

Computations.—All computations were made on a UNIVAC 1106 computer. Local programs were used for data reduction, statistical analysis of weighting schemes, and non-bonding energy calculations. In addition, local versions of entries nos. 7528, 7531, 7532, and 7535 in the 1966 'International World List of Crystallographic Programs' were used for Fourier analysis, and structure-factor and least-squares calculations; Johnson's ORTEP was used for thermal ellipsoid plotting and a program by Domenicano and Vaciago for computation of molecular parameters.

The results of the refinements are reported in Tables 1 and 2. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21786 (4 pp., 1 microfiche).*

DISCUSSION

The crystal structure of the complex consists of the packing of discrete $[ReH_2(NO)(PPh_3)_3]$ and benzene

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue (items less than 10 pp. are supplied as full size copies).

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TABLE 2

Parameters of the group atoms [a,b]

Atom	x	y	z
C(111)	152(7)	−1 010(8)	−716(11)
C(112)	−143(5)	−1 625(11)	−837(11)
C(113)	115(7)	−2 267(8)	−963(11)
C(114)	670(7)	−2 295(8)	−968(11)
C(115)	966(5)	−1 681(11)	−847(11)
C(116)	706(7)	−1 038(8)	−721(11)
C(121)	−178(11)	334(12)	−1 217(9)
C(122)	170(9)	151(12)	−1 714(12)
C(123)	181(8)	552(13)	−2 281(10)
C(124)	−156(11)	1 136(12)	−2 351(9)
C(125)	−506(9)	1 319(12)	−1 854(12)
C(126)	−516(8)	918(13)	−1 287(10)
C(131)	232(10)	235(15)	66(11)
C(132)	418(9)	928(14)	−20(10)
C(133)	760(11)	1 231(11)	434(13)
C(134)	917(10)	840(15)	974(11)
C(135)	731(9)	146(14)	1 061(10)
C(136)	388(11)	−155(11)	607(13)
C(211)	−2 338(9)	−783(18)	−870(11)
C(212)	−2 444(8)	−1 232(16)	−348(11)
C(213)	−2 934(10)	−1 577(14)	−303(10)
C(214)	−3 318(9)	−1 475(18)	−781(11)
C(215)	−3 212(8)	−1 027(16)	−1 303(11)
C(216)	−2 722(10)	−681(14)	−1 347(10)
C(221)	−1 360(11)	−1 035(13)	−1 563(12)
C(222)	−985(11)	−788(10)	−2 006(14)
C(223)	−719(8)	−1 268(14)	−2 408(12)
C(224)	−829(11)	−1 994(13)	−2 366(12)
C(225)	−1 205(11)	−2 241(10)	−1 922(14)
C(226)	−1 470(8)	−1 762(14)	−1 521(12)
C(231)	−1 835(13)	359(12)	−1 382(15)
C(232)	−1 894(10)	401(13)	−2 051(15)
C(233)	−2 042(7)	1 044(17)	−2 339(11)
C(234)	−2 130(13)	1 644(12)	−1 957(15)
C(235)	−2 071(10)	1 603(13)	−1 287(15)
C(236)	−1 924(7)	960(17)	−1 000(11)
C(311)	−1 948(12)	−744(13)	1 388(14)
C(312)	−2 476(11)	−750(13)	1 597(15)
C(313)	−2 675(8)	−1 338(17)	1 930(15)
C(314)	−2 347(12)	−1 921(13)	2 054(14)
C(315)	−1 819(11)	−1 915(13)	1 846(15)
C(316)	−1 619(8)	−1 327(17)	1 513(15)
C(321)	−2 205(9)	564(12)	672(13)
C(322)	−2 696(10)	346(10)	427(13)
C(323)	−3 082(8)	851(14)	269(13)
C(324)	−2 977(9)	1 574(12)	356(13)
C(325)	−2 486(10)	1 792(10)	601(13)
C(326)	−2 100(8)	1 287(14)	759(13)
C(331)	−1 306(11)	431(15)	1 522(11)
C(332)	−852(10)	817(12)	1 356(9)
C(333)	−620(9)	1 278(15)	1 804(13)
C(334)	−843(11)	1 353(15)	2 418(11)
C(335)	−1 297(10)	966(12)	2 584(9)
C(336)	−1 528(9)	505(15)	2 136(13)
C(411)	5 222(8)	−3 982(10)	−1 681(12)
C(412)	5 065(7)	−3 310(12)	−1 464(11)
