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Crystal and Molecular Structure of Tristriphenylphosphine Rhodium Carbonyl Hydride*

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The structure of tristriphenylphosphine rhodium carbonyl hydride, $RhH(CO)(P(C_6H_5)_3)_3$, is of interest because the compound is representative of a small class of stable transition-metal hydrides and because it contains five-coordinated rhodium, the stereochemistry of which has not been studied previously. The compound crystallizes with four molecules in space group $P2_1/n$ (C_{2h}^5) of the monoclinic system in a cell of dimensions $a = 10{\cdot}11$, b(unique axis) $= 33{\cdot}31$, $c = 13{\cdot}33$ Å, $\beta = 90{\cdot}0°$. The structure has been solved by conventional three-dimensional Patterson, least-squares, and Fourier techniques. In order to make the refinement of this 60 atom problem feasible, the nine phenyl rings have been treated as groups and constrained to their well-known geometry. In a difference Fourier synthesis calculated after this refinement the peak from the hydrogen atom attached to the rhodium is discernible. The conformation of the ligands around the rhodium atom is that of a trigonal bipyramid, with the three phosphorus atoms in the basal plane, the hydrogen at one apex, and the carbon of the carbonyl at the other. The rhodium atom lies 0·36 Å above the phosphorus plane toward the carbon of the carbonyl. The Rh–H distance is $1{\cdot}60 \pm 0{\cdot}12$ Å, a normal length for a covalent bond.

Introduction

There is extensive interest, both theoretical and practical, in the metal–hydrogen bond in transition metal hydrides. Spectroscopic studies of the transition–metal hydrides have led to considerable speculation and controversy concerning the nature of this metal–hydrogen bond, M–H. The abnormally large chemical shift to high fields of the proton has been interpreted in terms of an abnormally short bond in which the hydrogen is 'buried' in the metal orbitals (Cotton & Wilkinson, 1956; Cotton, 1958), and more recently in terms of a normal covalent bond with an M–H distance of 1·6 Å or so (Stevens, Kern & Lipscomb, 1962; Lohr & Lipscomb, 1964). The chemical shift data and the vibrational frequency assignments, while providing valuable comparative data for different compounds, do not yield direct information on the length and strength of the M–H bond. Definitive experiments to obtain such information have been rare, probably because the parent compounds, such as $HCo(CO)_4$, are extremely unstable, and the substituted compounds, though somewhat more stable, invariably contain bulky and complicated ligands such as the trialkyl- or triarylphosphines. One direct experiment is the broad line nuclear magnetic resonance study of $H_2Fe(CO)_4$ (Bishop, Down, Emtage, Richards & Wilkinson, 1959). Here the intramolecular H–H distance was determined to be $1{\cdot}88 \pm 0{\cdot}05$ Å on the assumption, difficult to justify, that intermolecular effects can be ignored. Since the geometry of the $H_2Fe(CO)_4$ molecule is unknown, the Fe–H bond length cannot be derived from this H–H bond length.

The present X-ray study of the structure of tristriphenylphosphine rhodium carbonyl hydride was undertaken because the compound is representative of a small class of stable transition-metal hydrides which heretofore have not been studied in detail by diffraction methods. The detailed knowledge of the conformation of the ligands about the rhodium is of interest in itself, because five-coordinated compounds have been studied infrequently, and five-coordinated rhodium not at all. Moreover it was felt that such information might possibly provide clues as to the nature of the Rh–H bond. At the outset we did not expect that we could locate the hydrogen atom in this structure; this we have done, and we find the Rh–H distance to be a normal covalent distance at $1{\cdot}60 \pm 0{\cdot}12$ Å.

Because of the interest in the metal–hydrogen bond, a preliminary account of this work has been published (La Placa & Ibers, 1963). In this paper we present the details of the study.

