The Low-Temperature X-ray Diffraction Studies of the Heptahydridobis(tertiaryphosphine)rhenium Complexes, [ReH₇{P(C₃H₇)₂(C₆H₅)}₂] and [ReH₇{P(C₆H₅)₃}₂]

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Abstract. Crystals of [ReH₇{P(C₃H₇)₂(C₆H₅)}₂] (I) and [ReH₇{P(C₆H₅)₃}₂] (II) grow as transparent prisms from petroleum ether in the monoclinic space groups $P2_1/n$ (I*a*), $P2_1/c$ (I*b*), and $A2/a$ (II), two crystalline forms being observed for (I). (I*a*): $M_r = 581 \cdot 8$, $a = 11 \cdot 271$ (5), $b = 13 \cdot 405$ (11), $c = 17 \cdot 017$ (8) Å, $\beta = 95 \cdot 53$ (4)°, $U = 2559$ (3) Å³ (200 K), $Z = 4$, $D_x = 1 \cdot 47$, $D_m = 1 \cdot 46$ g cm⁻³, $F(000) = 1176$; (I*b*): $M_r = 581 \cdot 8$, $a = 16 \cdot 058$ (9), $b = 12 \cdot 311$ (6), $c = 14 \cdot 307$ (7) Å, $\beta = 114 \cdot 27$ (4)°, $U = 2578$ (2) Å³ (210 K), $Z = 4$, $D_x = 1 \cdot 50$, $D_m = 1 \cdot 49$ g cm⁻³, $F(000) = 1176$; (II) $M_r = 717 \cdot 8$, $a = 18 \cdot 666$ (6), $b = 9 \cdot 301$ (6), $c = 18 \cdot 304$ (6) Å, $\beta = 108 \cdot 99$ (3)°, $U = 3005$ (3) Å³ (220 K), $Z = 4$, $D_x = 1 \cdot 56$, $D_m = 1 \cdot 54$ g cm⁻³, $F(000) = 1432$. $R = 0 \cdot 038$, $0 \cdot 046$ and $0 \cdot 031$ for (I*a*), (I*b*) and (II) respectively. The hydride ligands were not located. Mean Re–P bond lengths and P–Re–P bond angles are $2 \cdot 413$ (2), $2 \cdot 423$ (2) and $2 \cdot 427$ (2) Å, and $147 \cdot 0$ (1), $141 \cdot 0$ (1), and $138 \cdot 9$ (1)° for (I*a*), (I*b*), and (II), respectively.

Introduction. The title compounds belong to a series of transition-metal polyhydride complexes which have been known for some years (Malatesta, Freni & Valenti, 1961; Chatt & Coffey, 1969; Moss & Shaw, 1968; Douglas & Shaw, 1970; Pennella, 1971; Tebbe, 1973). However, very few have been structurally characterized by the exact location of the hydride ligands from single-crystal neutron-diffraction studies (Hart, Bau & Koetzle, 1977; Bau, Carroll, Hart, Teller & Koetzle, 1977). The recent study of [WH₆(PPr$_2^i$Ph)₃] (Howard, Gregson, Spencer & Turner, 1981; Gregson, Howard, Nicholls, Spencer & Turner, 1980) revealed a tricapped trigonal prismatic structure (C_{2v}) with the phosphine ligands occupying one capping and two eclipsed prism vertices, contrary to intuitive expectations of a D_{3h} structure with the phosphines placed at the capping positions. Bau (1978) reported preliminary results on [ReH₇(PMe₂Ph)₂] in which the P–Re–P angle of $146 \cdot 8$ (1)° is inconsistent with a structure having the phosphines placed at two of three capping positions. Single-crystal neutron-diffraction studies provide the best technique for accurately defining the structures of hydrido complexes of the type [ReH₇(PR₃)₂] and thus we embarked upon the synthesis

of various derivatives. In this paper we report the results of the full X-ray diffraction studies of [ReH₇(PPr$_2^i$Ph)₂] (I) and [ReH₇(PPh₃)₂] (II), preliminary to any neutron investigations.

Experimental. The method suggested by Baudry & Ephritikhine (1980) was used to synthesize (II) and suitable crystals were grown by slow cooling of a saturated dichloromethane solution. Complex (I) was prepared from [ReOCl₃(PPr$_2^i$Ph)₂] by a similar method and the crude material was purified by chromatography on alumina using petroleum ether as eluant. Slow cooling (293–277 K) of a saturated solution of (I) in petroleum ether gave large colourless prisms and plates (m.p. 364 K).