C(413)	5 411(9)	−2 733(9)	−1 518(12)
C(414)	5 915(8)	−2 827(10)	−1 789(12)
C(415)	6 072(7)	−3 498(12)	−2 005(11)
C(416)	5 726(9)	−4 076(9)	−1 951(12)
C(421)	5 050(10)	−5 121(13)	−782(10)
C(422)	4 781(8)	−5 681(13)	−482(12)
C(423)	4 970(9)	−5 960(11)	98(12)
C(424)	5 429(10)	−5 678(13)	379(10)
C(425)	5 698(8)	−5 119(13)	80(12)
C(426)	5 508(9)	−4 840(11)	−500(12)
C(431)	5 014(11)	−5 375(11)	−2 133(10)
C(432)	4 979(10)	−5 188(9)	−2 785(11)
C(433)	5 118(7)	−5 681(12)	−3 261(8)
C(434)	5 290(11)	−6 361(11)	−3 085(10)
C(435)	5 324(10)	−6 547(9)	−2 434(11)
C(436)	5 186(7)	−6 054(12)	−1 958(8)
C(511)	2 857(7)	−3 984(17)	−403(9)
C(512)	2 574(8)	−4 161(14)	153(9)
C(513)	2 052(6)	−3 923(15)	232(8)
C(514)	1 813(7)	−3 508(17)	−246(9)
C(515)	2 097(8)	−3 331(14)	−803(9)
C(516)	2 619(6)	−3 569(15)	−882(8)
C(521)	3 945(8)	−3 639(10)	−156(12)
C(522)	3 739(6)	−2 949(12)	−141(12)
C(523)	4 059(9)	−2 384(9)	62(13)
C(524)	4 583(8)	−2 509(10)	251(12)
C(525)	4 789(6)	−3 199(12)	235(12)
C(526)	4 470(9)	−3 761(9)	31(13)
C(531)	3 577(11)	−5 092(11)	79(10)
C(532)	3 447(7)	−5 773(13)	−140(8)
C(533)	3 448(10)	−6 346(10)	288(12)
C(534)	3 578(11)	−6 239(11)	936(10)
C(535)	3 708(7)	−5 558(13)	1 156(8)
C(536)	3 707(10)	−4 985(10)	727(12)
C(611)	2 581(11)	−4 380(15)	−2 480(15)
C(612)	2 812(8)	−3 777(17)	−2 757(16)
C(613)	2 490(12)	−3 253(13)	−3 032(15)
C(614)	1 938(11)	−3 332(15)	−3 029(15)
C(615)	1 707(8)	−3 934(17)	−2 752(16)
C(616)	2 029(12)	−4 458(13)	−2 477(15)
C(621)	2 617(10)	−5 624(12)	−1 625(11)
C(622)	2 681(8)	−6 357(13)	−1 701(10)
C(623)	2 408(10)	−6 827(9)	−1 299(12)
C(624)	2 070(10)	−6 564(12)	−819(11)
C(625)	2 006(8)	−5 831(13)	−743(10)
C(626)	2 279(10)	−5 361(9)	−1 146(12)
C(631)	3 181(11)	−5 608(13)	−2 870(10)
C(632)	2 789(8)	−5 699(14)	−3 339(13)
C(633)	2 885(9)	−6 134(13)	−3 873(11)
C(634)	3 373(11)	−6 479(13)	−3 937(10)
C(635)	3 767(8)	−6 388(14)	−3 469(13)
C(636)	3 671(9)	−5 953(13)	−2 935(11)
C(1) [c]	4 339(12)	−2 125(17)	−3 989(13)
C(2)	4 131(8)	−2 561(18)	−3 505(15)
C(3)	4 468(12)	−2 998(13)	−3 146(13)
C(4)	5 014(12)	−3 000(17)	−3 271(13)
C(5)	5 222(8)	−2 564(18)	−3 755(15)
C(6)	4 884(12)	−2 127(13)	− 4114(13)
H(112) [d]	−575	−1 603	−832
H(113)	−114	−2 746	−1 056
H(114)	872	−2 795	−1 065
H(115)	1 398	−1 702	−850
H(116)	937	−559	−627
H(122)	435	−302	−1 658
H(123)	454	410	−2 668
H(124)	−147	1 449	−2 793
H(125)	−769	1 774	−1 909
H(126)	−788	1 060	−899
H(132)	296	1 233	−440
H(133)	905	1 771	367
H(134)	1 184	1 075	1 329
H(135)	853	−157	1 483
H(136)	244	−695	674
H(212)	−2 145	−1 311	24
H(213)	−3 016	−1 926	103
H(214)	−3 700	−1 744	−746
H(215)	−3 511	−946	−1 675
H(216)	−2 640	−332	−1 754
H(222)	−899	−222	−2 038
H(223)	−426	−1 075	−2 752
H(224)	−622	−2 368	−2 678
H(225)	−1 290	−2 807	−1 890
H(226)	−1 762	−1 953	−1 175
H(232)	−1 825	−65	−2 348
H(233)	−2 087	1 077	−2 859
H(234)	−2 244	2 145	−2 180
H(235)	−2 140	2 071	−990
H(236)	−1 877	928	−478
H(312)	−2 731	−295	1 500
H(313)	−3 086	−1 341	2 092
H(314)	−2 502	−2 379	2 314
H(315)	−1 562	−2 369	1 943
H(316)	−1 208	−1 322	1 351
H(322)	−2 778	−216	360
H(323)	−3 464	681	79
H(324)	−3 277	1 968	234

