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Pentahydridorhenium: Crystal and Molecular Structure of $ReH_5(PMePh_2)_3$

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The crystal and molecular structure of the pentahydrido complex $ReH_5(PMePh_2)_3$ has been determined by X-ray diffraction techniques at room temperature and refined against neutron diffraction data obtained at 20 K to yield precise locations for all atoms. The two independent molecules in the unit cell possess essentially identical dodecahedral cores, with the three phosphines and one hydride in B (5-neighbor) positions and the remaining four hydrides in A (4-neighbor) sites. The mean Re–H bond distance is 1.688 (5) Å, which is in agreement with that found in K_2ReH_9 (1.68 (1) Å). At convergence, with anisotropic thermal parameters refined for all 174 atoms (1568 variables), agreement factors are $R(F^2) = 0.091$ and $R_w(F^2) = 0.090$ for all 11 374 independent neutron observations ($(\sin\theta)/\lambda \le 0.69$ Å^{-1}). Crystal data at 20.0 (5) K: $a = 17.935$ (3) Å, $b = 20.066$ (4) Å, $c = 10.403$ (1) Å, $\alpha = 91.72$ (1)°, $\beta = 100.64$ (1)°, $\gamma = 69.48$ (1)°, $V = 3443$ Å^3, triclinic, space group $P\bar{1}$, $Z = 4$, fw($C_{39}H_{44}P_3Re$) = 791.9. In solution, ^1H and $^{31}P\{^1H\}$ NMR measurements indicate that $ReH_5(PMePh_2)_3$ and $ReH_5(PMe_2Ph)_3$ are fluxional molecules, with magnetically equivalent hydrides and phosphines at 25 °C.

Introduction

The title compound, $ReH_5(PMePh_2)_3$, is one of a series of metal phosphine complexes with high coordination numbers of hydride ligands, called polyhydride complexes, the structures of which are of continuing interest.[1] However, to our knowledge only four single-crystal neutron diffraction studies of such polyhydride complexes giving precise bonding parameters for the hydride ligands have been reported to date: the classic 1964 study of K_2ReH_9[2] and, more recently, analyses of $OsH_4(PMe_2Ph)_3$,[3] $Re_2H_8(PEt_2Ph)_4$,[4] and $WH_6(PPh\text{-}i\text{-}Pr_2)_3$.[5] A neutron diffraction analysis of $ReH_7(PPh\text{-}i\text{-}Pr_2)_2$ has also been carried out, but the structure was found to be disordered, preventing unambiguous location of the hydrides.[6] The ReH_5L_3 system (L = tertiary phosphine) has been the subject of at least two X-ray diffraction studies,[7,8] in which the hydride ligands were not located, as was also the case of $ReH_3(PMe_2Ph)_3(\eta^2\text{-}C_5H_8)$.[9] We embarked upon the present low-temperature neutron diffraction study of $ReH_5(PMePh_2)_3$ in order to characterize the metal–hydrogen bonding and distinguish between the various possible eightfold polyhedral coordination geometries, e.g., the dodecahedron (D_{2d}-$\bar{4}2m$ symmetry), square antiprism (D_{4d}-$\bar{8}2m$), bicapped trigonal prism (C_{2v}-$mm2$), and the bicapped octahedra. In an X-ray diffraction study of $MoH_4(PMePh_2)_4$, where the hydrides were located, the coordination was found to be dodecahedral.[10] The coordination about rhenium has also been demonstrated to be dodecahedral in a recent X-ray study of $[(ReH_5(PMePh_2)_3)_2Cu]PF_6$,[11] prepared by reaction of ReH_5L_3 with Cu(I), in which three hydrides from each ReH_5L_3 moiety are bound to the central copper, in an octahedral[12] arrangement. The 18e ReH_5L_3 complexes can be activated by photodissociation with loss of phosphine[13] and the resultant highly reactive transient 16e ReH_5L_2 species utilized in hydrogenation and dehydrogenation and other reactions that constitute a diverse and rich chemistry.[9]

Table I. Experimental Parameters for the Neutron Diffraction Study

space group: $P\bar{1}$	$a = 17.935$ (3) Å
$V = 3443$ Å^3	$b = 20.066$ (4) Å
fw = 791.9	$c = 10.403$ (1) Å
D_{calcd}(20 K) = 1.527 g cm^{-3}	$\alpha = 91.72$ (1)°
D_{measd}(298 K) = 1.50 (1) g cm^{-3}	$\beta = 100.64$ (1)°
temp: 20.0 (5) K	$\gamma = 69.48$ (1)°

wavelength: 1.1611 (1) Å
monochromator: Ge, (220) reflecting plane
cryst color: beige/brown (298 K); colorless (120 K)[a]
cryst dimens: 2.0 × 1.1 × 0.6 mm
scan widths ($\Delta(2\theta)$): 2.8° ($0.00 < (\sin\theta)/\lambda < 0.431$ Å^{-1}); 3.2° ($0.431 < (\sin\theta)/\lambda < 0.494$ Å^{-1}); 2.00° + 2.00° tan θ ($0.494 < (\sin\theta)/\lambda < 0.688$ Å^{-1})
scan speeds: approx 1.75 s/step;[b] 60–100 steps/scan
abs coeff (μ): 2.33 cm^{-1}
transmission factors: 0.774–0.861
$R_{av} = 0.073 = \Sigma_{i=1}^{n_o}\Sigma_{j=1}^{m}|F_{ij}^2 - \bar{F}_i^2|/\Sigma_{i=1}^{n_o} m|\bar{F}_i^2|$ (upon averaging over $m = 2$ hemispheres)
obsd reflcns: 18 475
indep reflcns (n_o): 11 374
variable parameters (n_v): 1568
final agreement factors (for n_o data): $R_1 = 0.091 = \Sigma|F_o^2 - k^2F_c^2|/\Sigma|F_o^2|$; $R_2 = 0.090 = [\Sigma w(F_o^2 - k^2F_c)^2/\Sigma w(F_o^2)^2]^{1/2}$; $S = 1.208 = [\Sigma w(F_o^2 - k^2F_c^2)^2/(n_o - n_v)]^{1/2}$

[a] A crystal was cooled under an evacuated glass dome, to inspect for possible damage or phase change. [b] The exact duration of each step was determined by monitoring the incident beam intensity.

Experimental Section

All synthetic mainpulations were carried out under a N_2 atmosphere with use of standard Schlenk techniques. Proton NMR spectra were recorded on a Nicolet NT-360 (FT, 360 MHz) instrument and phosphorus NMR spectra on a Varian XL-100 (FT, phosphorus at 40.5 MHz) instrument. Phosphine chemical shifts are relative to external 85% H_3PO_4, with negative values upfield. Infrared spectra were obtained on a Perkin-Elmer 283 spectrophotometer.

