

## Structure of a Hydrazido(2–) Complex of Tungsten(V): Trichlorobis(dimethylphenylphosphine)[phenylhydrazido(2–)]tungsten(V)

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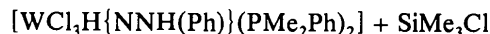
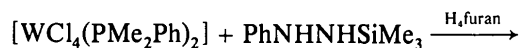
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### Abstract

Crystals of  $[\text{WCl}_3\{\text{NNH}(\text{Ph})\}(\text{PMe}_2\text{Ph})_2]$  are bright green and slightly air-sensitive.  $[\text{C}_{22}\text{H}_{28}\text{Cl}_3\text{N}_2\text{P}_2\text{W}]$ ,  $M_r = 672.6$ ,  $a = 26.048$  (4),  $b = 10.773$  (4),  $c = 19.529$  (2) Å,  $\beta = 104.53$  (1)°; monoclinic, space group  $P2_1/a$ ,  $U = 5304.9$  Å<sup>3</sup>,  $D_c = 1.684$  Mg m<sup>-3</sup>,  $Z = 8$ ,  $F(000) = 2632$ ,  $\mu(\text{Mo } K\alpha) = 4.89$  mm<sup>-1</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å]. Their structure was determined by the heavy-atom method, and refined to  $R = 0.036$  and  $R' = 0.041$  for 7065 reflections. There are two independent molecules in the crystal, almost identical in geometry and conformation, and related by a pseudo centre of symmetry. The hydrazido H atom of one molecule was found in a difference map; the parameters for the other were estimated, and both atoms refined satisfactorily. Both form hydrogen bonds to chloro groups of the opposite molecule, so that the two molecules form a dimer pair about the pseudo centre. The coordination about the W atoms is octahedral, and the hydrazido(2–) groups have dimensions typical of the linear, multiple-bonded W–N–N systems.

### Introduction

In the course of examining the reduction, to ammonia, of dinitrogen in its Mo and W complexes, a number of hydrazido(2–)–hydrido complexes have been prepared and their formulae established by spectroscopic methods (Chatt, Fakley, Hitchcock, Richards, Luong-Thi & Hughes, 1979). No crystalline product, suitable for X-ray analysis, has resulted from these preparations. Preparation of analogues of these compounds was attempted by the reaction:



and attempts were made to recrystallize the air-sensitive complex product from dichloromethane/ether. The resulting crystals were indeed most suitable

for crystal structure analysis [which has been reported briefly (Chatt, Fakley, Hitchcock, Richards, Luong-Thi & Hughes, 1979) and is described more fully here], but thereby were shown to have the composition: *trans*- $[\text{WCl}_3\{\text{NNH}(\text{Ph})\}(\text{PMe}_2\text{Ph})_2]$ . The phenylhydrazido(2–)–hydrido complex was thus shown to lose a hydrogen radical during the slow recrystallization process.

A similar hydrazido(2–)–hydrido complex,  $[\text{WCl}_3\text{H}(\text{NNH}_2)(\text{PMe}_2\text{Ph})_2]$ , prepared differently from its phenyl analogue above, was also shown to undergo a similar reaction during recrystallization, and the X-ray analysis of the solvated product, *cis*- $[\text{WCl}_3(\text{NNH}_2)(\text{PMe}_2\text{Ph})_2] \cdot \text{C}_4\text{H}_8\text{O}$ , has been recorded (Chatt, Fakley, Hitchcock, Richards, Luong-Thi & Hughes, 1979).

### Experimental

Crystals of this complex are bright green and slightly air-sensitive. A prism-shaped crystal, length 0.26 mm (parallel with the *b* axis), with diamond-shaped section of diameters 0.13 and 0.21 mm, was mounted on a glass fibre and coated with Araldite.

In addition to the absent festoons of *h0l* reflections having *h* odd, other reflections in this layer showed systematically strong diffraction where (*h*/2 + *l*) was even, and weak diffraction where (*h*/2 + *l*) was odd; this inferred a pseudo glide plane of symmetry, normal to *b*, with a shift of (*a*/4 + *c*/2).

Accurate cell dimensions were calculated from the centred settings of 25 reflections with  $12 < \theta < 15^\circ$ , on an Enraf–Nonius CAD-4 diffractometer using monochromated Mo *K*α radiation. Diffraction intensities for reflections having  $\theta$  in the range  $1.15 - 25^\circ$  were measured on the same instrument using a variable scan speed and a 3:2 goniometer:counter scanning ratio, as optimized by peak-analysis routines. Series of diffraction scans, at various  $\psi$  values, were also recorded for each of 17 reflections and their symmetry equivalents so that semi-empirical absorption factors could be calculated and applied by the method of Sheldrick,

Table 1. Atomic coordinates (fractional  $\times 10^4$ ) and isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ )

Estimated standard deviations are in parentheses and refer to the final digit(s) quoted. An asterisk denotes  $U_{eq}$ , the equivalent value of the anisotropic temperature factor coefficients, calculated from the expression:  $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$ . The  $U_{ij}$  values have been deposited.