Room-temperature single-crystal X-ray investigations preceded all low-temperature studies but only results from the latter are presented here. No phase changes were observed between 293 and 200 K, the lower temperature at which the diffracted intensities were recorded using a Nicolet *P*3*m* four-circle automated diffractometer, according to methods described earlier (Modinos & Woodward, 1974), using the parameters in Table 1. All structures were solved by Patterson and Fourier techniques, using the unique data

Table 1. *Additional crystal and experimental data for* [ReH₇(PPr$_2^i$Ph)₂] (I*a*, I*b*) *and* [ReH₇(PPh₃)] (II)

	(I*a*)	(I*b*)	(II)
λ (Å) Mo $K\alpha$	0·71069	0·71069	0·71069
μ(cm⁻¹)	49·4	49·1	41·3
U(Å³)(292K)	2635 (3)	2628 (2)	3074 (2)
D_x(292K)(g cm⁻³)	1·47	1·50	1·56
2θ range (°)	2·9–60	2·9–55	2·9–55
Independent data	6819	5940	3448
Data used	5515	5138	3113
$I > n\sigma(I)$: n	6	6	6
Crystal size (mm)	0·35 × 0·4 × 0·5	0·64 × 0·31 × 0·25	0·2 × 0·15 × 0·35
R (R')	0·038 (0·042)	0·046 (0·049)	0·031 (0·031)
Weighting scheme $[\sigma^2(F) + g\,|F^2\,|\,]^{-1}$: g	0·0012	0·0007	0·0005
Scan type	ω:2θ	ω	ω:2θ
Refinement		Block cascaded least squares	
Program system		*SHELXTL* (Nicolet XRD, 1981)	
Scattering factors		*International Tables for X-ray Crystallography* (1974) (anomalous-dispersion effects included)	
Function minimized		$\sum w(F_o - |F_c|)^2$	

(Table 1) corrected for the effects of Lorentz, polarization and of X-ray absorption. All the methyl H atoms were refined isotropically as members of rigid groups (H–C, 0·96 Å); phenyl H atoms were refined either isotropically or as atoms 'riding' (Busing & Levy, 1964) on the attached C atoms, as also were the tertiary H atoms of the Pr^i groups.

The non-hydrogen atoms were given anisotropic thermal parameters. Final difference density syntheses showed significant residuals (± 2 e Å^{-3}) only in positions very close to the Re atoms, and rather weak peaks in the regions where hydride ligands might be expected. However, these did not refine for any of the three structures. Low-angle (sin$\theta < 0 < 0·3$) difference density maps were calculated but failed to show the positions of the hydride ligands. In view of the appearance on these same maps of most of the aromatic and aliphatic H atoms, but also accepting that there are difficulties involved in locating H atoms from third-row elements, we were suspicious of a disorder amongst these core hydrides which would lead to a weaker and more diffuse density distribution and hence even less likelihood of locating these particular H atoms.

Discussion. Our X-ray analyses confirm the geometry of the ReP_2 skeleton determined originally by Bau *et al.* (1977), but unfortunately do not lead to the complete elucidation of the structures without the location of the hydride ligands. Atomic coordinates, important bond lengths and interbond angles are given in Tables 2–7. Fig. 1 and 2 show the skeletons of (I*a*) and (II) with their atomic numbering schemes.* Unit-cell packing diagrams are given in Figs. 3,4,5.

The major points of interest we report here are the structural variations involved in the two crystalline forms of (I). The difference in the unit-cell volumes is small (7 Å^3 at 293 K) yet there are significant variations in the molecular parameters, noticeably the Re–P separations, presumably a result of the packing modifications. We remarked in the first instance on the disparity in the chemically equivalent Re–P bonds for (I*a*) 2·404 (2) and 2·423 (2) Å, which led us directly to study (II), hoping to ascertain whether this observation was in any way related to the nature of the phosphine. However, since in (II) the molecule lies astride a twofold rotation axis (Fig. 2), the Re–P separations are necessarily equal, 2·427 (1) Å, and in fact longer than the mean for (I*a*) [2·413 (2) Å] with a correspondingly smaller P–Re–P angle of 138·9 (1)°.