ReH_5L_3 (L = PMe_2Ph or $PMePh_2$) was prepared from $ReCl_3L_3$[14] via the literature method.[15] $ReH_5(PMe_2Ph)_3$: ^1H NMR (C_6D_6) δ 7.2–7.4 m, 1.67 d (J_{PH} = 7 Hz), −6.10 q (J_{PH} = 19 Hz); $^{31}P\{^1H\}$ NMR: δ −16.5 s. $ReH_5(PMePh_2)_3$: ^1H NMR (C_6D_6) δ 7.4 m, 7.1 m, 1.90

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(1) Bau, R.; Carroll, W. E.; Hart, D. W.; Teller, R. G.; Koetzle, T. F. *Adv. Chem. Ser.* **1978**, *No. 167*, 73.
(2) Abrahams, S. C.; Ginsberg, A. P.; Knox, K. *Inorg. Chem.* **1964**, *3*, 558.
(3) Hart, D. W.; Bau, R.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 7557.
(4) Bau, R.; Carroll, W. E.; Hart, D. W.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872.
(5) Gregson, D.; Howard, J. A. K.; Spencer, J. L.; Turner, D.; Mason, S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1981**, *A37*, C-240.
(6) Mead, K. A.; Howard, J. A. K.; Spencer, J. L.; Gregson, D.; Mason, S. Abstracts, British Crystallographic Association Meeting, Durham, England, 1982.
(7) Ginsberg, A. P.; Abrahams, S. C.; Jamieson, P. B. *J. Am. Chem. Soc.* **1973**, *95*, 4751.
(8) Teller, R. G.; Carroll, W. E.; Bau, R. *Inorg. Chim. Acta* **1984**, *87*, 121.
(9) Green, M. A.; Huffman, J. C.; Caulton, K. G.; Rybak, W. K.; Ziolkowski, J. J. *J. Organomet. Chem.* **1981**, *218*, C39.
(10) Meakin, P.; Guggenberger, L. J.; Peet, W. G.; Muetterties, E. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 1467.
(11) Rhodes, L. F.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1983**, *105*, 5137.

0020-1669/84/1323-4012$01.50/0

d (J_{PH} = 7 Hz), −5.50 q (J_{PH} = 19 Hz); $^{31}P\{^1H\}$ NMR δ 5.6 s. Spectra were recorded at 25 °C.

Crystals for neutron diffraction were obtained as follows: 500 mg of $ReH_5(PMePh_2)_3$ was dissolved in 15 mL of hexane and 3 mL of toluene. The mixture was heated to the boiling point to effect solution and allowed to cool slowly to room temperature. Beige crystals formed over a period of 2–3 days.

Neutron Data Collection and Refinement of the Structure of $ReH_5(PMePh_2)_3$. A tabloid-shaped crystal of $ReH_5(PMePh_2)_3$ with volume 1.2 mm^3 was glued to a hollow-point aluminum pin. The mount was sealed under helium in an aluminum can, mounted in a closed-cycle refrigerator,[16] and placed on a four-circle diffractometer[17] at the Brookhaven High Flux Beam Reactor. The wavelength λ = 1.1611 (1) Å[18] of the Ge(220) monochromated neutron beam was calibrated with use of a KBr crystal (a_0 = 6.6000 (1) Å at 298 K).[19] The sample temperature was decreased at a rate of approximately 2° min^{-1} from 298 to 20.0 (5) K and remained constant thereafter.[20] The unit cell parameters listed in Table I were obtained from a least-square fit of the $\sin^2\theta$ values for 32 centered reflections (16 Friedel pairs). This cell corresponds to the reduced cell of highest symmetry.[21]

A total of 18 475 neutron intensity data was collected in the θ–2θ scan mode. The intensities of 2 monitor reflections measured every 100 reflections showed no significant variation throughout the data collection. Further experimental details are included in Table I.

Backgrounds were based on the intensity level of the outermost seven steps on either end of each scan. The net intensities were corrected for Lorentz and absorption[22] effects. The latter corrections were determined by numerical integration over a Gaussian grid of 8 × 6 × 10 points along the a^*, b^*, and c^* directions, respectively. Averaging of symmetry-related data resulted in 11 374 independent F_o^2 values, which were used in the structure refinement.

Initial coordinates of the 86 non-hydrogen atoms were taken from a concurrent X-ray analysis[23] and refined with isotropic thermal parameters against the neutron intensity data. At an intermediate stage of this refinement, the positions of all 88 H atoms were obtained from difference maps, and refinement continued with anisotropic thermal parameters for all 174 atoms. The final cycles of refinement were accomplished by means of a full-matrix least-squares procedure with blocks of up to 510 variable parameters.[24] The quantity minimized was $\sum[w(F_o^2 - k^2F_c^2)^2]$, with weights $w = 1/\sigma^2(F_o^2)$ and variances $\sigma^2(F_o^2) = \sigma_c^2(F_o^2) + (0.02F_o^2)^2$, where $\sigma_c^2(F_o^2)$ values were derived from counting statistics. A type I isotropic extinction correction[25] was included and was most significant for the 040 reflection, which had a factor of 0.97 dividing F_o^2. Final agreement factors are listed in Table I. The final difference-Fourier map was essentially featureless.