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{iso}$		<i>x</i>	<i>y</i>	<i>z</i>	$U_{iso}$
Molecule (I)					Molecule (I')				
W	1546.5 (1)	1024.9 (2)	924.6 (1)	38.3 (1)*	W'	968.0 (1)	1640.2 (3)	4117.1 (1)	44.1 (1)*
Cl(1)	1285 (1)	-310 (2)	1769 (1)	64 (1)*	Cl'(1)	1236 (1)	2899 (2)	3239 (1)	70 (1)*
Cl(2)	1121 (1)	-555 (2)	51 (1)	68 (1)*	Cl'(2)	1436 (1)	3241 (2)	4941 (1)	84 (1)*
Cl(3)	1761 (1)	2061 (2)	-44 (1)	65 (1)*	Cl'(3)	740 (1)	679 (2)	5092 (1)	79 (1)*
P(4)	2386 (1)	-278 (2)	1141 (1)	48 (1)*	P'(4)	138 (1)	2987 (2)	3893 (1)	59 (1)*
C(41)	2789 (3)	-179 (6)	2052 (3)	49 (2)	C'(41)	-265 (3)	2867 (7)	2995 (4)	56 (2)
C(42)	3042 (3)	932 (7)	2280 (4)	58 (2)	C'(42)	-531 (3)	1766 (8)	2758 (5)	81 (3)
C(43)	3358 (3)	1021 (8)	2966 (4)	70 (2)	C'(43)	-834 (4)	1627 (9)	2077 (5)	91 (3)
C(44)	3409 (3)	42 (8)	3425 (4)	71 (2)	C'(44)	-896 (4)	2592 (9)	1634 (5)	86 (3)
C(45)	3150 (3)	-1051 (8)	3205 (4)	69 (2)	C'(45)	-648 (4)	3682 (9)	1833 (5)	92 (3)
C(46)	2841 (3)	-1150 (7)	2522 (4)	64 (2)	C'(46)	-325 (3)	3848 (8)	2514 (4)	69 (2)
C(47)	2846 (3)	148 (7)	621 (4)	64 (2)	C'(47)	-306 (4)	2597 (9)	4444 (5)	92 (3)
C(48)	2272 (3)	-1913 (7)	964 (4)	67 (2)	C'(48)	248 (4)	4624 (8)	4055 (5)	89 (3)
P(5)	673 (1)	2159 (2)	603 (1)	51 (1)*	P'(5)	1827 (1)	449 (2)	4448 (1)	54 (1)*
C(51)	759 (3)	3799 (6)	788 (4)	54 (2)	C'(51)	1731 (3)	-1152 (7)	4168 (4)	54 (2)
C(52)	739 (3)	4280 (8)	1443 (4)	71 (2)	C'(52)	1808 (3)	-1556 (8)	3532 (4)	76 (2)
C(53)	838 (4)	5552 (9)	1594 (5)	89 (3)	C'(53)	1697 (4)	-2779 (10)	3319 (5)	94 (3)
C(54)	963 (4)	6292 (10)	1105 (5)	98 (3)	C'(54)	1520 (4)	-3578 (9)	3725 (5)	91 (3)
C(55)	987 (4)	5868 (11)	470 (6)	112 (4)	C'(55)	1443 (4)	-3220 (9)	4359 (5)	95 (3)
C(56)	883 (4)	4594 (9)	303 (5)	92 (3)	C'(56)	1539 (3)	-2003 (8)	4588 (5)	78 (2)
C(57)	196 (3)	1617 (8)	1070 (4)	75 (2)	C'(57)	2351 (3)	1042 (8)	4074 (4)	83 (3)
C(58)	318 (4)	2047 (9)	-315 (4)	90 (3)	C'(58)	2147 (4)	402 (9)	5386 (4)	87 (3)
N(1)	1816 (2)	2112 (5)	1572 (3)	43 (2)*	N'(1)	694 (2)	547 (5)	3474 (3)	49 (2)*
N(2)	1994 (3)	2891 (7)	2104 (3)	57 (3)*	N'(2)	544 (3)	-211 (6)	2932 (3)	58 (2)*
H(2)	1921 (30)	2760 (75)	2421 (36)	66 (28)	H'(2)	687 (22)	-63 (53)	2624 (28)	28 (17)
C(21)	2363 (3)	3826 (7)	2086 (4)	52 (2)	C'(21)	166 (3)	-1136 (6)	2884 (3)	50 (2)
C(22)	2520 (3)	4074 (7)	1473 (4)	57 (2)	C'(22)	-74 (3)	-1371 (7)	3440 (4)	57 (2)
C(23)	2907 (3)	4966 (7)	1488 (4)	62 (2)	C'(23)	-477 (3)	-2263 (7)	3346 (4)	65 (2)
C(24)	3128 (4)	5581 (9)	2093 (5)	83 (3)	C'(24)	-635 (3)	-2899 (8)	2730 (4)	73 (2)
C(25)	2966 (4)	5358 (9)	2699 (5)	86 (3)	C'(25)	-389 (3)	-2694 (8)	2193 (5)	80 (2)
C(26)	2574 (3)	4474 (8)	2714 (4)	74 (2)	C'(26)	9 (3)	-1809 (7)	2267 (4)	71 (2)
H(42)	2999	1661	1954	63	H'(42)	-499	1054	3094	86
H(43)	3551	1812	3128	75	H'(43)	-1008	814	1916	96
H(44)	3634	123	3919	76	H'(44)	-1131	2505	1146	91
H(45)	3185	-1770	3538	74	H'(45)	-696	4381	1486	98
H(46)	2650	-1946	2364	68	H'(46)	-140	4657	2655	74
H(47A)	3055	859	881	69	H'(47A)	-559	1980	4161	97
H(47B)	2652	406	133	69	H'(47B)	-500	3351	4544	97
H(47C)	3084	-565	589	69	H'(47C)	-105	2227	4902	97
H(48A)	2072	-2257	1298	72	H'(48A)	475	4850	3730	94
H(48B)	2618	-2354	1031	72	H'(48B)	435	4790	4560	94
H(48C)	2059	-2033	465	72	H'(48C)	-95	5093	3935	94
H(52)	656	3720	1809	76	H'(52)	1944	-969	3222	81
H(53)	814	5901	2059	94	H'(53)	1750	-3062	2854	99
H(54)	1042	7187	1220	103	H'(54)	1442	-4454	3563	97
H(55)	1077	6443	116	117	H'(55)	1317	-3837	4664	101
H(56)	899	4275	-171	96	H'(56)	1470	-1734	5047	83
H(57A)	364	1593	1590	80	H'(57A)	2186	1107	3554	88
H(57B)	71	766	902	80	H'(57B)	2658	453	4169	88
H(57C)	-115	2192	975	80	H'(57C)	2477	1872	4277	88
H(58A)	581	2100	-609	95	H'(58A)	1924	-137	5613	92
H(58B)	56	2740	-442	95	H'(58B)	2174	1257	5591	92
H(58C)	125	1237	-403	95	H'(58C)	2511	45	5463	92
H(22)	2356	3619	1026	62	H'(22)	42	-908	3897	62
H(23)	3023	5154	1049	67	H'(23)	-650	-2434	3739	70
H(24)	3413	6206	2100	88	H'(24)	-930	-3517	2666	79
H(25)	3131	5834	3139	91	H'(25)	-499	-3186	1745	85
H(26)	2451	4316	3151	79	H'(26)	183	-1661	1871	76

