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The X-ray Structures of $H_5Re(PMe_2Ph)_3$ and $H_7Re(PMe_2Ph)_2$

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The structures of $H_5Re(PMe_2Ph)_3$ and $H_7Re(PMe_2Ph)_2$ have been solved by single-crystal X-ray diffraction methods. Although the hydride ligands could not be directly located in this study, the overall structure of the complexes could be deduced from a knowledge of the central rhenium/phosphorus core of the molecules. The ReP_3 skeleton of $H_5Re(PMe_2Ph)_3$ has distorted pyramidal geometry (P–Re–P angles 149.5°, 101.9°, 99.8°) consistent with a dodecahedral structure for the H_5ReP_3 core. The ReP_2 backbone of $H_7Re(PMe_2Ph)_2$ is bent (P–Re–P angle 146.8°), suggesting a tricapped trigonal prismatic geometry for the H_7ReP_2 core in which the P atoms are placed in opposing axial and equatorial positions. Crystallographic details: $H_5Re(PMe_2Ph)_3$: space group $P2_1/c$ (monoclinic); $a = 6.876(3)$ Å, $b = 19.493(7)$ Å, $c = 19.646(8)$ Å, $\beta = 103.26(2)°$, $V = 2563.0$ Å^3, $Z = 4$; $R = 6.7\%$ for 2067 reflections. $H_7Re(PMe_2Ph)_2$: space group $P2_1/n$ (monoclinic); $a = 19.083(17)$ Å, $b = 6.337(4)$ Å, $c = 15.234(13)$ Å, $\beta = 93.72(4)°$, $V = 1834.0$ Å^3, $Z = 4$; $R = 5.0\%$ for 1672 reflections.

Introduction

During the past few years, we have been involved in the structural characterization of polyhydrido complexes of the form H_xML_y, where L is a tertiary phosphine. Most of these compounds were first prepared in the 1960's by Chatt, Shaw and co-workers [2–5] and are interesting structurally because of (a) their high co-ordination number and (b) the unusual feature of a large number of hydride ligands attached to the central metal atom. In earlier publications we have reported the results of neutron diffraction studies of $H_4Os(PMe_2Ph)_3$ [6] and $H_8Re_2(PEt_2Ph)_4$ [7] and the X-ray diffraction structure of $H_3Ir(PMe_2Ph)_3$ [8]. In this paper we describe the results of X-ray work on the eight-coordinate complex $H_5Re(PMe_2Ph)_3$ (*I*) and the nine-coordinate complex $H_7Re(PMe_2Ph)_2$ (*II*).

Experimental

All preparations were based on the original synthetic procedure of Chatt and co-workers [3] and were carried out under a nitrogen atmosphere with freshly distilled, dried and degassed solvents. Ethanol and chlorinated solvents used in the preparation of the chloride complexes were degassed by bubbling nitrogen through the solvents for half an hour prior to use. Drying agents for other solvents used in the preparation are Na/benzophenone for tetrahydrofuran (THF) and calcium hydride for hexane, toluene and benzene.

$ReCl_3(PMe_2Ph)_3$

First, 2.0 g of $KReO_4$ and 6 ml of 12 *N* HCl were added to 100 ml of ethanol in a Schlenk tube fitted with a condenser. Then 7.5 ml of PMe_2Ph was added and the mixture was heated at reflux for 18 hours. Upon cooling, an orange crystalline material precipitated. This solid was dissolved in 35 ml of CH_2Cl_2 and a pale yellow impurity removed by filtration. Recrystallization from CH_2Cl_2/ethanol yielded 4.1 g (84% yield) of the product as orange crystals.

$ReCl_4(PMe_2Ph)_2$

The tetrachloro species was prepared by addition of 0.05 g of $ReCl_3(PMe_2Ph)_3$ to 25 ml of CCl_4 and heating at reflux for 24 hours. Reducing the volume of the purple solution gave a purple solid, which was recrystallized from CH_2Cl_2/hexane yielding 0.30 g (70% yield) of $ReCl_4(PMe_2Ph)_2$.

$H_5Re(PMe_2Ph)_3$ (*I*)

The rhenium pentahydride was prepared by dissolving 0.35 g of $ReCl_3(PMe_2Ph)_3$ in 15 ml of THF and adding 0.15 g of $LiAlH_4$ in portions. The mixture was heated at reflux for 90 minutes and hydrolyzed with wet THF (10% water) after cooling to −20 °C. After removal of the THF *in vacuo*, the solid was extracted with hexane and isolated by removal of the solvent. Recrystallization from hexane or ethanol yielded clear crystals of $H_5Re(PMe_2Ph)_3$ (0.18 g, 61% yield). The product was identified via its ^1H NMR spectrum in d^6-benzene: δ 7.0–7.9 ppm

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[m, 15 H], 1.89 [d, 18 H, J(P–H) = 7 Hz], –5.56 [q, 5 H, J(P–H) = 18 Hz].