Table 2. *Atomic positional (fractional coordinates) parameters with estimated standard deviations in parentheses for* (I*a*) $\lfloor ReH_7(PPr_2^iPh)_2\rfloor$ (*form* 1)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq} (Å^2)
Re	0·95450 (2)	−0·03699 (1)	0·76112 (1)	0·0269 (1)
P(1)	0·84293 (10)	0·11132 (9)	0·78409 (7)	0·0237 (3)
P(2)	1·12320 (10)	−0·10912 (9)	0·70349 (7)	0·0225 (3)
C(11)	0·8987 (5)	0·1910 (4)	0·8682 (3)	0·028 (1)
C(12)	0·8472 (6)	0·2845 (4)	0·8773 (4)	0·035 (2)
C(13)	0·8826 (6)	0·3441 (5)	0·9419 (4)	0·043 (2)
C(14)	0·9678 (7)	0·3111 (6)	0·9993 (4)	0·046 (2)
C(15)	1·0182 (7)	0·2190 (6)	0·9920 (4)	0·046 (2)
C(16)	0·9844 (6)	0·1592 (5)	0·9270 (4)	0·036 (2)
C(1)	0·7919 (7)	0·1573 (6)	0·6198 (4)	0·044 (1)
C(2)	0·8280 (5)	0·2035 (4)	0·7022 (4)	0·030 (2)
C(3)	0·9429 (6)	0·2622 (5)	0·6989 (4)	0·038 (2)
C(4)	0·5995 (7)	0·0553 (6)	0·7443 (6)	0·054 (2)
C(5)	0·6870 (5)	0·0960 (4)	0·8106 (4)	0·038 (2)
C(6)	0·6869 (7)	0·0319 (5)	0·8851 (6)	0·054 (1)
C(21)	1·0924 (5)	−0·2078 (4)	0·6301 (3)	0·025 (1)
C(22)	1·1749 (5)	−0·2817 (4)	0·6165 (4)	0·032 (2)
C(23)	1·1489 (6)	−0·3532 (4)	0·5571 (4)	0·035 (2)
C(24)	1·0421 (6)	−0·3504 (5)	0·5109 (4)	0·037 (2)
C(25)	0·9608 (6)	−0·2771 (5)	0·5230 (4)	0·037 (1)
C(26)	0·9852 (5)	−0·2065 (4)	0·5817 (4)	0·030 (2)
C(7)	1·3299 (6)	−0·0578 (5)	0·6258 (5)	0·041 (1)
C(8)	1·2096 (5)	−0·0189 (4)	0·6487 (3)	0·028 (1)
C(9)	1·1370 (6)	0·0190 (5)	0·5744 (4)	0·034 (2)
C(10)	1·2922 (6)	−0·0875 (5)	0·8355 (4)	0·042 (2)
C(01)	1·2374 (5)	−0·1651 (4)	0·7751 (3)	0·027 (1)
C(02)	1·1895 (6)	−0·2539 (5)	0·8189 (4)	0·039 (2)

Table 3. *Atomic positional (fractional coordinates) parameters with estimated standard deviations in parentheses for* (I*b*) $[ReH_7(PPr_2^iPh)_2]$ (*form* 2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq} (Å^2)
Re	0·26269 (1)	0·43403 (2)	0·63042 (1)	0·0200 (4)
P(1)	0·26666 (9)	0·36639 (11)	0·79127 (10)	0·0197 (4)
P(2)	0·24712 (9)	0·60183 (12)	0·53624 (10)	0·0197 (4)
C(11)	0·1777 (4)	0·4166 (5)	0·8306 (5)	0·023 (2)
C(12)	0·1407 (4)	0·5212 (5)	0·8020 (5)	0·026 (2)
C(13)	0·0760 (5)	0·5624 (5)	0·8335 (5)	0·029 (2)
C(14)	0·0451 (5)	0·5004 (7)	0·8921 (5)	0·037 (2)
C(15)	0·0804 (5)	0·3973 (7)	0·9222 (6)	0·040 (3)
C(16)	0·1454 (5)	0·3555 (6)	0·8912 (5)	0·035 (2)
C(1)	0·1716 (5)	0·1688 (6)	0·7261 (5)	0·039 (2)
C(2)	0·2620 (4)	0·2161 (5)	0·8035 (3)	0·026 (2)
C(3)	0·3435 (5)	0·1608 (5)	0·7963 (5)	0·034 (2)
C(4)	0·3758 (4)	0·5288 (5)	0·9220 (5)	0·028 (2)
C(5)	0·3731 (4)	0·4044 (5)	0·9046 (5)	0·024 (2)
C(6)	0·3855 (4)	0·3446 (6)	1·0031 (5)	0·030 (2)
C(21)	0·3072 (4)	0·7239 (5)	0·6099 (4)	0·021 (2)
C(22)	0·3954 (4)	0·7112 (3)	0·6863 (5)	0·026 (2)
C(23)	0·4463 (5)	0·8028 (6)	0·7356 (5)	0·033 (2)
C(24)	0·4096 (5)	0·9058 (6)	0·7112 (5)	0·036 (2)
C(25)	0·3225 (6)	0·9178 (5)	0·6363 (5)	0·034 (2)
C(26)	0·2705 (5)	0·8279 (5)	0·5852 (5)	0·028 (2)
C(7)	0·3947 (5)	0·5897 (6)	0·4774 (5)	0·034 (2)
C(8)	0·2901 (4)	0·5973 (5)	0·4335 (5)	0·024 (2)
C(9)	0·2582 (5)	0·6921 (6)	0·3570 (5)	0·037 (2)
C(10)	0·0703 (5)	0·5694 (5)	0·3842 (6)	0·036 (2)
C(01)	0·1277 (4)	0·6495 (5)	0·4684 (5)	0·028 (2)
C(02)	0·0816 (5)	0·6745 (6)	0·5407 (5)	0·035 (2)