Orpen, Reichert & Raithby (1977). The intensities of two control reflections (indices 126 and 811), dropped steadily during the data collection, each by *ca* 9% overall; a deterioration factor was therefore applied in addition to Lorentz and polarization factors.

Structure amplitudes for 9318 unique reflections were derived.

### Structure analysis and refinement

The coordinates of the two independent W atoms were determined from a Patterson map and the remaining non-hydrogen atoms were located in successive electron-density maps. After some refinement of the parameters of the atoms (the W and Cl atoms allowed anisotropic thermal motion, the remainder refined isotropically), the coordinates of all H atoms (except the two of the hydrazido groups) were calculated (those of the methyl groups in staggered conformations) and allowed to 'ride' on the neighbouring C atoms. In later cycles, the P and N atoms were also refined with anisotropic temperature factors.

A Fourier difference synthesis then revealed one of the two hydrazido H atoms; the coordinates of the other were calculated, and positional and thermal parameters of these atoms were allowed to refine as independent parameters in the final least-squares cycles. At the conclusion of the refinement, when the atoms were refined in two large blocks (one per molecule), with 7065 reflections (*i.e.* all those with  $I > 2\sigma_I$ ) weighted according to counting *e.s.d.*'s, the agreement indices  $R$  and  $R'$  were 0.036 and 0.041.\* Final atomic coordinates and isotropic thermal parameters are in Table 1.

The scattering factors and real dispersion corrections used for C, H, N and P atoms were those incorporated in the refinement program *SHELX* (Sheldrick, 1976); for the W and Cl atoms, values for  $W^{6+}$  and  $Cl^-$  were taken from *International Tables for X-ray Crystallography* (1974).

### Computing

The diffractometer data were processed by the *CAD-4* program (Hursthouse, 1977) and absorption corrections applied in *EMPABS* (Sheldrick *et al.*, 1977). The program suite *SHELX* (Sheldrick, 1976) was used for the structure analysis and refinement. These programs were adapted for use on the Station's ICL System 4 computer by Dr J. D. Owen. Geometrical features of the structure were examined by programs for the Department's IBM 1130 computer (*X-RAY ARC*,

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35761 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1973). Most of the diagrams were drawn by the program *ORTEP* (Johnson, 1965) on the ICL System 4 computer.