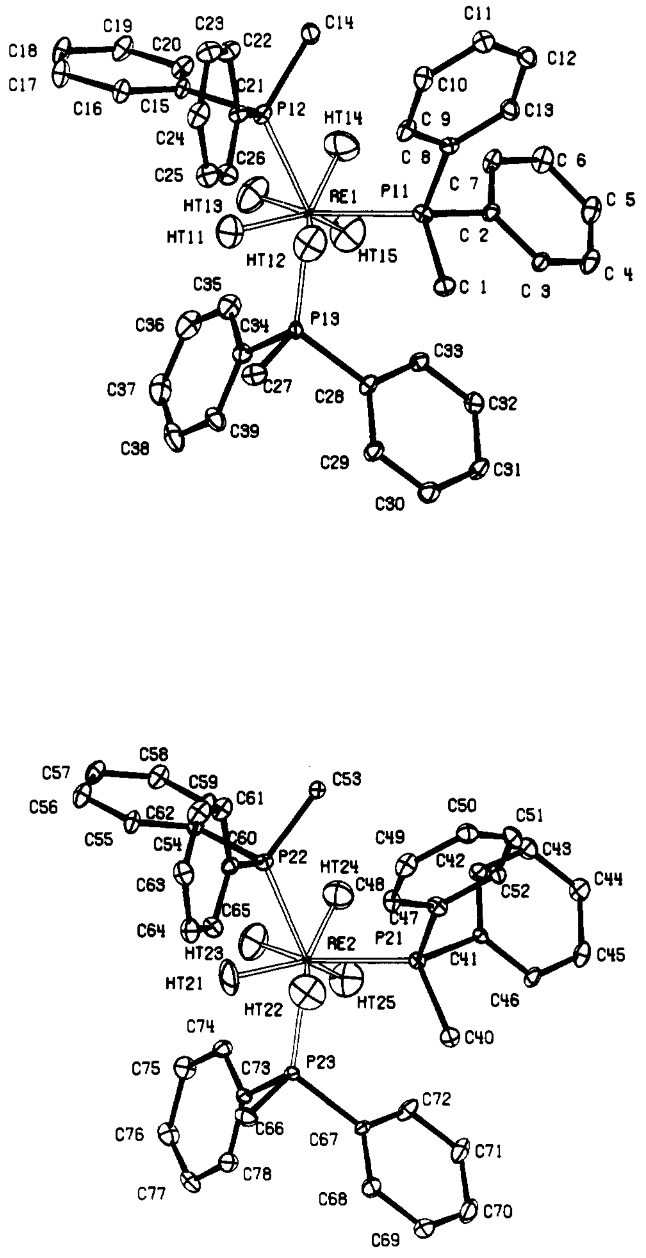

Figure 1. The two independent $ReH_5(PMePh_2)_3$ molecules with the atom-numbering scheme and thermal ellipsoids drawn to enclose 75% probability:[28] (top) molecule I; (bottom) molecule II. H atoms on the phosphine ligands have been removed for clarity.

Neutron scattering lengths employed were $b_H = -0.3741 \times 10^{-12}$ $b_C = 0.6648 \times 10^{-12}$, $b_P = 0.513 \times 10^{-12}$, and $b_{Re} = 0.92 \times 10^{-12}$ cm.[26] Computer programs used include DIFSYN[27] (a differential-Fourier

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(12) An octahedral $[FeH_6]^{4-}$ core has recently been found in X-ray and neutron diffraction studies of $FeH_6Mg_4Br_{3.5}Cl_{0.5}(C_4H_8O)_8$: Bau, R.; Ho, D. M.; Gibbins, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 4960. Bau, R.; Chiang, M.; Ho, D. M.; Gibbins, S. G.; Emge, T. J.; Koetzle, T. F., *Inorg. Chem.* **1984**, *23*, 2823.

(13) Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 695.

(14) Chatt, J.; Rowe, G. A. *J. Chem. Soc.* **1962**, 4019. Chatt, J.; Leigh, G. J.; Mingos, D. M. P.; Paske, R. J. *J. Chem. Soc. A* **1968**, 2636.

(15) Douglas, P. G.; Shaw, B. L. *Inorg. Synth.* **1977**, *17*, 64. Chatt, J.; Coffey, R. S. *J. Chem. Soc. A.* **1969**, 1963.

(16) Air Products and Chemicals, Inc., DISPLEX Model CS-202.

(17) McMullan, R. K. and in part Andrews, L. C.; Koetzle, T. F.; Reidinger, F.; Thomas, R.; Williams, G. J. B. "NEXDAS, Neutron and X-ray Data Acquisition System"; unpublished work. Dimmler, D. G.; Greenlaw, N.; Kelley, M. A.; Potter, D. W.; Rankowitz, S.; Stubblefield, F. W. *IEEE Trans. Nucl. Sci.* **1976**, *NS-23*, 398.

(18) Estimated standard deviations in units of the least significant digit are enclosed in parentheses.

(19) Donnay, J. D. H., Ondik, H. M., Eds. "Crystal Data Determinative Tables", 3rd ed.; U.S. Department of Commerce and Joint Committee on Powder Diffraction Standards: Washington, DC, 1973; Vol. 2, p C-164.

(20) Temperature readings were calibrated with reference to a magnetic phase transition in FeF_2 at T_N = 78.38 (1) K (Hutchings, M. T.; Schulhof, M. P.; Guggenheim, H. J. *Phys. Rev. B: Solid State* **1975**, *5*, 154).

(21) Lawton, S. L.; Jacobson, R. A. "The Reduced Cell and Its Crystallographic Applications", Report IS1141; Iowa State University: Ames, IA, 1962.

(22) Coppens, P.; Leiserowitz, L. L.; Rabinovich, D. *Acta Crystallogr.* **1965**, *18*, 1035.

(23) X-ray results (cell constants of the reduced cell based on Enraf-Nonius CAD4 diffractometer data at 298 K): a = 18.151 (4) Å, b = 20.411 (6) Å, c = 10.481 (3) Å, α = 91.55 (2)°, β = 100.57 (2)°, γ = 68.96 (2)°, V = 3560 Å^3, Z = 4. The density measured at 298 K by a neutral-density method was 1.50 (1) g cm^{-3}, confirming that the number of formula units, $ReH_5(PMePh_2)_3$, per unit cell is 4. A hemisphere of X-ray intensities (Mo Kα, λ = 0.71069 Å) was collected out to the limit $(\sin\theta)/\lambda$ = 0.481 Å^{-1}. Averaging of symmetry-equivalent reflection data gave 6106 non-zero independent F_o^2 values. The structure was solved by assuming space group $P\bar{1}$ with the aid of a Patterson synthesis, and all non-hydrogen atoms were located on the Fourier map and refined with use of a least-squares prcocedure.

(24) Least-squares refinements were carried out with UPALS83, a modified version of UPALS (Lundgren, J.-O. "Crystallographic Computer Programs", Report UUIC-B13-4-05; Institute of Chemistry, University of Uppsala: Uppsala, Sweden, 1982).

(25) Becker, P. J.; Coppens, P. *Acta. Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1975**, *A31*, 417.

(26) Koester, L.; Rauch, H.; Herkens, M.; Schröder, K. *Jahresber.—Kernforschungsanlage Jülich* **1981**, 1755.