Experimental

Excellent crystals of tristriphenylphosphine rhodium carbonyl hydride were very kindly supplied by L. Vaska. They had been prepared as described by Bath & Vaska (1963). Vaska had characterized the compound thoroughly by analytical, spectroscopic, and magnetic techniques and had concluded that it

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is monomeric, diamagnetic, and probably has a trigonal bipyramidal configuration. The chemical shift of the proton as well as other spectroscopic data were interpreted to indicate that the environment of the hydrogen in this compound is very similar to that of the hydrogen in the parent compounds, such as $HCo(CO)_4$ and $HRh(CO)_4$.

The yellow crystals are generally needle-like in habit. On the basis of precession and Weissenberg photographs these crystals were found to belong to the monoclinic system and to have a unit cell of dimensions $a = 10{\cdot}11 \pm 0{\cdot}05$, b(unique axis) $= 33{\cdot}31 \pm 0{\cdot}15$, $c = 13{\cdot}33 \pm 0{\cdot}07$ Å, $\beta = 90{\cdot}0 \pm 0{\cdot}1°$. Some of the crystals were twinned around [010] so that the intensities of the hkl and $hk\bar{l}$ reflections were equal. The prominent crystal faces are the forms {100}, {021}, and $\{02\bar{1}\}$. The only systematic absences are $h0l$ for $h+l$ odd and $0k0$ for k odd; the space group is probably $P2_1/n$ (C_{2h}^5) and a plausible structure has been found on this assumption. The density, as measured by flotation of the crystals in concentrated potassium tartrate solutions, is $1{\cdot}33 \pm 0{\cdot}02$ g.cm^{-3}, in good agreement with a density of 1·36 g.cm^{-3} calculated for four molecules in the unit cell. Thus all atoms lie in general positions, and there are no symmetry conditions imposed on the molecule.

Although the linear absorption coefficient μ for Cu $K\alpha$ radiation is 44·5 cm^{-1} while that for Mo $K\alpha$ is only 5·2 cm^{-1}, we decided to use Cu $K\alpha$ radiation in this study for the following reasons. Since the crystals are exceedingly well-formed, their dimensions can be accurately determined and a reliable absorption correction applied. Because of the very large cell (cell volume $V = 4489$ Å^3) the use of Cu $K\alpha$ rather than Mo $K\alpha$ radiation results in the loss of far fewer close-in reflections. Finally it has been our experience that better intensity data are obtained with Cu $K\alpha$ radiation, presumably because there is less interference from white radiation than there is in the case of Mo $K\alpha$ radiation.

A crystal of approximate linear dimensions 0·42 mm in length by 0·07 mm by 0·035 mm in cross section was selected for the photographic work. The indices of the faces were determined by optical goniometry and the dimensions of the faces were determined accurately through the use of a calibrated microscope eyepiece. The crystal had a total volume of 0·00104 mm^3 and a calculated weight of 1·41 micrograms. No protection of this crystal from air proved necessary: no visible change in the crystal occurred during the six weeks of photography, and photographs of the $0kl$ layer at the end of the experiment were identical with those taken initially. Data were collected at room temperature by the equi-inclination Weissenberg technique on a Nonius integrating camera. The layers $0kl$ to $7kl$ were collected. The intensities at angles higher than θ_{Cu} of 40° are generally very weak. With exposures of not too inconvenient a duration (69 hours) it was possible to obtain a reasonable fraction of the data within $\theta_{\text{Cu}} \leq 40°$. Of the approximately 2650 independent reflections within this range, the intensities of 1480 were accessible and sufficiently strong to be estimated reliably. The multiple film technique was used, and the intensities were estimated visually by comparison with a strip prepared from timed exposures of Ilford G industrial X-ray film to the filtered beam. The intensity estimates of reflections on the various films were reduced to average intensities, and then to relative values of F^2 by application of the appropriate Lorentz-polarization factors. An absorption correction was then applied, using a Gaussian integration technique for 512 grid points within the crystal. The ratio of maximum to minimum transmission factors for the 1480 reflections is only 1·18; the absorption correction is thus a small one. By comparison with data obtained from precession photographs and through the use of a modified Wilson-method calculation the relative values of F^2 were brought approximately to an absolute scale.