Table 4. *Atomic positional (fractional coordinates) parameters with estimated standard deviations in parentheses for* (II) [ReH$_7$(PPh$_3$)$_2$]

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq} (Å^2)
Re	0·75000	−0·01681 (2)	1·00000	0·0176 (1)
P	0·64550 (5)	0·07476 (10)	0·89278 (5)	0·0160 (3)
C(11)	0·6163 (3)	0·2583 (4)	0·9086 (3)	0·018 (1)
C(12)	0·6703 (3)	0·3681 (5)	0·9247 (3)	0·023 (1)
C(13)	0·6511 (3)	0·5091 (5)	0·9374 (3)	0·028 (1)
C(14)	0·5780 (3)	0·5394 (5)	0·9352 (3)	0·032 (1)
C(15)	0·5233 (3)	0·4321 (5)	0·9178 (3)	0·030 (2)
C(16)	0·5425 (3)	0·2920 (5)	0·9042 (3)	0·024 (1)
C(21)	0·5554 (3)	−0·0238 (4)	0·8652 (3)	0·019 (1)
C(22)	0·5100 (3)	−0·0394 (5)	0·7883 (3)	0·026 (1)
C(23)	0·4383 (3)	−0·1030 (6)	0·7693 (3)	0·034 (1)
C(24)	0·4117 (3)	−0·1490 (5)	0·8280 (3)	0·031 (1)
C(25)	0·4554 (3)	−0·1352 (5)	0·9047 (3)	0·029 (1)
C(26)	0·5276 (3)	−0·0749 (5)	0·9229 (3)	0·024 (1)
C(31)	0·6630 (3)	0·0965 (4)	0·8003 (3)	0·020 (1)
C(32)	0·6985 (3)	−0·0149 (5)	0·7733 (3)	0·029 (1)
C(33)	0·7119 (4)	−0·0015 (6)	0·7029 (3)	0·036 (2)
C(34)	0·6908 (3)	0·1220 (6)	0·6590 (3)	0·029 (1)
C(35)	0·6556 (3)	0·2318 (5)	0·6845 (3)	0·026 (1)
C(36)	0·6409 (3)	0·2195 (5)	0·7548 (3)	0·024 (1)

Table 5. *Selected bond lengths* (Å) *and interbond angles* (°) *with estimated standard deviations in parentheses for* (Ia) [ReH$_7$(PPr$_2^i$Ph)$_2$] *(form 1)*