TABLE 2 (*Continued*)

Atom	x	y	z
H(325)	−2 403	2 355	669
H(326)	−1 717	1 457	950
H(332)	−678	759	879
H(333)	−266	1 580	1 675
H(334)	−662	1 712	2 767
H(335)	−1 470	1 025	3 063
H(336)	−1 881	205	2 266
H(412)	4 673	−3 236	−1 253
H(413)	5 290	−2 209	−1 350
H(414)	6 186	−2 377	−1 830
H(415)	6 465	−3 572	−2 215
H(416)	5 849	−4 598	−2 120
H(422)	4 424	−5 900	−701
H(423)	4 761	−6 395	332
H(424)	5 577	−5 895	832
H(425)	6 056	−4 900	299
H(426)	5 718	−4 404	−733
H(432)	4 846	−4 659	−2 921
H(433)	5 091	−5 536	−3 767
H(434)	5 398	−6 744	−3 455
H(435)	5 459	−7 075	−2 297
H(436)	5 213	−6 199	−1 450
H(512)	2 760	−4 433	527
H(513)	1 832	−4 060	666
H(514)	1 407	−3 322	−184
H(515)	1 911	−3 008	−1 175
H(516)	2 840	−3 431	−1 315
H(522)	3 331	−2 851	−287
H(523)	3 899	−1 847	75
H(524)	4 832	−2 069	410
H(525)	5 198	−3 296	382
H(526)	4 631	−4 301	19
H(532)	3 347	−5 856	−644
H(533)	3 348	−6 876	118
H(534)	3 579	−6 685	1 271
H(535)	3 809	−5 474	1 661
H(536)	3 808	−4 454	899
H(612)	3 242	−3 716	−2 759
H(613)	2 669	−2 783	−3 248
H(614)	1 688	−2 923	−3 243
H(615)	1 278	−3 994	−2 749
H(616)	1 850	−4 927	−2 260
H(622)	2 945	−6 561	−2 074
H(623)	2 459	−7 398	−1 358
H(624)	1 858	−6 930	−505
H(625)	1 744	−5 626	−369
H(626)	2 230	−4 789	−1 086
H(632)	2 408	−5 430	−3 288
H(633)	2 579	−6 205	−4 238
H(634)	3 448	−6 817	−4 353
H(635)	4 148	−6 656	−3 519
H(636)	3 977	−5 882	−2 569
H(1)	4 077	−1 784	−4 269
H(2)	3 706	−2 559	−3 407
H(3)	4 307	−3 337	−2 768
H(4)	5 278	−3 340	−2 990
H(5)	5 648	−2 565	−3 851
H(6)	5 047	−1 787	−4 491