Solution of the structure

The positions of the Rh atom and the three P atoms were readily derived from an unsharpened three-dimensional Patterson function. These positions, together with scale and thermal parameters, were refined in a least-squares calculation. The conventional R factor was 34%. A difference Fourier synthesis was then computed and the approximate positions of the carbonyl group and of the 54 carbon atoms in the nine phenyl rings were derived.

Refinement of the structure

Because there are 60 atoms (not counting hydrogen) in the asymmetric unit, refinement of this structure by conventional full-matrix least-squares techniques is not feasible with currently available computers. (If individual isotropic thermal parameters are used, then there are 240 parameters to be refined and special techniques would be required to handle a problem of this size, particularly to handle the matrix inversion necessary to obtain error estimates. Moreover, the time required (for example on an IBM 7094 computer) would be excessive. It would probably have been possible to refine the structure through the use of some form of the block-diagonal method, but this is not without its difficulties (Hodgson & Rollett, 1963) and also requires extensive machine time owing to slowness of convergence. We therefore decided to treat the nine phenyl rings as groups and to carry out the refinement with these rings constrained to their well-known geometry. The position of each phenyl group is defined by six, rather than eighteen, positional parameters, and this in itself reduces the number of variables by 108. We had considered and rejected such a group refinement in the rhodium chloride 1,5-cyclooctadiene problem

(Ibers & Snyder, 1962) because we felt that the data were not too reliable, the contribution of the rings to the structure amplitudes was not too great (R, heavy atoms alone, 16%), and because the geometry of the rings was not known precisely. The present case is an ideal one for a group refinement, for the geometry of the rings is certain and the contribution of the rings to the structure amplitudes is considerable (R, heavy atoms alone, 34%).

Our program for group refinement is written for the IBM 7090 computer and is an extensive modification of the local version of the Busing–Levy ORFLS program for conventional least-squares refinements. As written it enables the simultaneous refinement of individual atoms and of groups of atoms to be carried out in any symmetry. The method employed is as follows. A transformation matrix $\mathbf{U}$ is defined such that

$$A = \mathbf{U}a \tag{1}$$

where a is the original cell and A an orthogonal cell of unit dimensions. A convenient transformation is one that gives A_2 parallel to a_2, A_3 parallel to $A_1 \times A_2$, and A_1 parallel to $a_2 \times a_3$. Define a set of orthogonal internal axes a' within a group and let x' be the positional coordinates (in Å) of a particular atom relative to these axes a'. Next define a transformation matrix $\mathbf{R}(\delta, \varepsilon, \eta)$ that in some manner gives

$$X = \mathbf{R}x' + X_c \tag{2}$$

where X are the positional coordinates (in Å) of the particular atom relative to the coordinate system A, and where X_c represents the position in the A system of the origin of coordinates a'. Then the fractional coordinates of the particular atom in the original a coordinate system are simply

$$x = \mathbf{U}^{tr}\mathbf{R}x' + x_c \tag{3}$$

where x_c represents the origin of the a' system in the a system. The form of $\mathbf{R}$ depends upon the choice of the rotations δ, ε, η which bring about the alignment (except for translation) of the a' system with the A system. Thus the angles δ, ε, η could be the conventional Eulerian angles. We have found it convenient to take them rather as successive rotations about the a' axes.

The calculation proceeds as follows. For non-group atoms the input parameters are the usual ones. For the groups the input parameters are the three components of x_c and the three angles δ, ε, η, together with the values of x' for each atom in the group. The coordinates x are derived in accordance with equation (3), and are then used in the normal way in the calculation of structure factors. Derivatives of these structure factors with respect to the six group variables are obtained through a differencing process. Although either isotropic or anisotropic thermal parameters can be applied to the non-group atoms, we have restricted the program to a single isotropic thermal parameter per group. Individual isotropic thermal parameters could have been included, but this is probably an unnecessary embellishment. In principle one can define anisotropic vibrations of the group along its principal axes, but since these need not intersect (Schomaker, 1964) and in any event are difficult to determine, this does not seem worthwhile in practice.