Re–P(1)	2·404 (2)	Re–P(2)	2·423 (2)
P(1)–C(11)	1·847 (5)	P(1)–C(2)	1·858 (5)
P(1)–C(5)	1·867 (6)	P(2)–C(21)	1·829 (5)
P(2)–C(8)	1·859 (5)	P(2)–C(01)	1·844 (5)
C(11)–C(12)	1·396 (7)	C(11)–C(16)	1·389 (7)
C(12)–C(13)	1·386 (9)	C(13)–C(14)	1·375 (9)
C(14)–C(15)	1·370 (10)	C(16)–C(15)	1·390 (9)
C(2)–C(1)	1·550 (8)	C(2)–C(3)	1·521 (8)
C(5)–C(4)	1·526 (10)	C(5)–C(6)	1·532 (10)
C(21)–C(22)	1·394 (7)	C(21)–C(26)	1·396 (7)
C(22)–C(23)	1·403 (8)	C(23)–C(24)	1·373 (9)
C(24)–C(25)	1·373 (9)	C(26)–C(25)	1·384 (8)
C(8)–C(7)	1·537 (8)	C(8)–C(9)	1·525 (7)
C(01)–C(10)	1·549 (8)	C(01)–C(02)	1·530 (8)
P(1)–Re–P(2)	147·0 (1)	Re–P(1)–C(11)	117·4 (2)
Re–P(1)–C(2)	116·0 (2)	C(11)–P(1)–C(2)	101·3 (2)
Re–P(1)–C(5)	117·9 (2)	C(11)–P(1)–C(5)	97·7 (3)
C(2)–P(1)–C(5)	103·6 (3)	Re–P(2)–C(21)	117·4 (2)
Re–P(2)–C(8)	114·4 (2)	C(21)–P(2)–C(8)	101·7 (2)
Re–P(2)–C(01)	114·8 (2)	C(21)–P(2)–C(01)	103·4 (2)
C(8)–P(2)–C(01)	103·3 (2)	P(1)–C(11)–C(12)	119·4 (4)
P(1)–C(11)–C(16)	122·8 (4)	C(12)–C(11)–C(16)	117·6 (5)
C(11)–C(12)–C(13)	121·0 (5)	C(12)–C(13)–C(14)	120·4 (6)
C(13)–C(14)–C(15)	119·5 (6)	C(14)–C(15)–C(16)	120·6 (6)
C(11)–C(16)–C(15)	121·0 (6)	P(1)–C(2)–C(1)	114·2 (4)
P(1)–C(2)–C(3)	110·9 (4)	C(1)–C(2)–C(3)	108·9 (5)
P(1)–C(5)–C(4)	114·6 (5)	P(1)–C(5)–C(6)	109·7 (4)
C(4)–C(5)–C(6)	111·1 (5)	P(2)–C(21)–C(22)	122·8 (4)
P(2)–C(21)–C(26)	119·4 (4)	C(22)–C(21)–C(26)	117·6 (4)
C(21)–C(22)–C(23)	120·6 (5)	C(22)–C(23)–C(24)	120·3 (5)
C(23)–C(24)–C(25)	119·7 (5)	C(24)–C(25)–C(26)	120·5 (5)
C(21)–C(26)–C(25)	121·2 (5)	P(2)–C(8)–C(7)	115·1 (4)
P(2)–C(8)–C(9)	111·6 (4)	C(7)–C(8)–C(9)	108·6 (5)
P(2)–C(01)–C(10)	111·9 (4)	P(2)–C(01)–C(02)	112·4 (4)
C(10)–C(01)–C(02)	109·6 (4)		

Table 6. *Selected bond lengths* (Å) *and interbond angles* (°) *with estimated standard deviations in parentheses for* (Ib) [ReH$_7$(PPr$_2^i$Ph)$_2$] *(form 2)*