### Description and discussion

There are two independent molecules of the complex  $[WCl_3\{NNH(Ph)\}(PMe_2Ph)_2]$  in the crystal. Atoms of one molecule are named W, Cl(1), *etc.*, and corresponding atoms of the other W', Cl'(1). The molecule of W, whose coordinates are in Table 1, is denoted as (I) and is shown, with the atom numbering scheme, in Fig. 1; the molecule of W', also in Table 1, is denoted as (I'). Other Roman numerals denote symmetry-related molecules, detailed at the foot of Table 4. Bold atom numbers, *e.g.* Cl(1), and for the tungsten atoms W, refer to atoms of either, or the general, molecule.

(I) and (I') are very similar in many respects and are related by a pseudo centre of symmetry with coordinates  $[0.12573(7), 0.13325(17), 0.25201(11)]$ , calculated as the weighted mean of the mid-points of all corresponding pairs of non-hydrogen atoms of the two molecules. The calculated mid-points of the outer ring atoms, *e.g.* C(55) and C(24), are furthest, *ca* 0.21 Å, from this point. The two molecules are connected about the pseudo centre by hydrogen bonds between the hydrazido H atoms, H(2), and the chloro groups, Cl(1), on the opposite molecules; the pair of molecules thus form a dimer, denoted as (I)/(I') and shown in Fig. 3.

The finding of one of the H(2) atoms in a difference map, the satisfactory refinement of both atoms, and the locations of the opposing Cl(1) atoms in ideal hydrogen-bonding positions, all confirm the ligand to be a phenylhydrazido(2-) rather than a phenyldiazenido(1-) ligand.

The dimensions for both molecules are in Table 2. All H atoms, except H(2), were in calculated, idealized positions, 1.0 Å from the bonded C atoms. The H atoms of the phosphine methyl groups were not allowed to refine away from a staggered conformation; they have not been included in any geometrical calculations.

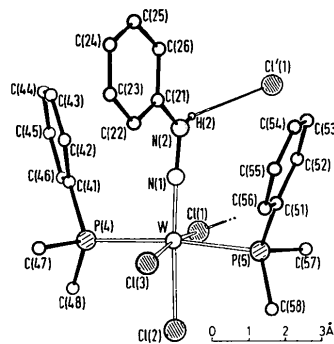


Fig. 1. Molecule (I), with atomic numbering scheme.