$H_7Re(PMe_2Ph)_2$ (II)

The rhenium heptahydride was prepared by dissolving 0.50 g of $ReCl_4(PMe_2Ph)_2$ in 15 ml of THF and adding 0.14 g of $LiAlH_4$ in portions. The mixture was heated at reflux for 30 minutes and hydrolyzed with wet THF. The solvent was removed *in vacuo* and the residue was extracted with methanol. Recrystallization from hexane yielded 0.11 g of $H_7Re(PMe_2Ph)_2$ (29% yield). The product was identified via its ^1H NMR spectrum in d^6-benzene: δ 7.0–7.9 ppm [m, 10 H], 2.05 [d, 12 H, J(P–H) = 7 Hz], –4.75 [t, 7 H, J(P–H) = 19 Hz].

X-ray Analyses of $H_5Re(PMe_2Ph)_3$ (I) and $H_7Re(PMe_2Ph)_2$ (II)

Precession photographs of *I* and *II* showed systematic extinctions [(0k0, k = 2n + 1) and (h0l, l = 2n + 1) for *I*; (0k0, k = 2n + 1) and (h0l, h + l = 2n + 1) for *II*] indicating space groups $P2_1/c$ and $P2_1/n$, respectively. Because *I* slowly oxidizes in air, the crystal used for data collection was mounted in a glass capillary. Crystal and refinement details for each complex are reported in Table I.

For *I*, a diamond-shaped crystal of dimensions 0.31 mm × 0.34 mm × 0.56 mm was mounted approximately along its a* axis. Accurate centering of 45 reflections on a Nonius CAD-3 diffractometer allowed the calculation of an orientation matrix and unit cell parameters.

For *II*, an approximately tetragonally-shaped crystal (0.35 mm × 0.35 mm × 0.65 mm) was mounted on a glass fiber approximately along its b* axis. Least-squares refinement of 36 carefully-centered reflections yielded cell constants and an orientation matrix used in subsequent data collection.

Data were collected on a Nonius CAD-3 diffractometer with Zr-filtered MoKα radiation to a (sin θ/λ) limit of 0.54 $Å^{-1}$ in the $\theta/2\theta$ scan mode (10°/min scan rate). Each reflection was scanned a maximum of six times, depending on intensity. Background radiation for each reflection was counted at the beginning and at the end of each scan, for a duration (t_b) of one-half of the scan time (t_s). The intensities of three standard reflections [(4 1 0), (1 9 0), and (0 0 8) for *I*; (0 4 0), (9 1 0), and (0 1 –9) for *II*] were collected at intervals of 50 reflections. No systematic fluctuations were observed in these monitor reflections for either compound. Two quadrants of data were collected for each compound: (+h, ±k, ±l, 5442 reflections for *I*; ±h, ±k, +l, 4200 reflections for *II*).

The intensity (*I*) and the standard deviation of the intensity [σ(*I*)] for each reflection were calculated as:

$$I = [C - (t_s/t_b)B]$$

$$\sigma(I) = [C + (t_s/t_b)^2\ b + (pI)^2]^{1/2}$$

where C is the integrated intensity of the reflection, B the background count, and p = 0.04 for *I* and 0.03 for *II*. Values for F_o^2 were obtained after correcting for Lorentz and polarization effects. An empirical absorption correction was also applied to each data set, with transition coefficients (normalized to unity) ranging from 1.100 to 0.846 for *I* and 1.540 to 0.521 for *II*. Equivalent reflections were merged and those with F_o^2 values less than $3\sigma(F_o^2)$ were rejected, leaving 2067 and 1672 reflections for the subsequent structure analyses of *I* and *II*, respectively.

Patterson maps [9] revealed the locations of the Re and P atoms for each molecule. Successive cycles of structure factor calculations and difference-Fourier syntheses allowed the location of all non-hydrogen

TABLE I. Crystal Data and Details of Refinement for $H_7Re(PMe_2Ph)_2$ and $H_5Re(PMe_2Ph)_3$.