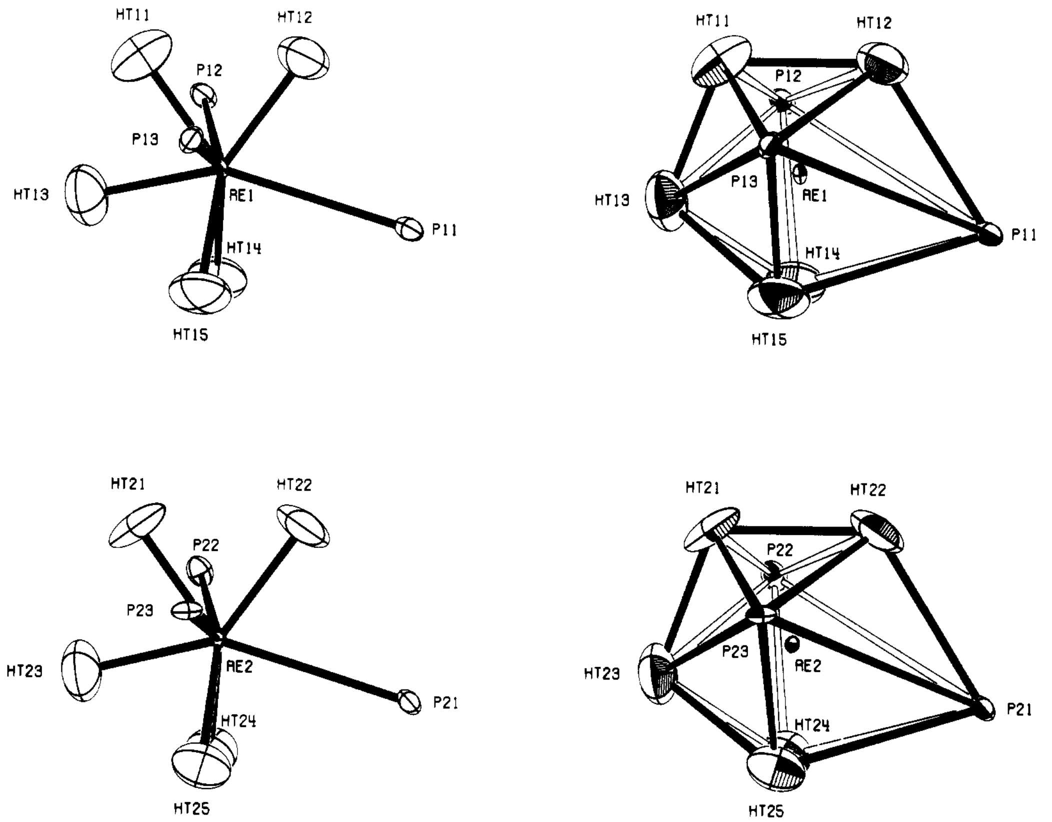

Figure 2. Perspective views of the ReH_5P_3 cores illustrating the dodecahedral coordination, with thermal ellipsoids as in Figure 1: (top) molecule I; (bottom) molecule II.

refinement procedure), a modified version of the full-matrix least-squares program UPALS,[24] the absorption procedure of Coppens, Leiserowitz, and Rabinovich,[22] Johnson's ORTEP2,[28] and locally written programs.

Results and Discussion

The molecules ReH_5L_3 (L = PMe_2Ph and $PMePh_2$) exhibit infrared spectra that are broad and not structurally enlightening. They are fluxional molecules, showing sharp ^1H NMR quartets for the Re–H hydrogens and a $^{31}P\{^1H\}$ singlet at 25 °C. At −60 °C the $^{31}P\{^1H\}$ spectrum of $ReH_5(PMe_2Ph)_3$ in CH_2Cl_2 is resolved into two chemical shifts (−13.8 ppm, intensity 2; −22.1 ppm, intensity 1) with poorly resolved doublet and triplet structure, respectively ($J \approx 13$ Hz). The ^1H NMR spectrum (CD_2Cl_2) at −80 °C exhibits two broad resonances (i.e., no well-defined coupling to P) at −6.23 ppm (110 Hz half-width, intensity 2) and −7.19 ppm (43 Hz half-width, intensity 3). Previously, ^1H NMR spectra were reported by Ginsberg, Abrahams, and Jamieson[7] for $ReH_5(PEtPh_2)_3$ and $ReH_5(AsEtPh_2)_3$. The NMR and X-ray results[7,8] are consistent with the presence of a molecular mirror plane of symmetry (but no C_3 axis) in the equilibrium geometry of ReH_5L_3. However, various polyhedral coordination geometries are possible with this symmetry element. The neutron diffraction study of $ReH_5(PMePh_2)_3$ provides definitive information regarding the molecular structure. The $PMePh_2$ analogue was selected because of its favorable crystal growth properties.

The structures of the two crystallographically independent $ReH_5(PMePh_2)_3$ molecules with corresponding numbering schemes are presented in Figure 1. The final atomic coordinates are listed in Table II. The interatomic distances and angles for the ReH_5P_3 cores and mean bonding parameters for the phosphine ligands are given in Table III.

The two $ReH_5(PMePh_2)_3$ molecules possess essentially identical distorted dodecahedral cores (see Figure 2) and differ significantly only in the orientations of the phenyl rings on one of the phosphine ligands (labelled P11 and P21). There are two types of hydride ligands in each polyhedron about rhenium, namely, the four hydrides that occupy 4-neighbor A sites[29] and the fifth (HT13 and HT23 in molecules I and II, respectively), which occupies a 5-neighbor B site. The three phosphine ligands occupy the remaining B sites. A similar dodecahedral disposition of hydride and phosphine ligands about rhenium has been found in $[ReH_5(PMePh_2)_3]_2Cu^{+}$,[11] while $MoH_4(PMePh_2)_4$[10] exhibits a symmetrical arrangement of A-site hydrides and B-site phosphines. In fact, phosphine ligands generally seem to occupy the B sites in these polyhydride complexes. As was mentioned above, the hydrides were not located in X-ray studies of $ReH_5(PPh_3)_3$[7] and $ReH_5(PMe_2Ph)_3$,[8] but one would expect these compounds to be dodecahedral, by analogy with the present structure. The dimeric species $Re_2H_8(PEt_2Ph)_4$[4] exhibits square-antiprismatic geometry, disregarding the Re–Re interaction.

The dodecahedral coordination geometry in $ReH_5(PMePh_2)_3$ may be characterized as consisting of two orthogonal A_2B_2 trapezoidal planes.[30] One of these planes, the "equatorial" plane (P11, HT11, HT12, and HT13 in molecule I), is an approximate mirror plane of symmetry for the core (the symmetry inferred by NMR spectroscopy) and includes the Re atom. Displacements from the least-squares plane are 0.005 (1) and 0.007 (1) Å, respectively, for Re1 and Re2. However, the Re atom is displaced by 0.251 (2) Å from the

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(27) McMullan, R. K., unpublished work.

(28) Johnson, C. K. *Oak Ridge Natl. Lab.*, *[Rep.] ORNL (U.S.)* **1976**, *ORNL-5138*.

(29) Hoard, J. L.; Silverton, J. V. *Inorg. Chem.* **1963**, *2*, 235.

(30) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748. The dihedral angles ϕ, which are zero for a dodecahedron of D_{2d} symmetry with planar A_2B_2 units, average $\phi = 2$ (1)° for the present structure.

(31) Ciani, G.; Giusto, D.; Manassero, M.; Albinati, A. *J. Chem. Soc., Dalton Trans.* **1976**, 1943.