Re–P(1)	2·423 (2)	Re–P(2)	2·423 (2)
P(1)–C(11)	1·844 (7)	P(1)–C(2)	1·863 (6)
P(1)–C(5)	1·868 (5)	P(2)–C(21)	1·861 (5)
P(2)–C(8)	1·864 (7)	P(2)–C(01)	1·852 (5)
C(11)–C(12)	1·406 (8)	C(11)–C(16)	1·400 (10)
C(12)–C(13)	1·388 (10)	C(13)–C(14)	1·368 (11)
C(14)–C(15)	1·385 (10)	C(16)–C(15)	1·390 (11)
C(2)–C(1)	1·533 (8)	C(2)–C(3)	1·516 (10)
C(5)–C(4)	1·550 (8)	C(5)–C(6)	1·529 (9)
C(21)–C(22)	1·397 (7)	C(21)–C(26)	1·392 (8)
C(22)–C(23)	1·401 (8)	C(23)–C(24)	1·382 (9)
C(24)–C(25)	1·376 (9)	C(26)–C(25)	1·397 (8)
C(8)–C(7)	1·535 (9)	C(8)–C(9)	1·537 (8)
C(01)–C(10)	1·536 (8)	C(01)–C(02)	1·532 (11)
P(1)–Re–P(2)	141·0 (1)	Re–P(1)–C(11)	117·0 (2)
Re–P(1)–C(2)	116·4 (2)	C(11)–P(1)–C(2)	103·8 (3)
Re–P(1)–C(5)	113·3 (2)	C(11)–P(1)–C(5)	101·4 (3)
C(2)–P(1)–C(5)	103·0 (2)	Re–P(2)–C(21)	117·6 (2)
Re–P(2)–C(8)	115·2 (2)	C(21)–P(2)–C(8)	101·4 (3)
Re–P(2)–C(01)	114·2 (2)	C(21)–P(2)–C(01)	103·0 (3)
C(8)–P(2)–C(01)	103·6 (3)	P(1)–C(11)–C(12)	120·4 (5)
P(1)–C(11)–C(16)	122·7 (5)	C(12)–C(11)–C(16)	116·9 (6)
C(11)–C(12)–C(13)	121·6 (6)	C(12)–C(13)–C(14)	120·3 (6)
C(13)–C(14)–C(15)	119·7 (7)	C(14)–C(15)–C(16)	120·4 (7)
C(11)–C(16)–C(15)	121·1 (6)	P(1)–C(2)–C(1)	111·9 (4)
P(1)–C(2)–C(3)	111·7 (5)	C(1)–C(2)–C(3)	111·6 (5)
P(1)–C(5)–C(4)	110·0 (3)	P(1)–C(5)–C(6)	113·9 (4)
C(4)–C(5)–C(6)	110·1 (5)	P(2)–C(21)–C(22)	118·4 (4)
P(2)–C(21)–C(26)	122·1 (3)	C(22)–C(21)–C(26)	119·2 (5)
C(21)–C(22)–C(23)	119·9 (5)	C(22)–C(23)–C(24)	120·7 (5)
C(23)–C(24)–C(25)	119·1 (6)	C(24)–C(25)–C(26)	121·3 (6)
C(21)–C(26)–C(25)	119·7 (5)	P(2)–C(8)–C(7)	112·1 (4)
P(2)–C(8)–C(9)	114·6 (5)	C(7)–C(8)–C(9)	109·0 (6)
P(2)–C(01)–C(10)	111·5 (4)	P(2)–C(01)–C(02)	113·2 (4)
C(10)–C(01)–C(02)	110·9 (5)		

Table 7. *Selected bond lengths* (Å) *and interbond angles* (°) *with estimated standard deviations in parentheses for* (II) [ReH$_7$(PPh$_3$)$_2$]

Re–P	2·427 (1)	Re–P'*	2·427 (1)
P–C(11)	1·843 (4)	P–C(21)	1·836 (4)
P–C(31)	1·837 (5)	C(11)–C(12)	1·397 (6)
C(11)–C(16)	1·391 (6)	C(12)–C(13)	1·399 (6)
C(13)–C(14)	1·380 (8)	C(14)–C(15)	1·390 (7)
C(16)–C(15)	1·395 (6)	C(21)–C(22)	1·394 (5)
C(21)–C(26)	1·403 (7)	C(22)–C(23)	1·400 (7)
C(23)–C(24)	1·389 (8)	C(24)–C(25)	1·380 (6)
C(26)–C(25)	1·396 (6)	C(31)–C(32)	1·403 (7)
C(31)–C(36)	1·395 (6)	C(32)–C(33)	1·397 (8)
C(33)–C(34)	1·383 (7)	C(34)–C(35)	1·375 (7)
C(36)–C(35)	1·405 (7)		
P–Re–P'*	138·9 (1)	Re–P–C(11)	113·5 (1)
Re–P–C(21)	118·1 (1)	C(11)–P–C(21)	102·4 (2)
Re–P–C(31)	116·6 (1)	C(11)–P–C(31)	101·1 (2)
C(21)–P–C(31)	102·9 (2)	P–C(11)–C(12)	118·7 (3)
P–C(11)–C(16)	122·5 (3)	C(12)–C(11)–C(16)	118·7 (4)
C(11)–C(12)–C(13)	120·9 (4)	C(12)–C(13)–C(14)	119·4 (4)
C(13)–C(14)–C(15)	120·4 (4)	C(14)–C(15)–C(16)	119·9 (5)
C(11)–C(16)–C(15)	120·5 (4)	P–C(21)–C(22)	122·1 (4)
P–C(21)–C(26)	119·5 (4)	C(22)–C(21)–C(26)	118·2 (4)
C(21)–C(22)–C(23)	120·8 (5)	C(22)–C(23)–C(24)	119·4 (4)
C(23)–C(24)–C(25)	121·0 (4)	C(24)–C(25)–C(26)	119·1 (5)
C(21)–C(26)–C(25)	121·3 (4)	P–C(31)–C(32)	119·3 (3)
P–C(31)–C(36)	122·2 (3)	C(32)–C(31)–C(36)	118·5 (4)
C(31)–C(32)–C(33)	120·4 (4)	C(32)–C(33)–C(34)	120·5 (5)
C(33)–C(34)–C(35)	119·8 (5)	C(34)–C(35)–C(36)	120·5 (4)
C(31)–C(36)–C(35)	120·4 (4)		