The present refinement was carried out on F, with unit weights assigned for $F \leq 80$ electrons and with weights taken as $(80/F)^2$ for $F > 80$ electrons. The atomic scattering factors used were those tabulated by Ibers (1962) for the neutral atoms. Templeton's (1962) tabulation of f' and f'' for Rh and P (Cu $K\alpha$ radiation) were used and the effects of anomalous dispersion were included in the calculated structure factors (Ibers & Hamilton, 1964). The internal axial system a' was placed with origin at the center of mass of the ring and the coordinates x' were chosen to give a planar phenyl ring with C–C = 1·392 Å and C–H = 1·08 Å. To be refined were the three positional and one thermal parameter for each of the six non-group atoms, and the three positional, three angular, and one thermal parameter for each of the nine groups. In addition to these 87 parameters, the scale was occasionally adjusted, and in the later stages of the refinement the Rh and P atoms were allowed to vibrate anisotropically. One cycle of refinement, preceded and followed by a structure factor calculation, requires about 9 minutes of IBM 7094 computer time.

Scheringer (1963) has discussed some of the obvious advantages of a group refinement and has described a program for such refinements that is similar to, but less general than, the one described here. It is clear from Scheringer's examples and from the present work that a group of atoms will shift smoothly over a surprisingly large distance, and hence the starting parameters for the group need not be very accurate. In Table 1 we list the initial values of the parameters for the nine phenyl rings and the final values achieved after three cycles of refinement. For convenience the derived parameters of the carbon atoms are given in Table 2. Owing to some errors in arithmetic some of the rings were badly misplaced and the resultant angular shifts were as great as 40° (corresponding to shifts of individual carbon atoms of over 1·3 Å). Thus a refinement of a group of atoms is an efficacious way of achieving convergence or near convergence with minimal computing time. If there are cases where it is justified, then after the group refinement the constraints on the atoms can be relaxed and refinement to a final structure achieved in a minimum number of additional cycles. The conventional R factor after the group refinement with isotropic thermal parameters on the non-group atoms was 7·5%.

A three-dimensional difference Fourier synthesis was next computed. It was surprisingly smooth with a maximum peak height of 0·6 e.Å^{-3}. The difference

Table 1. *Initial and final values of the group parameters*

Group	x_c (Å)		y_c (Å)		z_c (Å)		δ (rad.)*		ε (rad.)		η (rad.)		B (Å^2)
	in.	fin.	in.	fin.	in.	fin.	in.	fin.	in.	fin.	in.	fin.	fin.
P(1)R(1)	−4·11	−4·104(11)†	11·11	11·125(12)	5·58	5·508(12)	2·16	2·331(12)	2·53	2·560(11)	2·26	2·147(12)	4·25(29)
P(1)R(2)	−2·37	−2·374(12)	15·77	15·743(12)	5·79	5·811(11)	0·13	0·087(11)	2·70	2·622(10)	3·02	2·938(12)	3·80(29)
P(1)R(3)	5·86	5·841(12)	4·66	4·604(11)	−0·07	−0·018(12)	2·04	1·826(10)	0·19	0·241(10)	3·99	4·052(11)	4·28(29)
P(2)R(1)	−1·16	−1·190(11)	6·99	6·959(10)	3·99	3·950(11)	1·33	1·189(10)	3·14	3·139(10)	0·99	0·922(10)	3·65(27)
P(2)R(2)	3·30	3·277(10)	8·31	8·345(11)	2·17	2·287(10)	2·04	2·605(11)	0·49	0·507(10)	6·18	6·194(11)	3·43(26)
P(2)R(3)	2·69	2·699(12)	6·29	6·241(13)	6·90	6·882(14)	1·80	1·929(42)	5·16	4·993(13)	0·66	1·017(42)	5·73(33)
P(3)R(1)	−3·86	−3·866(11)	2·87	2·865(12)	5·11	5·127(10)	1·81	1·823(10)	6·05	6·121(10)	2·87	2·844(10)	3·91(28)
P(3)R(2)	1·97	2·003(9)	15·77	15·766(12)	3·14	3·086(12)	3·14	3·211(10)	3·39	3·427(10)	1·95	1·907(11)	3·78(28)
P(3)R(3)	−3·28	−3·278(13)	14·80	14·831(11)	0·71	0·677(13)	4·62	4·439(22)	5·18	5·208(11)	1·57	1·423(23)	4·79(29)