[a] $x, y, z \times 10^4$. [b] Isotropic mean thermal parameters of the 19 groups are 3.2(2), 4.8(3), 5.4(3), 4.9(4), 4.9(3), 5.6(3), 5.8(4), 4.8(3), 4.6(3), 4.1(3), 4.3(3), 4.0(3), 4.3(3), 4.4(3), 4.4(3), 6.7(4), 4.5(3), 5.0(3), and 8.1(5) Å². [c] Carbon atoms of the benzene molecule. [d] Hydrogen atoms have the same labels and thermal factors as the carbon atoms to which they are linked.

solvent molecules in the ratio 2 : 1. All the intermolecular contacts are normal, except for some involving phenyl hydrogen atoms, which were somewhat shorter than the sum of the van der Waals radii, probably owing to the rigid-body refinement of the phenyl groups and to the location of the hydrogen atoms in idealized positions. Figure 1 shows a projection of the structure down the *c* axis.

The two crystallographically independent $[ReH_2(NO)(PPh_3)_3]$ molecules exhibit similar geometries, especially in their inner co-ordination spheres (Figure 2). We shall refer to the molecule containing Re(1) as molecule (I) and to the other as molecule (II). All the important interatomic distances and angles are reported in Table 3. The rhenium atoms show strongly distorted octahedral co-ordination, with one phosphine ligand, the nitrosyl group, and the two hydrido-ligands (themselves *cis*) lying in equatorial positions, the other two phosphine ligands being axial and markedly bent towards the hydrido-atoms.

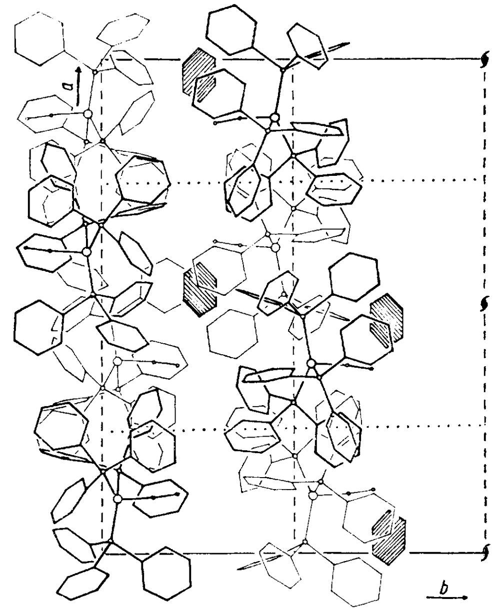

FIGURE 1 Projection of the structure down the *c* axis

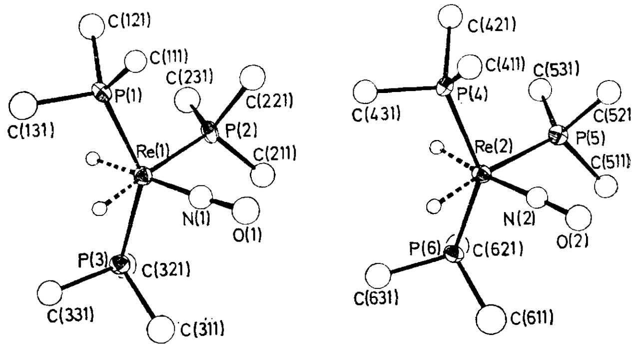

FIGURE 2 ORTEP drawing of the inner co-ordination sphere in the two independent $[ReH_2(NO)(PPh_3)_3]$ molecules