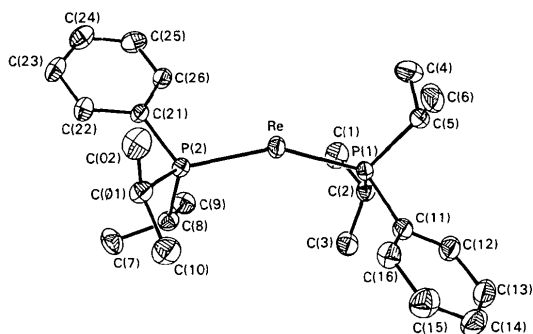* Atom P' is related to atom P by the twofold rotation axis.

Fig. 1. Molecular structure of [ReH₇(PPr₂ᶦPh)₂], form (Ia); the numbering scheme is common to (Ia) and (Ib), hence (Ib) is omitted for brevity.
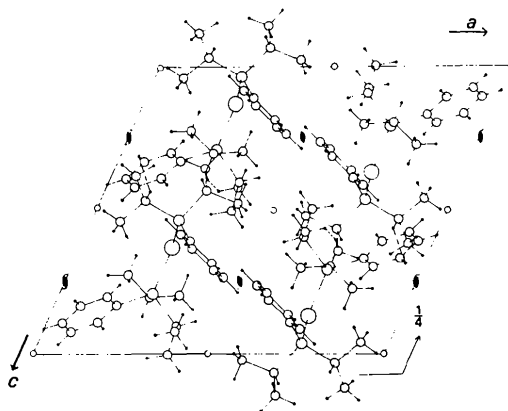

Fig. 4. Unit-cell contents of (Ib) viewed along **b** towards the origin.
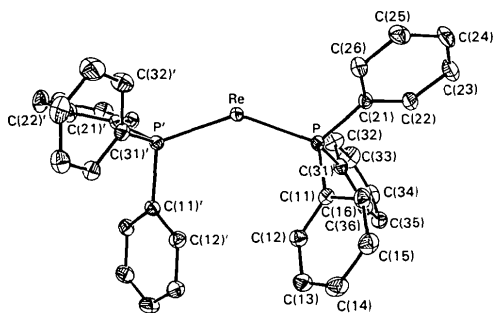

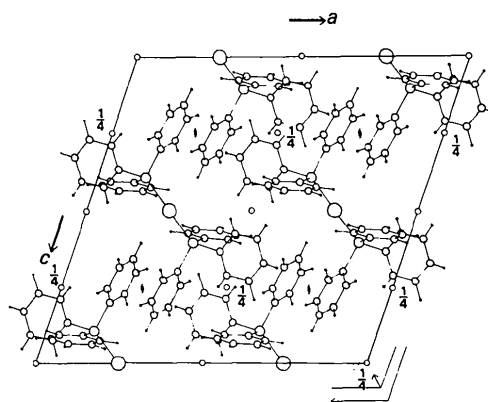Fig. 2. Molecular structure and atomic numbering scheme for [ReH₇(PPh₃)₂].

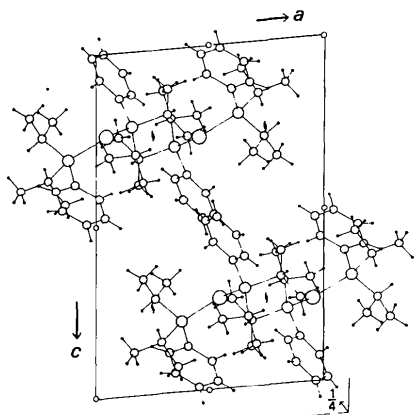Fig. 5. Unit-cell contents of (II) viewed along **b** towards the origin.