Table II. Atomic Positional and Equivalent Isotropic Thermal Parameters (Å^2) (All Quantities ×10^4): Results of the 20 K Neutron Diffraction Study

ATOM	X	Y	Z	UISO
RE1	7440(1)	2335(1)	507(1)	21(4)
P11	8482(2)	1259(1)	1462(3)	67(9)
P12	6378(2)	2477(1)	1687(3)	65(9)
P13	7801(2)	2317(1)	-1567(3)	63(9)
HT11	6564(3)	2635(3)	-567(5)	269(18)
HT12	7220(3)	1623(3)	-132(5)	232(18)
HT13	7025(3)	3227(3)	398(5)	257(18)
HT14	7724(3)	2614(3)	2016(5)	244(18)
HT15	8234(3)	2618(3)	643(5)	270(19)
C1	8744(1)	524(1)	343(2)	94(8)
C2	9462(1)	1314(1)	2200(2)	69(7)
C3	10181(1)	887(1)	1816(2)	83(7)
C4	10918(1)	966(1)	2350(2)	105(8)
C5	10952(1)	1459(1)	3312(2)	120(8)
C6	10240(1)	1883(1)	3719(2)	114(8)
C7	9500(1)	1818(1)	3159(2)	97(7)
C8	8273(1)	789(1)	2770(2)	67(7)
C9	7534(1)	675(1)	2563(2)	86(7)
C10	7341(1)	313(1)	3509(2)	95(8)
C11	7888(1)	58(1)	4672(2)	95(8)
C12	8630(1)	164(1)	4889(2)	99(8)
C13	8822(1)	525(1)	3939(2)	93(8)
C14	6651(1)	2416(1)	3482(2)	95(7)
C15	5598(1)	3370(1)	1447(2)	61(7)
C16	4805(1)	3491(1)	786(2)	81(7)
C17	4238(1)	4182(1)	578(2)	106(7)
C18	4448(1)	4757(1)	1058(2)	108(7)
C19	5238(1)	4644(1)	1719(2)	110(7)
C20	5811(1)	3956(1)	1904(2)	89(7)
C21	5741(1)	1920(1)	1330(2)	67(7)
C22	5270(1)	1846(1)	2223(2)	98(7)
C23	4773(1)	1433(1)	1926(2)	106(8)
C24	4740(1)	1098(1)	735(2)	105(8)
C25	5201(1)	1173(1)	-158(2)	113(8)
C26	5693(1)	1585(1)	140(2)	86(7)
C27	7221(1)	1930(1)	-2810(2)	106(9)
C28	8848(1)	1858(1)	-1810(2)	79(7)
C29	9027(1)	1465(1)	-2920(2)	103(8)
C30	9831(1)	1147(1)	-3088(2)	119(8)
C31	10463(1)	1216(1)	-2168(2)	96(8)
C32	10289(1)	1607(1)	-1057(2)	85(7)
C33	9489(1)	1925(1)	-885(2)	78(7)
C34	7623(1)	3192(1)	-2344(2)	85(7)
C35	7532(1)	3795(1)	-1587(2)	123(8)
C36	7394(1)	4452(1)	-2179(3)	149(8)
C37	7334(1)	4518(1)	-3522(3)	158(9)
C38	7436(1)	3919(1)	-4281(3)	153(9)
C39	7587(1)	3258(1)	-3686(2)	115(8)
H1A	9206(3)	43(3)	843(5)	255(18)
H1B	8943(3)	690(3)	-485(5)	307(21)
H1C	8191(3)	411(3)	-20(5)	284(20)
H3	10171(3)	493(3)	1067(5)	273(19)
H4	11467(3)	641(3)	2012(5)	283(19)
H5	11517(3)	1526(3)	3718(5)	272(19)
H6	10259(3)	2267(3)	4488(5)	317(20)
H7	8937(3)	2167(3)	3451(5)	266(18)
H9	7100(3)	881(3)	1664(5)	241(18)
H10	6759(3)	242(3)	3326(5)	283(20)
H11	7744(3)	-228(3)	5406(5)	255(19)
H12	9065(3)	-39(3)	5798(5)	272(19)
H13	9397(3)	607(3)	4124(5)	257(19)
H14A	7063(3)	1880(3)	3801(5)	311(19)
H14B	6958(3)	2793(3)	3766(5)	317(21)
H14C	6124(3)	2559(3)	3969(5)	317(20)
H16	4631(3)	3040(2)	415(5)	234(17)
H17	3626(3)	4265(3)	49(5)	268(18)
H18	4014(3)	5301(2)	897(6)	287(19)
H19	5405(3)	5088(3)	2067(5)	278(19)
H20	6422(3)	3873(3)	2382(5)	265(18)
H22	5276(3)	2113(3)	3150(5)	242(18)
H23	4408(3)	1397(3)	2631(5)	267(20)
H24	4357(3)	777(3)	503(5)	284(20)
H25	5174(3)	907(3)	-1100(5)	265(20)
H26	6050(3)	1638(3)	-565(5)	238(19)
H27A	7368(3)	1377(3)	-2526(5)	302(21)
H27B	6587(3)	2210(3)	-2780(6)	337(21)
H27C	7314(3)	1967(3)	-3804(5)	324(22)
H29	8543(3)	1396(3)	-3656(5)	320(20)
H30	9963(3)	841(3)	-3968(5)	333(21)
H31	11090(3)	965(3)	-2297(5)	240(18)
H32	10783(3)	1673(3)	-326(5)	244(18)
H33	9357(3)	2227(3)	-18(5)	270(19)
H35	7564(4)	3735(3)	-546(5)	302(21)
H36	7324(4)	4915(3)	-1574(6)	378(24)
H37	7213(3)	5033(3)	-3979(6)	347(22)