Table 2. Bond distances (Å) and angles (°) with *e.s.d.*'s in parentheses

	Molecule (I)	Molecule (I')		Molecule (I)	Molecule (I')		Molecule (I)	Molecule (I')
W-Cl(1)	2.411 (2)	2.424 (2)	W-Cl(3)	2.379 (2)	2.371 (2)	W-P(5)	2.520 (2)	2.519 (2)
W-Cl(2)	2.468 (2)	2.463 (2)	W-P(4)	2.543 (2)	2.548 (2)	W-N(1)	1.737 (5)	1.739 (5)
P(4)-C(41)	1.827 (6)	1.809 (7)	P(5)-C(51)	1.806 (7)	1.807 (7)	N(1)-N(2)	1.325 (8)	1.316 (8)
P(4)-C(47)	1.813 (9)	1.816 (10)	P(5)-C(57)	1.812 (9)	1.817 (10)	N(2)-H(2)	0.71 (8)	0.80 (6)
P(4)-C(48)	1.806 (8)	1.802 (9)	P(5)-C(58)	1.804 (8)	1.814 (8)	N(2)-C(21)	1.400 (10)	1.388 (9)
C(41)-C(42)	1.385 (10)	1.392 (11)	C(51)-C(52)	1.394 (11)	1.378 (12)	C(21)-C(22)	1.384 (11)	1.405 (11)
C(42)-C(43)	1.388 (10)	1.375 (12)	C(52)-C(53)	1.412 (13)	1.390 (13)	C(22)-C(23)	1.386 (11)	1.401 (10)
C(43)-C(44)	1.368 (12)	1.336 (13)	C(53)-C(54)	1.345 (15)	1.329 (15)	C(23)-C(24)	1.351 (11)	1.355 (11)
C(44)-C(45)	1.371 (11)	1.350 (13)	C(54)-C(55)	1.336 (16)	1.360 (15)	C(24)-C(25)	1.374 (14)	1.377 (13)
C(45)-C(46)	1.379 (10)	1.395 (11)	C(55)-C(56)	1.421 (15)	1.387 (13)	C(25)-C(26)	1.401 (13)	1.390 (12)
C(46)-C(41)	1.375 (10)	1.397 (11)	C(56)-C(51)	1.373 (13)	1.404 (12)	C(26)-C(21)	1.397 (10)	1.378 (10)
Cl(1)-W-Cl(2)	84.6 (1)	83.5 (1)	C(41)-P(4)-C(47)	103.4 (3)	104.9 (4)	C(52)-C(51)-C(56)	118.0 (7)	118.3 (7)
Cl(1)-W-Cl(3)	170.4 (1)	171.2 (1)	C(41)-P(4)-C(48)	105.7 (3)	105.5 (4)	C(51)-C(52)-C(53)	120.4 (8)	120.2 (8)
P(4)-W-Cl(1)	86.3 (1)	86.7 (1)	C(47)-P(4)-C(48)	103.9 (4)	102.6 (5)	C(52)-C(53)-C(54)	119.4 (9)	120.9 (10)
P(4)-W-Cl(2)	93.8 (1)	94.1 (1)	P(4)-C(41)-C(42)	118.3 (5)	120.1 (6)	C(53)-C(54)-C(55)	122.1 (10)	120.8 (10)
P(4)-W-Cl(3)	92.1 (2)	90.4 (2)	P(4)-C(41)-C(46)	122.8 (5)	122.6 (6)	C(54)-C(55)-C(56)	119.5 (11)	120.3 (10)
Cl(2)-W-Cl(3)	85.9 (1)	87.9 (1)	C(42)-C(41)-C(46)	118.9 (6)	117.3 (6)	C(55)-C(56)-C(51)	120.6 (9)	119.5 (8)
P(4)-W-Cl(1)	87.3 (1)	88.4 (1)	C(41)-C(42)-C(43)	119.3 (7)	122.1 (8)	W-N(1)-N(2)	174.4 (5)	170.5 (6)
P(4)-W-Cl(2)	86.6 (1)	85.8 (1)	C(42)-C(43)-C(44)	121.0 (7)	119.2 (9)	N(1)-N(2)-H(2)	116 (6)	112 (4)
P(4)-W-Cl(3)	176.2 (2)	172.9 (2)	C(43)-C(44)-C(45)	119.8 (7)	121.3 (8)	N(1)-N(2)-C(21)	122.9 (7)	124.2 (7)
Cl(3)-W-P(4)	91.6 (1)	90.8 (1)	C(44)-C(45)-C(46)	119.4 (7)	121.1 (9)	H(2)-N(2)-C(21)	120 (6)	123 (4)
Cl(3)-W-P(5)	87.3 (1)	87.6 (1)	C(45)-C(46)-C(41)	121.5 (7)	118.9 (8)	N(2)-C(21)-C(22)	120.9 (6)	121.5 (6)
N(1)-W-P(4)	97.4 (2)	98.3 (2)	W-P(5)-C(51)	111.5 (2)	111.2 (2)	N(2)-C(21)-C(26)	117.3 (7)	119.1 (7)
N(1)-W-P(5)	173.9 (1)	174.1 (1)	W-P(5)-C(57)	114.1 (3)	115.2 (3)	C(22)-C(21)-C(26)	121.7 (7)	119.4 (7)
P(5)-W-N(1)	94.4 (2)	94.9 (2)	W-P(5)-C(58)	114.8 (3)	115.2 (3)	C(21)-C(22)-C(23)	119.1 (6)	119.0 (6)
P(5)-W-N(1)	91.7 (2)	91.0 (2)	C(51)-P(5)-C(57)	105.9 (4)	105.9 (4)	C(22)-C(23)-C(24)	120.4 (8)	121.0 (8)
W-P(4)-C(41)	112.9 (2)	112.7 (3)	C(51)-P(5)-C(58)	105.7 (4)	105.8 (4)	C(23)-C(24)-C(25)	120.8 (9)	119.9 (8)
W-P(4)-C(47)	115.4 (2)	114.0 (3)	C(57)-P(5)-C(58)	103.6 (4)	102.4 (4)	C(24)-C(25)-C(26)	121.3 (8)	120.5 (8)
W-P(4)-C(48)	114.4 (3)	115.9 (3)	P(5)-C(51)-C(52)	121.1 (6)	122.3 (6)	C(25)-C(26)-C(21)	116.7 (8)	120.1 (8)
			P(5)-C(51)-C(56)	120.7 (6)	119.3 (6)			

Each W atom is six-coordinate, bonding three chloro groups, two phosphine groups in *trans* arrangement, and the nitrogen atom, N(1), of the phenylhydrazido ligand. The coordination pattern approximates an octahedron, with the W atoms displaced by *ca* 0.16 Å towards the hydrazido group from the 'equatorial' plane of the P atoms, Cl(1) and Cl(3) (Table 3, planes A).