* δ, ε, η are successive rotations about the a_2', a_1', a_3' axes; for convenience, x_c, y_c, z_c are in Å.

† Numbers in parentheses here and in subsequent tables are estimated standard deviations.

Table 2. *Derived parameters for group carbon atoms**

Group atom	x	y	z
P(1)R(1)C(1)	−0·3225(15)	0·35802(52)	0·4706(13)
P(1)R(1)C(2)	−0·3593(17)	0·32021(57)	0·5053(10)
P(1)R(1)C(3)	−0·4427(17)	0·29616(40)	0·4479(14)
P(1)R(1)C(4)	−0·4893(15)	0·30992(51)	0·3559(13)
P(1)R(1)C(5)	−0·4526(17)	0·34774(56)	0·3212(10)
P(1)R(1)C(6)	−0·3692(17)	0·37179(40)	0·3785(14)
P(1)R(2)C(1)	−0·2244(18)	0·43648(41)	0·4878(12)
P(1)R(2)C(2)	−0·3470(14)	0·45508(52)	0·4777(13)
P(1)R(2)C(3)	−0·3574(13)	0·49122(52)	0·4259(13)
P(1)R(2)C(4)	−0·2452(18)	0·50876(41)	0·3841(12)
P(1)R(2)C(5)	−0·1226(14)	0·49015(51)	0·3941(13)
P(1)R(2)C(6)	−0·1122(13)	0·45402(51)	0·4460(13)
P(1)R(3)C(1)	0·4483(13)	0·12797(51)	0·0236(13)
P(1)R(3)C(2)	0·5532(18)	0·11330(47)	0·0805(11)
P(1)R(3)C(3)	0·6826(15)	0·12353(52)	0·0556(13)
P(1)R(3)C(4)	0·7071(13)	0·14843(53)	−0·0263(14)
P(1)R(3)C(5)	0·6022(18)	0·16310(48)	−0·0832(11)
P(1)R(3)C(6)	0·4728(15)	0·15287(51)	−0·0582(12)
P(2)R(1)C(1)	0·0100(12)	0·19333(50)	0·2967(13)
P(2)R(1)C(2)	−0·0272(15)	0·22146(52)	0·3686(11)
P(2)R(1)C(3)	−0·1550(17)	0·23705(43)	0·3683(11)
P(2)R(1)C(4)	−0·2455(12)	0·22450(49)	0·2960(13)
P(2)R(1)C(5)	−0·2083(14)	0·19637(51)	0·2241(11)
P(2)R(1)C(6)	−0·0805(17)	0·18079(45)	0·2244(11)
P(2)R(2)C(1)	0·2626(15)	0·21912(42)	0·2223(12)
P(2)R(2)C(2)	0·1939(11)	0·25459(51)	0·2039(12)
P(2)R(2)C(3)	0·2554(15)	0·28599(39)	0·1532(13)
P(2)R(2)C(4)	0·3856(15)	0·28191(42)	0·1208(12)
P(2)R(2)C(5)	0·4544(11)	0·24644(51)	0·1392(12)
P(2)R(2)C(6)	0·3929(15)	0·21504(39)	0·1899(13)
P(2)R(3)C(1)	0·2312(20)	0·18329(64)	0·4159(11)
P(2)R(3)C(2)	0·3184(19)	0·21353(56)	0·4448(14)
P(2)R(3)C(3)	0·3541(16)	0·21760(49)	0·5451(17)
P(2)R(3)C(4)	0·3027(20)	0·19142(63)	0·6166(11)
P(2)R(3)C(5)	0·2156(19)	0·16117(56)	0·5878(14)
P(2)R(3)C(6)	0·1798(17)	0·15711(50)	0·4874(17)
P(3)R(1)C(1)	−0·5139(12)	0·07571(54)	0·3678(13)
P(3)R(1)C(2)	−0·4142(17)	0·04777(40)	0·3501(13)
P(3)R(1)C(3)	−0·2826(15)	0·05806(46)	0·3669(13)
P(3)R(1)C(4)	−0·2508(12)	0·09631(52)	0·4015(13)
P(3)R(1)C(5)	−0·3505(17)	0·12425(39)	0·4192(12)
P(3)R(1)C(6)	−0·4821(14)	0·11395(48)	0·4024(13)
P(3)R(2)C(1)	0·1890(16)	0·51331(38)	0·2021(13)
P(3)R(2)C(2)	0·2306(16)	0·50373(45)	0·2988(12)
P(3)R(2)C(3)	0·2398(16)	0·46373(54)	0·3282(10)
P(3)R(2)C(4)	0·2072(15)	0·43331(38)	0·2610(13)
P(3)R(2)C(5)	0·1655(16)	0·44288(46)	0·1643(12)
P(3)R(2)C(6)	0·1564(16)	0·48288(54)	0·1349(10)
P(3)R(3)C(1)	−0·2612(19)	0·43988(55)	−0·0411(11)
P(3)R(3)C(2)	−0·3974(18)	0·44594(55)	−0·0377(12)
P(3)R(3)C(3)	−0·4605(13)	0·45130(53)	0·0542(15)
P(3)R(3)C(4)	−0·3873(18)	0·45060(55)	0·1427(11)
P(3)R(3)C(5)	−0·2511(18)	0·44454(56)	0·1393(12)
P(3)R(3)C(6)	−0·1881(13)	0·43918(55)	0·0474(15)