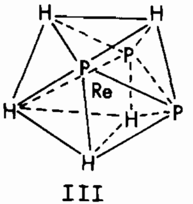
		$H_7Re(PMe_2Ph)_2$	$H_5Re(PMe_2Ph)_3$
Crystal type		monoclinic	monoclinic
Space group		$P2_1/n$ (#14n)	$P2_1/c$ (#14)
Cell constants	*a*	19.083(17) Å	6.876(3) Å
	b	6.337(4) Å	19.493(7) Å
	c	15.234(13) Å	19.646(8) Å
	β	93.72(4)°	103.26(2)°
	V	1834.0 $Å^3$	2563.0 $Å^3$
Number of molecules in the unit cell		4	4
Calculated density		1.70 $g\text{-}cm^{-3}$	1.57 $g\text{-}cm^{-3}$
Observed density		1.70 $g\text{-}cm^{-3}$	1.58 $g\text{-}cm^{-3}$
Sin θ/λ data collection limit		0.54 $Å^{-1}$	0.54 $Å^{-1}$
Reflections used in analysis ($F > 3\sigma F$)		1672	2067
Final agreement factors		$R(F) = 0.050$	$R(F) = 0.067$
		$R(wF) = 0.055$	$R(wF) = 0.075$

atoms. Three cycles of full-matrix least-squares refinement resulted in agreement factors of $R = 0.072$ for *I* and $R = 0.053$ for *II* [10]. At this point, calculated phenyl hydrogen positions were added to the coordinate list. Several more cylces of full-matrix least-squares refinement (in which the temperature factors of the Re and P atoms were allowed to vary anisotropically), with fixed hydrogen contributions, resulted in final agreement factors of $R = 0.067$ and $R = 0.052$ for *I* and *II*, respectively. In the final cycle of refinement, the largest parameter shifts were 1/4 of their estimated standard deviations. Attempts to locate the hydridic hydrogens with difference Fourier maps of decreasing ($\sin \theta/\lambda$) maxima [11] revealed several large peaks near the Re atoms. However, these peaks gave unreasonable bond lengths and angles and are probably due to ripple peaks from the metal atoms. Final atomic positions and thermal parameters are reported in Table II for $H_5Re(PMe_2Ph)_3$ and Table III for $H_7(PMe_2Ph)_2$.

Discussion

Selected bond distances and angles for $H_5Re(PMe_2Ph)_3$ and $H_7Re(PMe_2Ph)_2$ are reported in Tables IV and V. Stereoscopic unit cell plots are illustrated in Figs. 1 and 2.

Although the hydride ligands were not located in either X-ray study, an analysis of the rhenium–phosphorus geometries can provide clues about the overall coordination geometries about the metal atoms in the complexes [12]. For $H_5Re(PMe_2Ph)_3$ (Fig. 3), the relevant parameters to consider are the P–Re–P bond angles (149.5(2))°, 101.9(2)°, and 99.8(2)°] and the distance of the Re atom from the plane formed by the three P atoms (0.36 Å). These features are consistent with a dodecahedral geometry for $H_5Re(PMe_2Ph)_3$, as shown in *III*.



III

The metal–phosphine geometry of this complex parallels that of an earlier partial structure determination of $H_5Re(PPh_3)_3$ [13a]. In that study, decomposition of the crystal in the X-ray beam precluded a

TABLE II. Final Atomic Parameters for $H_5Re(PMe_2Ph)_3$.[a]

Atom	x	y	z	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re	2001(1)	2547(1)	4991(1)	128(2)	18(2)	15(3)	21(2)	1(1)	2(1)
P(1)	4585(8)	2622(3)	5997(3)	152(12)	29(2)	19(2)	22(7)	19(8)	3(3)
P(2)	177(8)	3041(3)	3937(3)	202(16)	26(2)	21(2)	29(9)	−2(9)	3(3)
P(3)	2518(9)	1416(3)	4635(3)	165(15)	21(2)	35(2)	16(8)	37(9)	0(3)
C(1)	5633(35)	1822(12)	6430(12)	4.37(0.47)					
C(2)	3997(39)	3087(13)	6721(14)	5.63(0.58)					
C(3)	6791(41)	3064(14)	5970(14)	5.83(0.58)					
C(4)	7431(40)	1552(13)	6338(13)	5.59(0.58)					
C(5)	8125(43)	934(15)	6687(16)	6.30(0.65)					
C(6)	7121(50)	668(16)	7052(18)	7.21(0.73)					
C(7)	5452(44)	884(15)	7228(15)	6.42(0.67)					
C(8)	4482(40)	1468(14)	6873(15)	5.72(0.59)					
C(9)	−1019(31)	3872(11)	4063(11)	3.72(0.43)					
C(10)	1775(39)	3283(13)	3299(14)	5.62(0.58)					
C(11)	−1980(44)	2572(14)	3389(14)	6.81(0.63)					
C(12)	−43(40)	4482(14)	3995(14)	5.53(0.57)					
C(13)	−962(51)	5134(17)	4108(17)	7.88(0.78)					
C(14)	−2686(53)	5123(17)	4294(17)	8.16(0.82)					
C(15)	−3677(46)	4504(17)	4362(17)	7.56(0.75)					
C(16)	−2771(34)	3900(11)	4247(11)	4.21(0.46)					
C(17)	934(33)	1120(11)	3809(12)	4.10(0.45)					
C(18)	5014(42)	1162(15)	4529(15)	6.48(0.65)					
C(19)	2079(46)	733(16)	5242(17)	7.28(0.73)					
C(20)	1459(38)	1222(14)	3174(14)	5.65(0.58)					
C(21)	229(40)	1007(13)	2551(15)	5.59(0.56)					
C(22)	−1541(41)	729(14)	2568(15)	5.88(0.60)					
C(23)	−2086(38)	642(12)	3196(15)	5.21(0.54)					
C(24)	−895(33)	794(11)	3780(13)	4.01(0.45)					