The coordination dimensions, Fig. 2, in the two molecules are almost identical. The almost linear W-N-N systems appear typical of *M*-hydrazido(2-) complexes, with multiple-bond character in both W-N and N-N bonds; the W-N lengths, quite short at 1.74 Å, seem reasonable for *W<sup>v</sup>* complexes in comparison with lengths in Table XVI of the review by Chatt, Dilworth & Richards (1978), and in the *M<sup>IV</sup>* complexes described by Chatt, Fakley, Richards, Hanson & Hughes (1979). The lengths of the mutually *trans* W-P bonds are perhaps shorter than extrapolations for *W<sup>v</sup>*-P bonds in the curves given by Aslanov, Mason, Wheeler & Whimp (1970); the slight differences between the W-P(4) and W-P(5) lengths probably result from steric effects. The W-Cl bond lengths are also closer to values expected for *W<sup>IV</sup>* complexes. The mutually *trans* chloro groups are at significantly different distances from the W atoms; the involvement of the Cl(1) atoms in hydrogen bonds lengthens the W-Cl(1) contacts appreciably. The *trans* influence of the hydrazido ligand lengthens the W-Cl(2) bonds; these are about 0.09 Å longer than the W-Cl(3) bonds, showing an increase of the expected magnitude (Heath, Mason & Thomas, 1974).

In the phenylhydrazido ligands, the coordinates of the H(2) atoms refined satisfactorily and these atoms are not significantly displaced from the planes of the N-N groups (Table 3, plane C). Each of these H atoms is directed towards and is within good hydrogen-bonding distance of the Cl(1) atom of the opposite half of the dimer. Dimensions in this hydrogen-bonded dimer ring are also in Fig. 2.

The phenylhydrazido groups lie roughly in the 'central' plane, *i.e.* that of the three Cl atoms (Table 3, planes B) of each monomer. The hydrazido groups are rotated 19–21° from the central planes; the rotations are away from the neighbouring phenyl group of the P(5) phosphine ligand and towards the hydrogen-

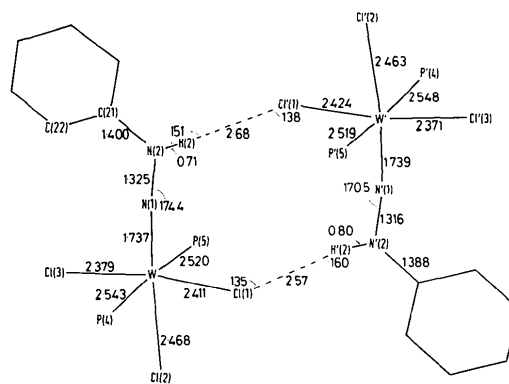


Fig. 2. Dimensions (Å and degrees) about the W atoms and in the hydrogen-bonded dimer ring.

Table 3. Mean planes

(a) Deviations (Å) from mean planes. Of the two deviations for each atom, the first refers to molecule (I), the second to molecule (I'). E.s.d.'s for deviations of atoms included in the calculation of the mean planes are: Cl 0.002–0.003; P 0.002; N 0.006–0.007; C 0.005–0.012 Å. For additional atoms, e.s.d.'s for deviations are shown in parentheses.

Plane (A): equatorial plane

Cl(1) –0.034, 0.026; Cl(3) –0.033, 0.031; P(4) 0.029, –0.025; P(5) 0.032, –0.021; W 0.165 (1), –0.151 (1); N(1) 1.900 (5), –1.885 (6); C(47) 0.064 (8), –0.048 (9); C(57) –0.162 (8), 0.409 (9)

Plane (B): central plane

Cl(1) 0.0, 0.0; Cl(2) 0.0, 0.0; Cl(3) 0.0, 0.0; W –0.037 (1), 0.051 (2); N(1) –0.120 (6), 0.196 (6); Cl'(1) –2.053 (6), 2.195 (6)

Plane (C): hydrazido group

N(1) 0.0, 0.0; N(2) 0.0, 0.0; C(21) 0.0, 0.0; H(2) 0.09 (8), –0.03 (6); C(22) –0.15 (2), 0.06 (2); C(26) 0.19 (2), –0.11 (2), Cl'(1) –0.86 (3), 0.67 (3)

Plane (D): about C(21)

N(2) –0.002, 0.003; C(21) 0.007, –0.011; C(22) –0.003, 0.004; C(26) –0.003, 0.005; N(1) –0.161 (10), 0.088 (10); H(2) –0.01 (8), –0.01 (6)

Plane (E): phenyl group of hydrazido ligand

C(21) –0.011, 0.010; C(22) 0.005, –0.007; C(23) 0.005, –0.003; C(24) –0.012, 0.013; C(25) 0.002, –0.010; C(26) 0.011, –0.005; N(2) –0.079 (10), 0.087 (10)

Plane (F): phenyl group of P(4) phosphine ligand

C(41) 0.009, –0.002; C(42) –0.012, –0.008; C(43) 0.007, 0.017; C(44) 0.003, –0.011; C(45) –0.004, –0.002; C(46) –0.004, 0.007; P(4) 0.018 (10), –0.008 (11); C(47) 1.47 (1), –1.47 (2); C(48) 0.50 (1), –0.48 (2)