H38	7397(4)	3957(3)	-5344(6)	365(24)
H39	7673(3)	2794(3)	-4295(5)	298(21)
RE2	7290(1)	7276(1)	5912(1)	20(4)
P21	8348(2)	6277(1)	5293(3)	56(9)
P22	6229(2)	7445(1)	4062(3)	66(9)
P23	7691(2)	7192(1)	8216(3)	52(9)
HT21	6432(3)	7508(3)	6511(5)	251(18)
HT22	7135(3)	6512(3)	6255(5)	239(18)
HT23	6856(3)	8158(3)	5994(5)	260(18)
HT24	7517(3)	7647(3)	4663(5)	231(18)
HT25	8071(3)	7563(3)	6338(5)	245(18)
C40	8900(1)	5545(1)	6499(2)	86(8)
C41	9158(1)	6476(1)	4740(2)	61(7)
C42	8960(1)	6919(1)	3617(2)	86(8)
C43	9560(1)	7048(1)	3097(2)	103(8)
C44	10369(1)	6753(1)	3721(2)	103(8)
C45	10577(1)	6329(1)	4859(2)	103(8)
C46	9972(1)	6189(1)	5364(2)	85(7)
C47	8072(1)	5742(1)	3934(2)	79(7)
C48	7358(1)	5598(1)	3859(2)	77(7)
C49	7149(1)	5152(1)	2922(2)	102(8)
C50	7654(1)	4845(1)	2024(2)	102(8)
C51	8362(1)	4994(1)	2075(2)	106(8)
C52	8568(1)	5438(1)	3026(2)	83(7)
C53	6492(1)	7327(1)	2431(2)	81(8)
C54	5507(1)	8366(1)	3854(2)	75(7)
C55	4696(1)	8553(1)	3957(2)	97(7)
C56	4177(1)	9265(1)	3797(2)	107(8)
C57	4467(1)	9797(1)	3520(2)	108(8)
C58	5279(1)	9612(1)	3408(2)	111(8)
C59	5797(1)	8905(1)	3585(2)	88(8)
C60	5555(1)	6927(1)	4004(2)	74(7)
C61	5079(1)	6844(1)	2819(2)	90(8)
C62	4600(1)	6427(1)	2773(2)	108(8)
C63	4577(1)	6086(1)	3908(2)	103(8)
C64	5034(1)	6174(1)	5095(2)	104(8)
C65	5514(1)	6595(1)	5148(2)	89(8)
C66	7127(1)	6782(1)	9030(2)	104(8)
C67	8748(1)	6712(1)	8999(2)	65(7)
C68	8967(1)	6179(1)	9977(2)	122(8)
C69	9777(1)	5858(1)	10578(2)	145(8)
C70	10378(1)	6065(1)	10220(2)	139(8)
C71	10161(1)	6591(1)	9223(2)	118(8)
C72	9355(1)	6912(1)	8626(2)	96(7)
C73	7539(1)	8023(1)	9111(2)	61(7)
C74	7282(1)	8688(1)	8457(2)	85(7)
C75	7154(1)	9307(1)	9171(2)	106(8)
C76	7282(1)	9269(1)	10534(2)	106(8)
C77	7556(1)	8607(1)	11192(2)	102(8)
C78	7684(1)	7990(1)	10479(2)	92(7)
H40A	8462(3)	5347(3)	6801(6)	288(20)
H40B	9206(3)	5733(3)	7359(5)	262(19)
H40C	9346(3)	5110(3)	6101(5)	281(19)
H42	8325(3)	7149(3)	3144(5)	263(19)
H43	9400(3)	7375(3)	2201(5)	269(20)
H44	10839(3)	6858(3)	3308(5)	280(20)
H45	11195(3)	6100(3)	5344(6)	289(20)
H46	10145(3)	5847(3)	6238(5)	237(19)
H48	6954(3)	5845(3)	4534(5)	229(18)
H49	6593(3)	5050(3)	2884(5)	264(20)
H50	7489(4)	4492(3)	1299(5)	299(21)
H51	8762(3)	4755(3)	1390(5)	268(20)
H52	9129(3)	5542(3)	3054(5)	244(19)
H53A	6849(4)	6769(3)	2326(5)	336(22)
H53B	5958(3)	7498(3)	1651(5)	273(19)
H53C	6854(3)	7652(3)	2350(5)	286(21)
H55	4460(3)	8151(3)	4168(6)	288(20)
H56	3550(3)	9404(3)	3903(6)	321(21)
H57	4074(3)	10350(3)	3421(5)	251(18)
H58	5504(3)	10027(3)	3209(6)	291(20)
H59	6431(3)	8770(3)	3517(5)	263(19)
H61	5082(3)	7102(3)	1924(5)	252(20)
H62	4227(3)	6380(3)	1842(5)	280(20)
H63	4206(3)	5752(3)	3872(5)	239(19)
H64	5015(3)	5913(3)	5991(5)	296(21)
H65	5881(3)	6657(3)	6072(5)	239(19)
H66A	7275(3)	6764(3)	10099(5)	294(21)
H66B	6489(3)	7090(3)	8705(6)	320(21)
H66C	7229(4)	6244(3)	8679(6)	327(22)
H68	8516(3)	6009(3)	10269(5)	295(20)
H69	9942(3)	5443(3)	11340(6)	337(21)
H70	11005(3)	5825(3)	10704(5)	325(20)
H71	10630(3)	6747(3)	8929(6)	300(20)
H72	9193(3)	7322(3)	7848(5)	261(19)
H74	7177(3)	8712(3)	7397(5)	244(19)
H75	6934(4)	9830(3)	8659(5)	274(20)
H76	7174(3)	9754(3)	11083(5)	273(20)
H77	7675(4)	8572(3)	12263(5)	280(21)
H78	7910(3)	7476(3)	10998(5)	246(19)