[a] Positional and anisotropic thermal parameters have been multiplied by 10^4. The form of the anisotropic thermal parameter is $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl))$.

TABLE III. Final Atomic Parameters for $H_7Re(PMe_2Ph)_2$.[a]

Atom	x	y	z	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re	4345(1)	5084(1)	7338(1)	171(2)	2259(18)	353(4)	59(4)	65(3)	−90(14)
P(1)	3790(2)	6833(5)	8500(3)	223(13)	2017(92)	391(22)	91(58)	79(25)	72(71)
P(2)	5357(2)	3232(5)	6906(3)	212(13)	1817(89)	448(24)	216(55)	69(25)	−59(68)
C(1)	3044(9)	8474(24)	8172(11)	5.36(0.36)					
C(2)	4311(9)	8619(22)	9170(10)	4.75(0.33)					
C(3)	3440(7)	5043(20)	9291(9)	3.38(0.24)					
C(4)	3851(10)	4319(24)	9987(12)	5.35(0.37)					
C(5)	3617(10)	2827(25)	10578(12)	5.65(0.38)					
C(6)	2944(10)	2119(25)	10427(12)	5.70(0.39)					
C(7)	2505(11)	2819(27)	9750(13)	6.42(0.43)					
C(8)	2777(10)	4276(25)	9154(12)	5.77(0.40)					
C(9)	5810(8)	1558(22)	7733(10)	4.84(0.34)					
C(10)	5195(9)	1478(24)	5949(11)	5.07(0.34)					
C(11)	6046(7)	4917(19)	6572(10)	3.71(0.25)					
C(12)	6558(7)	5725(18)	7200(9)	3.21(0.25)					
C(13)	7044(9)	7131(22)	6973(11)	4.97(0.34)					
C(14)	7078(9)	7758(22)	6138(11)	4.84(0.34)					
C(15)	6619(9)	6973(23)	5499(11)	4.95(0.34)					
C(16)	6091(9)	5588(22)	5726(11)	4.98(0.37)					

[a] Positional and anisotropic thermal parameters have been multiplied by 10^4. The form of the anisotropic thermal parameter is $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl))$.

TABLE IV. Selected Distances (in Å) and Angles (in degrees) in $H_5Re(PMe_2Ph)_3$.

Bond distances			
Re–P(1)	2.340(5)	P(1)–C(1)	1.840(23)
Re–P(2)	2.365(6)	P(1)–C(2)	1.756(24)
Re–P(3)	2.365(6)	P(1)–C(3)	1.810(22)
Average Re–P	2.357(8)	P(2)–C(9)	1.859(23)
		P(2)–C(10)	1.906(24)
		P(2)–C(11)	1.861(23)
		P(3)–C(17)	1.828(22)
		P(3)–C(18)	1.843(28)
		P(3)–C(19)	1.857(27)
		Average P–C	1.840(14)
Bond angles			
P(1)–Re–P(2)	149.5(2)		
P(1)–Re–P(3)	99.8(2)		
P(2)–Re–P(3)	101.9(2)		
Re–P(1)–C(1)	118.6(8)	C(1)–P(1)–C(2)	101.3(11)
Re–P(1)–C(2)	115.6(9)	C(1)–P(1)–C(3)	100.4(12)
Re–P(1)–C(3)	119.9(9)	C(2)–P(1)–C(3)	97.3(12)
Re–P(2)–C(9)	113.6(7)	C(9)–P(2)–C(10)	102.2(10)
Re–P(2)–C(10)	113.9(8)	C(9)–P(2)–C(11)	100.7(11)
Re–P(2)–C(11)	120.0(8)	C(10)–P(2)–C(11)	104.1(11)
Re–P(3)–C(17)	117.2(7)	C(17)–P(3)–C(18)	101.3(12)
Re–P(3)–C(18)	119.4(9)	C(17)–P(3)–C(19)	101.1(12)
Re–P(3)–C(19)	114.9(9)	C(18)–P(3)–C(19)	100.0(12)
Average Re–P–C	117.0(9)	Average C–P–C	100.9(6)