All the Re–P distances are as expected.[13] However they are of two types: axial, mean 2.39 Å, and equatorial, both these being longer as a consequence of the structural *trans* influence of the hydrido-ligands. These distances [Re(1)–P(2) 2.439(7), and Re(2)–P(5) 2.498(8) Å] exhibit the largest difference between corresponding bond lengths in the two molecules, probably to some extent due to

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[13] See, for example, V. G. Albano, P. L. Bellon, and G. Ciani, *J. Organometallic Chem.*, 1971, **31**, 75 and refs. therein.

correlation in the refinement of the positional parameters of P(2) and P(5), leading to not too accurate values for Re–P (see Experimental section), and, in part, to different non-bonding contacts.

TABLE 3

Selected interatomic distances and angles in the two $[ReH_2(NO)(PPh_3)_3]$ molecules

(*a*) Distances (Å)

Molecule (I)		Molecule (II)	
Re(1)–P(1)	2.370(7)	Re(2)–P(4)	2.401(6)
Re(1)–P(2)	2.439(7)	Re(2)–P(5)	2.498(8)
Re(1)–P(3)	2.403(8)	Re(2)–P(6)	2.386(8)
Re(1)–N(1)	1.77(2)	Re(2)–N(2)	1.73(2)
N(1)–C(1)	1.25(3)	N(2)–O(2)	1.24(3)
P(1)–C(111)	1.83(2)	P(4)–C(411)	1.84(2)
P(1)–C(121)	1.84(2)	P(4)–C(421)	1.84(2)
P(1)–C(131)	1.86(3)	P(4)–C(431)	1.83(2)
P(2)–C(211)	1.84(3)	P(5)–C(511)	1.87(2)
P(2)–C(221)	1.85(3)	P(5)–C(521)	1.84(2)
P(2)–C(231)	1.79(3)	P(5)–C(531)	1.87(2)
P(3)–C(311)	1.88(3)	P(6)–C(611)	1.82(3)
P(3)–C(321)	1.83(3)	P(6)–C(621)	1.88(3)
P(3)–C(331)	1.80(3)	P(6)–C(631)	1.89(3)
P(1) · · · P(2)	3.70(1)	P(4) · · · P(5)	3.79(1)
P(2) · · · P(3)	3.85(1)	P(5) · · · P(6)	3.79(1)
P(1) · · · N(1)	3.29(2)	P(4) · · · N(2)	3.28(2)
P(2) · · · N(1)	3.03(3)	P(5) · · · N(2)	2.95(2)
P(3) · · · N(1)	3.24(3)	P(6) · · · N(2)	3.32(2)

(*b*) Angles (°)

Molecule (I)		Molecule (II)	
P(1)–Re(1)–P(2)	100.6(2)	P(4)–Re(2)–P(5)	101.2(2)
P(1)–Re(1)–P(3)	143.4(3)	P(4)–Re(2)–P(6)	143.0(3)
P(2)–Re(1)–P(3)	105.3(2)	P(5)–Re(2)–P(6)	101.6(3)
P(1)–Re(1)–N(1)	104.2(8)	P(4)–Re(2)–N(2)	104.1(7)
P(2)–Re(1)–N(1)	90.7(8)	P(5)–Re(2)–N(2)	86.3(8)
P(3)–Re(1)–N(1)	101.0(8)	P(6)–Re(2)–N(2)	106.2(7)
Re(1)–N(1)–O(1)	175(2)	Re(2)–N(2)–O(2)	177(2)
Re(1)–P(1)–C(111)	118.2(7)	Re(2)–P(4)–C(411)	117.4(7)
Re(1)–P(1)–C(121)	120.3(9)	Re(2)–P(4)–C(421)	122.3(8)
Re(1)–P(1)–C(131)	111.6(8)	Re(2)–P(4)–C(431)	110.6(9)
Re(1)–P(2)–C(211)	118.7(8)	Re(2)–P(5)–C(511)	116.4(7)
Re(1)–P(2)–C(221)	109.0(9)	Re(2)–P(5)–C(521)	109.4(8)
Re(1)–P(2)–C(231)	122.2(10)	Re(2)–P(5)–C(531)	120.9(8)
Re(1)–P(3)–C(311)	116.4(9)	Re(2)–P(6)–C(611)	115.4(10)
Re(1)–P(3)–C(321)	117.5(9)	Re(2)–P(6)–C(621)	117.9(8)
Re(1)–P(3)–C(331)	115.0(10)	Re(2)–P(6)–C(631)	113.3(9)
C(111)–P(1)–C(121)	102(1)	C(411)–P(4)–C(421)	102(1)
C(111)–P(1)–C(131)	101(1)	C(411)–P(4)–C(431)	101(1)
C(121)–P(1)–C(131)	101(1)	C(421)–P(4)–C(431)	101(1)
C(211)–P(2)–C(221)	103(1)	C(511)–P(5)–C(521)	101(1)
C(211)–P(2)–C(231)	96(1)	C(511)–P(5)–C(531)	103(1)
C(221)–P(2)–C(231)	106(1)	C(521)–P(5)–C(531)	104(1)
C(311)–P(3)–C(321)	105(1)	C(611)–P(6)–C(621)	105(1)
C(311)–P(3)–C(331)	96(1)	C(611)–P(6)–C(631)	101(1)
C(321)–P(3)–C(331)	104(1)	C(621)–P(6)–C(631)	102(1)