Plane (G): phenyl group of P(5) phosphine ligand

C(51) –0.001, 0.002; C(52) 0.005, 0.003; C(53) –0.008, –0.005; C(54) 0.005, –0.001; C(55) 0.001, 0.010; C(56) –0.002, –0.008; P(5) 0.116 (12), –0.098 (11); C(57) –0.78 (2), 0.74 (2); C(58) –0.92 (2), 1.04 (2)

(b) Angles (°) between the normals to planes (e.s.d.'s ca 1.0°)

B–C 18.8, 21.1; B–E 16.6, 19.9; B–F 28.3, 29.4; B–G 21.5, 24.9; C–D 8.0, 4.1; D–E 2.4, 2.6

Between the corresponding planes in molecules (I) and (I')

A–A' 2.0, B–B' 2.8, C–C' 3.6, D–D' 7.0, E–E' 7.0, F–F' 0.3, G–G' 6.7

bonded Cl(1) of the opposite monomer. There are small rotations, 8.0° in (I) and 4.1° in (I'), about the N–C bond, between the hydrazido and phenyl group planes.

The two dimethylphenylphosphine groups in each molecule form a staggered arrangement about the P...P vectors, such that C(47) and C(57) lie close to the equatorial plane. The phosphine groups appear closely related by a pseudo twofold symmetry axis coincident with the W–Cl(2) bond.

This arrangement of phosphine and phenylhydrazido ligands is very similar to that of the rhenium com-

Table 4. Shorter interatomic non-bonded contacts (Å)

E.s.d.'s for distances not involving hydrogen atoms are shown in parentheses.

(a) Within the dimer (I)/(I')

<i>a</i>	<i>b</i>	<i>a</i> ... <i>b</i>	<i>a</i>	<i>b</i>	<i>a</i> ... <i>b</i>
Cl(1)	C'(52)	3.628 (8)	Cl'(1)	C(52)	3.728 (8)
C(44)	C'(57)	3.481 (12)	C'(44)	C(57)	3.462 (12)
Cl(3)	H(22)	2.82			
C(48)	H(46)	2.66	C'(48)	H'(46)	2.67
C(57)	H(52)	2.79	C'(57)	H'(52)	2.77
C(58)	H(56)	2.81	C'(58)	H'(56)	2.87

(b) Between dimers

<i>a</i> or <i>a<sub>j</sub></i>	<i>b<sub>i</sub></i> or <i>b</i>	<i>a</i> ... <i>b<sub>i</sub></i> <i>b</i> ... <i>a<sub>j</sub></i>	<i>i</i>	<i>j</i>
Cl(3)	C(48)	3.616 (8)	(VI)	(VI)
C(42)	C'(44)	3.677 (12)	(II)	(VIII)
C(44)	Cl'(2)	3.670 (8)	(IV) <sub>a</sub>	(IV)
C(45)	Cl'(2)	3.591 (8)	(IV) <sub>a</sub>	(IV)
C(45)	C'(24)	3.692 (11)	(II) <sub>a</sub>	(VIII) <sub>a</sub>
C(58)	C'(26)	3.699 (11)	(VII) <sub>a</sub>	(VII) <sub>a</sub>
C(23)	C'(43)	3.624 (12)	(II)	(VIII)
C(24)	C'(43)	3.608 (13)	(II)	(VIII)
Cl'(3)	C'(23)	3.706 (8)	(IX) <sub>a</sub>	(IX) <sub>a</sub>
C'(46)	C'(24)	3.644 (12)	(I) <sub>b</sub>	(I) <sub>a</sub>
C'(54)	C'(58)	3.641 (13)	(IV) <sub>a</sub>	(IV)
C(45)	H'(24)	2.89	(II) <sub>a</sub>	(VIII) <sub>a</sub>
C(23)	H'(43)	2.87	(II)	(VIII)
C(24)	H'(43)	2.80	(II)	(VIII)
Cl'(2)	H(45)	2.89	(IV)	(IV) <sub>a</sub>
C'(24)	H'(46)	2.95	(I) <sub>a</sub>	(I) <sub>b</sub>

*i* and *j* denote symmetry-related positions. The two molecules of a dimer (e.g. II and II') are not distinguished in the Roman numerals in this table; they have the same symmetry operators.

(I)	<i>x</i> , <i>y</i> , <i>z</i>	(VI)	$\frac{1}{2} - x$ , $\frac{1}{2} + y$ , $-z$
(II)	$\frac{1}{2} + x$ , $\frac{1}{2} - y$ , <i>z</i>	(VII)	$-x$ , $1 - y$ , $-z$
(III)	$1 - x$ , $1 - y$ , $1 - z$	(VIII)	$-\frac{1}{2} + x$ , $\frac{1}{2} - y$ , <i>z</i>
(IV)	$\frac{1}{2} - x$ , $\frac{1}{2} + y$ , $1 - z$	(IX)	$-x$ , $1 - y$ , $1 - z$
(V)	$1 - x$ , $1 - y$ , $-z$		

Subscripts *a* and *b* indicate translations parallel to **b** from the positions above, e.g. (I)<sub>a</sub> *x*,  $-1 + y$ , *z*; (I)<sub>b</sub> *x*,  $1 + y$ , *z*.