TABLE V. Selected Distances (in Å) and Angles (in degrees) in $H_7Re(PMe_2Ph)_2$.[a]

Bond distances			
Re–P(1)	2.396(4)	P(1)–C(1)	1.808(17)
Re–P(2)	2.395(4)	P(1)–C(2)	1.781(18)
Average Re–P	2.396(1)	P(1)–C(3)	1.816(14)
		P(2)–C(9)	1.818(15)
		P(2)–C(10)	1.841(17)
		P(2)–C(11)	1.796(14)
		Average P–C	1.810(8)
Bond angles			
P(1)–Re–P(2)	146.8(1)	C(1)–P(1)–C(2)	101.0(7)
		C(1)–P(1)–C(3)	102.8(7)
Re–P(1)–C(1)	116.3(6)	C(2)–P(1)–C(3)	103.6(7)
Re–P(1)–C(2)	117.3(6)	C(9)–P(2)–C(10)	103.9(7)
Re–P(1)–C(3)	113.8(4)	C(9)–P(2)–C(11)	102.7(7)
Re–P(2)–C(9)	116.8(5)	C(10)–P(2)–C(11)	102.8(7)
Re–P(2)–C(10)	114.7(4)	Average C–P–C	102.8(4)
Re–P(2)–C(11)	114.1(4)		
Average Re–P–C	115.5(6)		
P(1)–C(3)–C(4)	120.6(12)		
P(1)–C(3)–C(8)	120.3(11)		
P(2)–C(11)–C(12)	120.6(11)		
P(3)–C(11)–C(16)	123.3(12)		
Average P–C–C	121.2(7)		

[a] Standard deviations of mean values ($\bar{x}$) are calculated as $[\Sigma(x_i - \bar{x})^2/n(n-1)]^{1/2}$. The resulting deviations are to be regarded as rough estimates of uncertainty in cases where $n \leq 3$.

complete structure determination, but an analysis of the Patterson map yielded the characteristic one-large/two-small pattern of P–Re–P angles corresponding to structure *III* (134.3, 107.2, 107.1°).

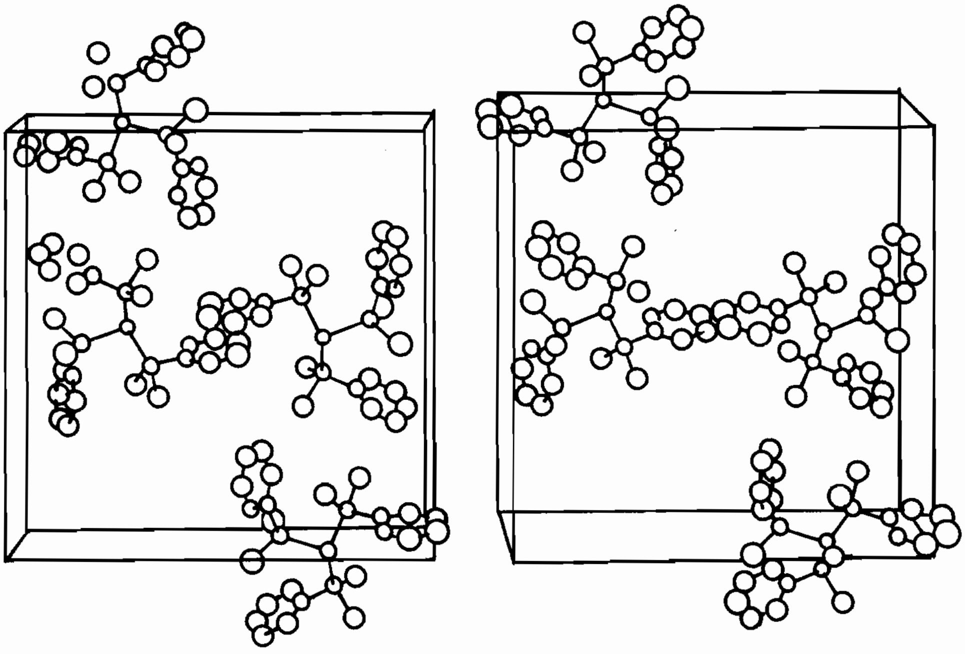


Fig. 1. A stereoscopic unit cell plot of $H_5Re(PMe_2Ph)_3$.