Table III. Selected Distances (Å) and Angles (deg)

A. ReH$_5$P$_3$ Core			
Bond Distances			
Re1–HT11	1.676 (5)	Re2–HT21	1.676 (5)
Re1–HT12	1.698 (5)	Re2–HT22	1.709 (5)
Re1–HT13	1.678 (5)	Re2–HT23	1.671 (5)
Re1–HT14	1.700 (5)	Re2–HT24	1.695 (5)
Re1–HT15	1.690 (5)	Re2–HT25	1.676 (5)
Re1–P11	2.398 (3)	Re2–P21	2.396 (3)
Re1–P12	2.383 (3)	Re2–P22	2.383 (3)
Re1–P13	2.359 (3)	Re2–P23	2.365 (3)
Interatomic Distances			
HT11···HT12	1.975 (7)	HT21···HT22	1.995 (7)
HT11···HT13	1.845 (7)	HT21···HT23	1.859 (6)
HT11···P12	2.474 (5)	HT21···P22	2.512 (5)
HT11···P13	2.495 (5)	HT21···P23	2.497 (5)
HT12···P11	2.435 (5)	HT22···P21	2.452 (5)
HT12···P12	2.801 (6)	HT22···P22	2.847 (5)
HT12···P13	2.640 (5)	HT22···P23	2.655 (6)
HT13···HT14	2.045 (7)	HT23···HT24	2.010 (7)
HT13···HT15	2.054 (7)	HT23···HT25	2.052 (7)
HT13···P12	2.706 (5)	HT23···P22	2.733 (6)
HT13···P13	2.913 (6)	HT23···P23	2.881 (5)
HT14···HT15	1.834 (6)	HT24···HT25	1.820 (7)
HT14···P11	2.678 (5)	HT24···P21	2.662 (6)
HT14···P12	2.485 (5)	HT24···P22	2.449 (5)
HT15···P11	2.739 (6)	HT25···P21	2.688 (5)
HT15···P13	2.416 (5)	HT25···P23	2.402 (5)
P11···P12	3.753 (4)	P21···P22	3.704 (4)
P11···P13	3.618 (3)	P21···P23	3.671 (4)
Mean Values[a]			
Re–HT	1.688 (5)	HT···HT	1.95 (3)
Re–P short	2.373 (6)	P···HT	2.62 (13)
long	2.397 (3)	P···P	3.69 (3)
Bond Angles			
HT11–Re1–HT12	71.7 (3)	HT21–Re2–HT22	72.2 (3)
HT11–Re1–HT13	66.8 (3)	HT21–Re2–HT23	67.5 (3)
HT11–Re1–HT14	130.9 (3)	HT21–Re2–HT24	130.2 (3)
HT11–Re1–HT15	127.2 (3)	HT21–Re2–HT25	128.4 (3)
HT12–Re1–HT13	138.4 (3)	HT22–Re2–HT23	139.7 (3)
HT12–Re1–HT14	137.6 (3)	HT22–Re2–HT24	138.5 (3)
HT12–Re1–HT15	135.8 (2)	HT22–Re2–HT25	133.7 (3)
HT13–Re1–HT14	74.5 (3)	HT23–Re2–HT24	73.3 (2)
HT13–Re1–HT15	75.2 (3)	HT23–Re2–HT25	75.6 (3)
HT14–Re1–HT15	65.5 (3)	HT24–Re2–HT25	65.4 (2)
HT11–Re1–P11	142.3 (2)	HT21–Re2–P21	143.3 (2)
HT11–Re1–P12	72.8 (2)	HT21–Re2–P22	74.2 (2)
HT11–Re1–P13	74.2 (2)	HT21–Re2–P23	74.2 (2)
HT12–Re1–P11	70.6 (2)	HT22–Re2–P21	71.1 (2)
HT12–Re1–P12	84.9 (2)	HT22–Re2–P22	86.5 (2)
HT12–Re1–P13	79.4 (2)	HT22–Re2–P23	79.6 (2)
HT13–Re1–P11	150.9 (2)	HT23–Re2–P21	149.2 (2)
HT13–Re1–P12	81.6 (2)	HT23–Re2–P22	82.8 (2)
HT13–Re1–P13	90.8 (2)	HT23–Re2–P23	89.4 (2)
HT14–Re1–P11	79.6 (2)	HT24–Re2–P21	79.2 (2)
HT14–Re1–P12	72.8 (2)	HT24–Re2–P22	71.6 (2)
HT14–Re1–P13	136.4 (2)	HT24–Re2–P23	135.4 (2)
HT15–Re1–P11	82.1 (2)	HT25–Re2–P21	80.5 (2)
HT15–Re1–P12	136.2 (2)	HT25–Re2–P22	135.7 (2)
HT15–Re1–P13	71.1 (2)	HT25–Re2–P23	70.6 (2)
P11–Re1–P12	103.4 (2)	P21–Re2–P22	101.6 (2)
P11–Re1–P13	99.0 (2)	P21–Re2–P23	100.9 (2)
P12–Re1–P13	146.5 (2)	P22–Re2–P23	148.0 (2)
B. Phosphine Ligands			
Mean Bond Distances[a]			
P–C	1.838 (2)	C–H(methyl)	1.090 (1)
C–C	1.397 (1)	C–H(phenyl)	1.089 (1)
Mean Bond Angles[a]			
Re–P–C	117.0 (7)	C–C(P)–C[b]	118.7 (1)
P–C–C	120.6 (4)	C–C–C	120.3 (1)
C–P–C	101.0 (4)	H–C–H(methyl)	109.0 (2)

[a] Esd's of mean values are calculated as $\sigma(\bar{x}) = [\Sigma_{i=1}^{n}(x_i - \bar{x})^2/n(n-1)]^{1/2}$. For the case $n = 2$, $\sigma = \sigma(\bar{x})$ or the average of the individual esd's, whichever is larger. [b] C(P) are the C atoms bonded to P.

perpendicular plane (P12, P13, HT14, HT15 in molecule I), in the direction toward the ligand that is farthest from the center of the equatorial plane (i.e., P11 or P21). Thus, the projected image of the ReH$_5$P$_3$ core differs from that of a D_{2d}-symmetry dodecahedron (a pentagon) only by the longer Re1–P11 or Re2–P21 distance, compared to Re–H (see Figure 2). The difference between the distorted dodecahedron of ReH$_5$(PMePh$_2$)$_3$ and a cisoid bicapped octahedron resides primarily in the equatorial plane, which would be square for the octahedron, compared to the trapezoidal geometry for the dodecahedron. The longest leg of this trapezoid (P11–HT13 or P21–HT23) intersects the edge defined by the two would-be capping ligands (HT14 and HT15 or HT24 and HT25).

Table IV summarizes salient structural features of ReH$_5$(PMePh$_2$)$_3$ and a number of related polyhydride complexes studied by X-ray diffraction techniques. The metal–phosphorus core geometry in ReH$_5$(PMePh$_2$)$_3$ compares well with that listed for the other six compounds. As mentioned above, the hydrides were located for MoH$_4$(PMePh$_2$)$_4$, which also exhibits dodecahedral coordination. However, the mean H–Mo–H angle of 61 (1)° is significantly smaller than the mean H–Re–H angle of 71 (1)° in ReH$_5$(PMePh$_2$)$_3$. This difference is to be expected as a consequence of including a fourth bulky phosphine ligand in the Mo compound.

The Re–P bonds in ReH$_5$(PMePh$_2$)$_3$ are grouped into two categories: the shorter Re1–P12, Re1–P13 and Re2–P22, Re2–P23, with a mean distance of 2.373 (6) Å, and the longer Re1–P11 and Re2–P21, mean 2.397 (3) Å (see Table III). The P12–Re1–P13 and P22–Re2–P23 angles average 147.3 (8)°, compared to 101 (1)° for the other four P–Re–P angles. The difference in length of the two sets of Re–P bonds in ReH$_5$(PMePh$_2$)$_3$, which also is found[32] in complexes listed in Table IV, may be ascribed to the trans effect. In fact, Re1–P11 (or Re2–P21) is more nearly trans to Re–H than the other Re–P bonds. Thus, the largest H–Re–P angles are HT13–Re1–P11 and HT23–Re2–P21, mean value 150.1 (9)°, and HT11–Re1–P11 and HT21–Re2–P21, mean value 142.8 (5)°. Steric arguments may also be applicable here because the long Re–P bond involves the P atom which has two small-angle contacts with the other phosphines. The shortest intracore H···H distance is HT24···HT25 (1.820 (7) Å), comparable to the closest H···H contacts found in other metal hydrides.[1,33] As discussed elsewhere,[3] hydride ligands in general donate electron density which accumulates on the metal atom and may be involved in multiple bonding, e.g., between rhenium and phosphorus. However, the Re–P bond distances in the title pentahydrido compound do not vary significantly from those of the di- or trihydrido complexes ReH$_2$(NO)(PPh$_3$)$_3$[31] or ReH$_3$(η^2-C$_5$H$_8$)(PMe$_2$Ph)$_3$,[9] as indicated in Table IV, and the Re–P distances in ReH$_7$L$_2$ complexes[8,32] also fall in the same range.