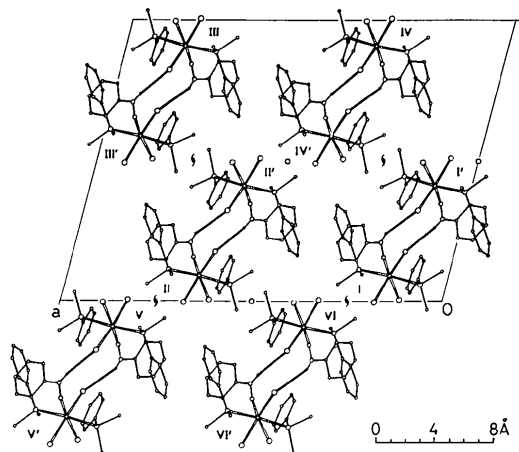


Fig. 3. Projection down the *b* axis. Roman numerals denote symmetry positions and are listed in Table 4.

Table 5. *Intermolecular contacts about symmetry positions*

E.s.d.'s for all distances are 0.01 Å.

(a) About  $(\frac{1}{2}, y, 0)$  and  $(\frac{1}{2}, y, \frac{1}{2})$ 

Atom in dimer (II)/(II')	Atom in dimer (VI)/(VI')	Distance	Atom in dimer (IV)/(IV')	Atom in dimer (I)/(I')	Distance
Cl(2)	C(57)	3.75 Å			
Cl(2)	C'(44)	3.88 *	Cl'(2)	C(44)	3.67 Å
			Cl'(2)	C(45)	3.59
C(54)	C(58)	3.76 *	C'(54)	C'(58)	3.64
			C'(55)	C'(57)	3.88
			C'(55)	C'(58)	3.88
C(58)	C'(25)	3.78 *	C'(58)	C(25)	3.82
C(58)	C'(26)	3.70 *	C'(58)	C(26)	3.73

(b) About  $(\frac{1}{2}, y, \frac{1}{2})$  and  $(\frac{1}{2}, y, 0)$ 

Atom in molecule (II')	Atom in molecule (IV')	Distance	Atom in molecule (VI)	Atom in molecule (I)	Distance
Cl'(3)	C'(47)	3.88 Å *	Cl(3)	C(47)	3.74
			Cl(3)	C(48)	3.62
Cl'(3)	C'(22)	3.78			
Cl'(3)	C'(23)	3.71 *	Cl(3)	C(23)	3.88

N.B. Subscript indicators on symmetry operators [(I), etc.] have been ignored in this table.

\* See text.

plex:  $[\text{Re}(\text{NH}_3)\text{Cl}_2(\text{PMe}_2\text{Ph})_2(\text{NNHPh})]\text{Br}$  (Mason, Thomas, Zubieta, Douglas, Galbraith & Shaw, 1974). The mean planes of all the phenyl groups are good (Table 3), but some of the substituent atoms are considerably displaced from these planes; in particular, the P(5) atoms are displaced by up to 0.12 Å from the planes of C(51) – (56).

In the crystal, the dimer pairs form discrete units, which are connected by van der Waals forces. Table 4 lists the shorter intermolecular contacts. In projection, Fig. 3, the packing arrangements about certain inversion centres and screw axes appear very similar. Short contacts between dimer pairs across the inversion centres at  $(\frac{1}{2}, y, 0)$  ( $y = 0$  and  $\frac{1}{2}$ ) and about the screw axis at  $(\frac{1}{2}, y, \frac{1}{2})$  are compared in Table 5(a) and those across the inversion centres at  $(\frac{1}{2}, y, \frac{1}{2})$  ( $y = 0$  and  $\frac{1}{2}$ ) and about the screw axis at  $(\frac{1}{2}, y, 0)$ , where the arrangements also look alike in projection, are compared in Table 5(b).

The contacts marked with an asterisk in Table 5 are similar, in both distance and direction, whether about an inversion centre or a screw axis. The packing of the dimers about these symmetry elements thus appears equally satisfactory. Some of the slight differences in arrangements of the two halves of the dimer presumably result from deviations of groups to improve these and supporting interactions (the non-asterisked contacts in the table) about the different symmetry elements.

The approximate inversion symmetry of the dimer pair, together with its placement with respect to the screw axis, leads to two non-symmetry-related monomeric components in two such dimer pairs (e.g. I and IV') having almost indistinguishable alignments in projection down the *b* axis with relative displacements of  $(a/4, c/2)$ ; this is the origin of the pseudo-systematic absence referred to above.

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