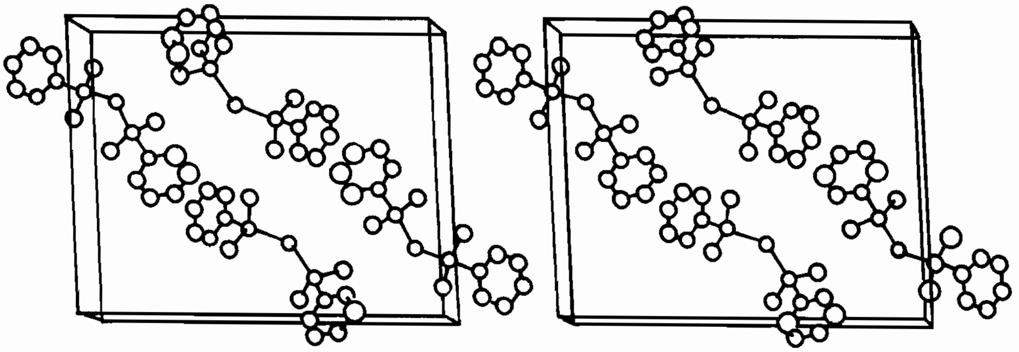


Fig. 2. A stereoscopic unit cell plot of $H_7Re(PMe_2Ph)_2$.

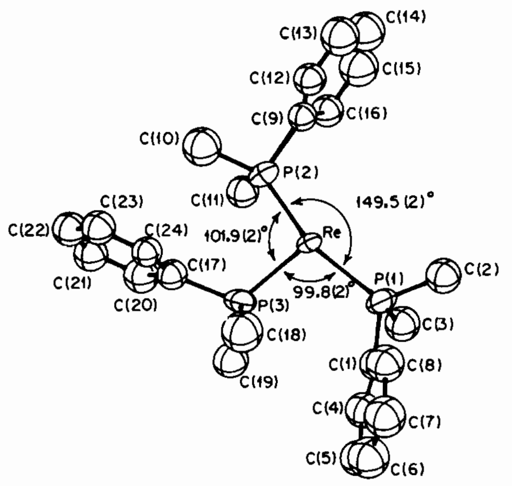


Fig. 3. A molecular plot of $H_5Re(PMe_2Ph)_3$. Phenyl hydrogens are omitted for clarity.

A very recent neturon-diffraction study [13b] of compound closely related to ours, $H_5Re(PMePh_2)_3$, has confirmed structure *III*, again with the same pattern of P–Re–P angles: [146.5(2), 103.4(2), 99.0(2)°] and [148.0(2), 101.6(2), 100.9(2)°] for the two independent molecules in the unit cell. These three studies suggest that the nature of the phosphine ligand has little effect on the coordination geometry of this particular class of eight-coordinate complexes. The dodecahedral geometry *III*, incidentally, has also been confirmed by the X-ray analysis of another eight-coordinate polyhydride complex, $H_4Mo(PMe_2Ph)_4$ [14], a study in which the hydride ligands (as in the neutron study of $H_5Re(PMePh_2)_3$ [13b]) were actually located.

The ReP_2 geometry of $H_7Re(PMe_2Ph)_2$ is illustrated in Fig. 4. The central P–Re–P backbone is found to be distinctly bent, with an angle of

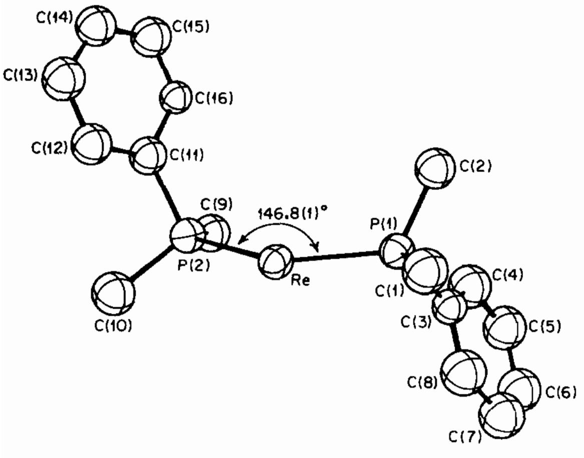
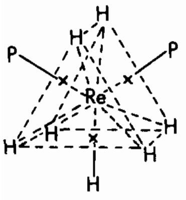
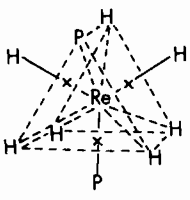


Fig. 4. Molecular plot of $H_7Re(PMe_2Ph)_2$. Phenyl hydrogens have been omitted for clarity.