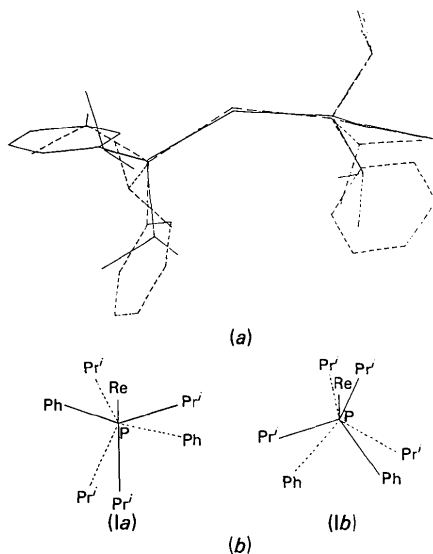Fig. 3. Unit-cell contents of (Ia) viewed along **b** towards the origin.

Fig. 6.(a) Projection of (Ia) and (Ib) onto the ReP₂ plane of (Ia) [(Ia) continuous line, (Ib) dashed line]. (b) Relative orientation of phenyl groups for (Ia) and (Ib), viewed along P(1)—P(2) vector.

The second modification of (I), which grew under apparently identical conditions from equivalently prepared solutions, was discovered whilst checking samples for the neutron diffraction experiment. A full structural study at approximately the same temperature was carried out to determine exactly the differences which would cause such a significant unit-cell, albeit small volume, change. Both crystalline forms are stable and not apparently interconvertible. The relative rotation of the ligand groups about the Re–P vectors which results in a different molecular packing and the subsequent changes observed are illustrated in Fig. 6. Fig. 6(a) shows a projection of the two forms onto the ReP$_2$ plane of (Ia), while Fig. 6(b) shows schematically the *staggered v gauchoid* orientations of the phenyl groups viewed along the Re–P(1) vector. In (Ia) the phenyl groups are oriented almost perpendicular to the ReP$_2$ plane (mean angle 84°) whilst in (Ib), they lie at a mean angle of 54° to this plane. The shortest intra- and intermolecular contacts are quite similar for both complexes and are discussed below.

In (Ib) the Re–P distances are equal with a value, 2·423 (2) Å, between those observed for (Ia) and (II), and an intermediate P–Re–P angle of 141°. The values for the Re–P separations all fall within previously recorded ranges, *i.e.* 2·333–2·498 Å; the longer value (2·498 Å) observed by Ciani, Giusto, Manassero & Albinati (1976) is attributed to the *trans* influence of a hydride ligand and the shortest (2·333 Å) derives from the neutron diffraction study of [Re$_2$H$_8$(PPhEt$_2$)$_4$] by Bau *et al.* (1977).

The geometries of the ligand atoms are not particularly unusual for any of the three compounds and show a variation of P–C distances which relates to the donor–acceptor characters of the ligand groups, namely the mean P–C(phenyl) > mean P–C(Pr^i), and similarly the 'tetrahedral' angles around the P atoms show the angles Re–P–C > C–P–C (mean values 116 *v* 102°), a feature that has been observed previously (Ashworth, Berry, Howard, Laguna & Stone, 1980; Auburn *et al.*, 1980). Consequent upon the slightly smaller angles C–P–C for (Ia), the intramolecular close contacts of < 3 Å between the two α-C atoms of the two isopropyl groups and between these and the α-C atoms of the phenyl groups are all less than in (Ib). This is more marked for the phosphine group closest to the Re atom, *i.e.* P(1). The shortest intermolecular contacts occur between the idealized positions of the H atoms of adjacent molecules, H(phenyl)···H(methyl) 2·25 Å in (Ia) and in (Ib), whilst in (II) it is between two phenyl H atoms related by a centre of symmetry (2·26 Å). These close contacts are illustrated in the unit-cell packing diagrams for (Ia) and (Ib), Figs. 3 and 4.

Without conclusive evidence for the hydride ligand positions to define completely the molecular geometry, we would conclude that the variations in the skeletal geometry arise from the subtle ligand orientational differences which result in dissimilar packing arrangements of these chemically identical molecules.

However, there remains the possibility of a different basic geometry for each of the two complexes (Ia) and (Ib), either the mono-capped square antiprism or the predicted tricapped trigonal prism. This we hope to be able to resolve from the neutron diffraction experiments.

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