The Re–N distances agree with corresponding values for $[ReBr_4(NO)(HOEt)]^-$ [1.723(15) Å],[1] $[ReBr_4(NCMe)(NO)]^-$ [1.771(11) Å],[1] and for a number of second- and third-row transition-metal nitrosyls. The N–O distances are somewhat longer than usually found, but are not unique {see 1.24(3) Å in $[Ir(NO)(PPh_3)_3]$ (ref. 14)}. The Re–N–O interactions are essentially linear, establishing the presence of NO^+ ligands. The rather low ν(NO) stretching frequency (at 1 640 cm^{-1}) [2] is, once more, not indicative of a bent metal–nitrosyl interaction, but is consistent with the presence of long N–O bond lengths. A possible explanation for the lengthening is that the *trans*-hydrido-ligand makes the Re–N bond poorer in σ but stronger in π character, with a consequent decrease in N–O bond-order.

The main feature of the present structure determination consists of the distorted co-ordination geometry of the $[ReH_2(NO)(PPh_3)_3]$ molecule. Both the direct and indirect location of the hydrido-hydrogen atoms (see Experimental section) are indicative of the fact that these atoms lie in the plane containing Re, the NO group, and the P atom of the equatorial phosphine, with a H–Re–H angle in the range 90—100°. The co-ordination of the four equatorial ligands does not therefore show large deviations from ideal octahedral geometry. A very large deviation consists of the bending of the two axial phosphines toward the hydrido-ligands, the P–Re–P angle being 143.4(3) in molecule (I) and 143.0(3)° in molecule (II). Distortions of the same kind have been observed in similar structures, due to the low steric hindrance of the hydrido-ligands. The P–M–P axial angle in *mer*-$[IrH_3(PPh_3)_3]$ [153.0(3)°],[15] $[Ir(CO)H_2(PPh_3)_3]^+$ [151.4(2)°],[16] *cis*-$[FeH_2\{PPh(OEt)_2\}_4]$ [136.7(1)°],[17] and *cis*-$[RuH_2(PPh_3)_4]$ [116.4(2)°] [18] decreases according to the bulkiness of the various ligands. In particular, our value is *ca.* 8° smaller than that for $[Ir(CO)H_2(PPh_3)_3]^+$ and seems to confirm that nitrosyl nitrogen possesses a larger non-bonded radius than carbonyl carbon in transition-metal complexes.[19]

The bonding parameters within the triphenylphosphine ligands are unexceptional. The P–C bond lengths are in the range 1.79—1.89 Å, mean 1.84 Å. The Re–P–C angles exhibit the usual enlargement [means: 116.5 molecule (I) and 116.0° molecule (II)] with respect to the tetrahedral value; the C–P–C angles show a corresponding decrease [means: 101 molecule (I) and 102° molecule (II)].

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