146.8(1)°. Structural data on nine-coordinate molecules indicate that the tricapped trigonal prism is by far the most preferred geometry [15] and the structure of $H_7Re(PMe_2Ph)_2$ can be rationalized in terms of this model. One can envisage several ways in which a bent P–Re–P backbone can be accommodated in a tricapped trigonal prism: a structure with equatorial–equatorial phosphines (*IV*), axial–equatorial (*V*), or axial–axial (*VI*). The 'normal' values expected for the P–Re–P angles in the three cases (*i.e.*, in the absence of steric effects) are 120° for *IV*, 139.1° for *V* and 100.0° for *VI*. It is clear that, for structures *IV* and *VI*, a fair amount of distortion would have to take place in order for the P–Re–P angle to expand to the observed value of 146.8°. This distortion is presumably largely caused by steric effects arising from the relatively bulky phosphine ligands. The axial–equatorial model *V*, on the other hand, is the least crowded arrangement, and would be the one favored solely on steric grounds. At first glance, the ^1H NMR data [3], which indicate the presence of two equivalent phosphorus atoms, might argue against structure *V*, but it should be kept in mind that virtually all polyhydride/phosphine complexes are fluxional on the NMR time-scale [16].

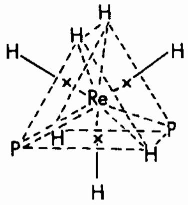


IV

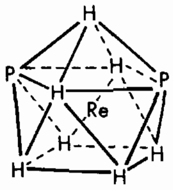


V

Very recent neutron-diffraction work by Howard, Spencer and co-workers on two different crystalline modifications of $H_7Re(PPr^i_2Ph)_2$ [17] also revealed a bent backbone (P–Re–P = 141.0°, 147.0°), but unambiguous location of the hydride ligands was prevented by complicated disorder effects. Nevertheless, sufficient detail was seen, through the partial resolution of the hydride peaks, to allow the authors to suggest a monocapped square-prismatic structure (*VII*) for $H_7Re(PPr^i_2Ph)_2$, as an alternative to the tricapped trigonal prismatic structure *IV–VI*.

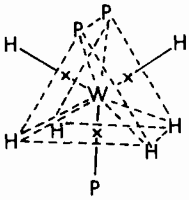


VI

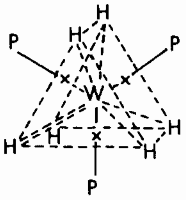


VII

The same authors also examined the related nine-coordinate complex $H_6W(PPr^i_2Ph)_3$, again with neutron diffraction [18]. In that compound they found a WP_3 skeleton which was planar, but curiously distorted from three-fold symmetry. The unexpected two-large/one-small pattern of P–W–P angles in $H_6W(PPr^i_2Ph)_3$ [126.49(5)°, 125.53(6)°, 107.89(6)°] led Howard, Spencer *et al.* to suggest structure *VIII* (ax–ax–eq) over the more symmetrical all-equatorial structure *IX*. (The W–P distances in $H_6W(PPr^i_2Ph)_3$, incidentally, also show a two-long/one-short pattern consistent with structure *VIII*: W–P = 2.524(1), 2.519(2) Å, 2.424(2)) [18].



VIII



IX

In summary, our X-ray structural results on $H_7Re(PMe_2Ph)_2$ are consistent with any of the models *IV* to *VI* (or, indeed, even *VII*) but on steric arguments we prefer structure *V*. The final assignment must await more definitive hydride positions from a neutron diffraction analysis.

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References

1 (a) Present address: Sohio Corp., Warrensville Research Center, Cleveland, OH 44128, U.S.A.
(b) Present address: Air Products & Chemicals, Inc., P.O. Box 538, Allentown, PA 18105, U.S.A.

2 (a) J. R. Moss and B. L. Shaw, *Chem. Commun.*, 632 (1968).
(b) B. Bell, J. Chatt, G. J. Leigh and T. Ito, *Chem. Commun.*, 34 (1972).
(c) J. R. Moss and B. L. Shaw, *J. Chem. Soc., Dalton*, 1910 (1972).