Re–H distances in the present structure range from 1.676 (5) to 1.709 (5) Å, with a mean value of 1.688 (5) Å. This value agrees to within experimental error with those of 1.68 (1) Å obtained in K$_2$ReH$_9$[2] and 1.669 (7) Å for terminal bonds in Re$_2$H$_8$(PEt$_2$Ph)$_4$.[4] These values may be compared to M–H terminal distances for other third-row metals: Ta–H, 1.774 (3) Å;[34] W–H, 1.732 (3) Å;[5] Os–H, 1.659 (3) Å;[3] Ir–H, 1.59 Å;[35] Pt–H, 1.610 (2) Å.[36] The diminution in the M–H dis-

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(32) Interestingly, in the case of ReH$_7$(PPh-*i*-Pr$_2$)$_2$, which has been crystallized in two forms, X-ray studies show the Re–P distances in one form to differ (2.404 (2) vs. 2.423 (2) Å) while those in the other form are equal (2.423 (2) Å). The Re–H distance in ReH$_7$(PPh$_3$)$_2$, which has crystallographic C_2 symmetry, is 2.427 (1) Å (see Howard, J. A. K.; Mead, K. A.; Spencer, J. L. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 555). In H$_7$Re(PMe$_2$Ph)$_2$, the Re–P distances are 2.396 (4) and 2.395 (4) Å.[8]

(33) Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* **1981**, *44*, 1.

(34) Wilson, R. D.; Koetzle, T. F.; Hart, D. W.; Kvick, Å.; Tipton, D. L.; Bau, R. *J. Am. Chem. Soc.* **1977**, *99*, 1775.

Table IV. Core Geometries of $ReH_5(PMePh_2)_3$ and Related Molecules

molecule	mean M-P bond dist, Å[a]	mean P-M-P angle, deg[a] type I	mean P-M-P angle, deg[a] type II	dist of M to 3 P plane, Å[a]	ref
$ReH_5(PMePh_2)_3$	2.381 (6)	147.2 (8)	101.2 (9)	0.40 (2)	this study
$ReH_5(PPh_3)_3$[b]	2.54 (2)	134.3	107.2	0.49	7
$ReH_5(PMe_2Ph)_3$	2.357 (8)	149.5 (2)	101 (1)	0.36 (1)	8
$[ReH_5(PMePh_2)_3]_2Cu^+$[c]	2.40 (1)	146 (1)	98 (2)	0.52 (1)	11
$ReH_3(PMe_2Ph)_3(\eta^2\text{-}C_5H_8)$	2.38 (2)	156.5 (2)	96 (2)	0.37 (1)	9
$ReH_2(PPh_3)_3(NO)$	2.42 (2)	143.2 (3)	102 (1)	0.46 (2)	31
$MoH_4(PMePh_2)_4$[d]	2.47 (2)	143 (1)	96 (2)	0.65 (3)	10

[a] Esd's of mean values are calculated as $\sigma(\bar{x}) = [\Sigma_{i=1}^{n}(x_i - \bar{x})^2/n(n-1)]^{1/2}$. For the case $n = 2$, $\sigma = \sigma(\bar{x})$ or the average of the individual esd's, whichever is larger. [b] The ReP_3 geometry was derived from atomic positions obtained by Patterson methods. [c] The mean Re–H distance is 1.54 (6) Å. [d] The mean Mo–H bond distance is 1.70 (3) Å.

Table V. H···H Interatomic Distances (Å)[a]

Intramolecular ($D \leq 2.20$)			
HT13···H35	2.010	HT23···H74	1.933
HT12···H26	2.053	HT22···H65	2.138
HT15···H33	2.124	HT25···H5	2.203
Intermolecular ($D \leq 2.30$)			
H19···H49	2.119	H78···H42[b]	2.258
H48···H37[b]	2.149	H76···H9[c]	2.289
H13···H30[b]	2.173	HT11···H62[d]	2.274
H14B···H39[b]	2.183		

[a] Esd's are in the range 0.007–0.009 Å. [b] $x, y, 1 + z$. [c] $x, 1 + y, 1 + z$. [d] $1 - x, 1 - y, -z$.

tances as one passes across the periodic table from group 5A to 8 is evident. Bridging M–H distances are typically 0.1–0.2 Å longer than the terminal distances quoted here,[37] as was specifically found to be the case for rhenium in $Re_2H_8(PEt_2Ph)_4$ (Re–H(bridging) = 1.878 (7) Å compared to Re–H(terminal) = 1.669 (7) Å).

The geometry of the phosphine ligands is quite normal (see mean bonding parameters in Table III). The C–C and C–H bond distances are as expected, with equivalent mean methyl and phenyl C–H distances.

As shown in Table V, the shortest H···H distances involving the phosphines correspond to intramolecular contacts between phenyl-ring hydrogens and the hydrides that occupy the more accessible B sites (HT13 and HT23). Also presented in Table V are intermolecular H···H distances, which primarily involve phenyl H atoms of translationally related molecules (e.g., ±*c*). None of these distances are abnormally short, and the crystal packing of $ReH_5(PMePh_2)_3$ exhibits weakly interacting layers of molecules in the *ac* plane centered at $y \approx {}^1/_4$ and $y \approx {}^3/_4$. The cores of molecules I and II are related by a pseudo *b* glide plane that is perpendicular to the crystallographic *c* axis at $z \approx {}^1/_3$. The packing contacts involve weak interactions between the large $PMePh_2$ ligands, which occupy the majority of the unit-cell volume, with the phenyl rings arranged in a herringbone motif in the *bc* plane near $x = 0$ and $x = {}^1/_2$.

Summary

A neutron diffraction study of $ReH_5(PMePh_2)_3$ has established the geometry about the 8-coordinate Re atoms to be that of a distorted dodecahedron. The Re–H bond distances range from 1.671 (5) to 1.709 (5) Å with a mean of 1.688 (5) Å, and Re–P bonds range from 2.359 (3) to 2.398 (3) Å. The two types of P–Re–P angles average 101 (1)° and 147.3 (8)°, with the longer Re–P bond in each molecule opposite the wider angle. The distance from Re to the 3 P atom plane is, when one averages over molecules I and II, 0.40 (2) Å. The crystal packing is entirely normal, with no unusually short H···H contacts.

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Registry No. $ReH_5(PMePh_2)_3$, 92077-24-2; $ReH_5(PMe_2Ph)_3$, 92077-25-3.

Supplementary Material Available: A unit-cell packing diagram (Figure S1) and listings of anisotropic thermal parameters for all atoms (Table S1), bond distances and angles for the phosphine ligands (Table S2), selected least-squares planes (Table S3), and observed and calculated squared structure factors (72 pages). Ordering information is given on any current masthead page.

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(35) Emge, T. J.; Koetzle, T. F.; Albinati, A.; Venanzi, L. M. Abstracts, American Crystallographic Association Meeting, Columbia, MO, 1983; p 22.

(36) Chiang, M. Y.; Bau, R.; Minghetti, G.; Bandini, A. L.; Banditelli, G.; Koetzle, T. F. *Inorg. Chem.* **1984**, *23*, 122.

(37) Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176.