3 (a) J. Chatt and G. A. Rowe, *J. Chem. Soc.*, 4019 (1962).
(b) J. Chatt, J. D. Garforth, N. P. Johnson and G. A. Rowe, *J. Chem. Soc.*, 601 (1964).
(c) J. Chatt, G. J. Leigh, D. M. P. Mingos and R. J. Paske, *J. Chem. Soc.*, 2636 (1968).
(d) J. Chatt and R. S. Coffey, *J. Chem. Soc., (A)*, 1963 (1969).

4 (a) P. G. Douglas and B. L. Shaw, *Chem. Commun.*, 624 (1969).
(b) G. J. Leigh, J. J. Levinson and S. D. Robinson, *Chem. Commun.*, 705 (1969).
(c) P. G. Douglas and B. L. Shaw, *J. Chem. Soc., (A)*, 334 (1970).
(d) B. Bell, J. Chatt and G. J. Leigh, *J. Chem. Soc., Dalton*, 997 (1973).

5 (a) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 3371 (1963).
(b) J. Chatt, R. S. Coffey and B. L. Shaw, *J. Chem. Soc.*, 7391 (1965).
(c) B. E. Mann, C. Masters and B. L. Shaw, *Chem. Commun.*, 703 (1970).
(d) B. E. Mann, C. Masters and B. L. Shaw, *Chem. Commun.*, 846 (1970).

6 D. W. Hart, R. Bau and T. F. Koetzle, *J. Am. Chem. Soc., 99*, 7557 (1977).

7 R. Bau, W. E. Carroll, R. G. Teller and T. F. Koetzle, *J. Am. Chem. Soc., 99*, 3872 (1977).

8 R. Bau, W. E. Carroll, D. W. Hart, R. G. Teller and T. F. Koetzle, *Adv. Chem. Ser., 167*, 73 (1978).

9 The major computations in this work were performed using CRYM, an amalgamated set of crystallographic programs developed by R. E. Marsh and co-workers at the California Insitute of Technology.

10 $R = \Sigma|F_o - |F_c||/\Sigma|F_o|; R_w = \{\Sigma w|F_o - |F_c||^2/\Sigma w F_o^2\}^{1/2}$.

11 (a) S. J. La Placa and J. A. Ibers, *Acta Cryst., 18*, 511 (1965).
(b) S. W. Kirtley, J. P. Olsen and R. Bau, *J. Am. Chem. Soc., 98*, 4532 (1973).

12 (a) B. A. Frenz and J. A. Ibers in 'Transition Metal Hydrides', E. L. Mutterties, (ed.), p. 33, Marcel Dekker, New York, 1971.
(b) H. D. Kaesz and R. B. Saillant, *Chem. Rev., 72*, 231 (1972).
(c) A. P. Ginsberg, *Transition Metal Chem., 1*, 112 (1965).
(d) R. G. Teller and R. Bau, *Structure and Bonding, 44*, I (1981).

13 (a) A. P. Ginsberg, S. C. Abrahams and P. B. Jamieson, *J. Am. Chem. Soc., 95*, 4731 (1973).
(b) T. J. Emge, T. F. Koetzle, J. W. Bruno and K. G. Caulton, *Inorg. Chem.*, submitted for publication.

14 P. Meakin, L. J. Guggenberger, W. G. Peet, E. L. Muetterties and J. P. Jesson, *J. Am. Chem. Soc., 95*, 1467 (1973).

15 E. L. Muetterties, *Quart. Rev., 21*, 109 (1967).

16 J. P. Jesson, in 'Transition Metal Hydrides', E. L. Muetterties (ed.), p. 75, Marcel Dekker, New York, 1971.

17 (a) K. A. Mead, J. A. K. Howard, J. L. Spencer, D. Gregson and S. Mason, Abstracts, British Crystallographic Association Meeting, Durham, England, April, 1982.
(b) For the corresponding X-ray structural studies on $H_7Re(PPr^i_2Ph)_2$, see J. A. K. Howard, K. A. Mead and J. L. Spencer, *Acta Cryst., C39*, 555 (1983).

18 (a) J. A. K. Howard, D. Gregson, J. L. Spencer and D. Turner, *Acta Cryst., A37*, C-240 (1981).
(b) The preliminary X-ray work on $H_6W(Pr^i_2PhP)_3$ is reported in: D. Gregson, J. A. K. Howard, J. N. Nicholls, J. L. Spencer and D. G. Turner, *J.C.S. Chem. Commun.*, 572 (1980).
(c) D. Gregson, S. A. Mason, J. A. K. Howard, J. L. Spencer and D. G. Turner, *Inorg. Chem.*, submitted for publication.