* C(1) is attached to P; other C atoms are numbered in succession so that C(4) is *para* to C(1).

Fourier synthesis shows several interesting features. Slight peaks are apparent at the positions of all of the phenyl carbon atoms attached to phosphorus (the 'C(1)' atoms). Clearly the single isotropic thermal parameter for the ring is slightly too high for the C(1) carbon atom, as is to be expected. In the region of the Rh and P atoms there are indications of an-

Table 3. *Parameters of non-group atoms*

Atom	x	y	z	B or β_{11}*	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	0·22696(17)	0·113302(56)	0·22315(14)	0·00452(20)	0·000352(19)	0·00288(12)	0·000047(67)	0·00013(12)	−0·000058(59)
P(1)	0·28161(55)	0·11137(21)	0·05283(48)	0·00498(76)	0·000467(78)	0·00514(55)	0·00025(23)	0·00125(52)	0·00000(20)
P(2)	0·18089(58)	0·17624(18)	0·28816(50)	0·00445(74)	0·000363(74)	0·00458(56)	0·00047(19)	0·00098(52)	−0·00046(17)
P(3)	0·31340(56)	0·06639(18)	0·33328(50)	0·00301(76)	0·000473(86)	0·00417(54)	0·00003(20)	0·00056(51)	−0·00016(17)
C	0·0640(26)	0·09039(75)	0·2064(19)	3·46(63) (Å^2)					
O	−0·0415(18)	0·07631(52)	0·1966(13)	4·65(43) (Å^2)					
H	0·377(12)	0·1290(36)	0·2168(90)						

* Equivalent isotropic temperature factors (Hamilton, 1959) for Rh, P(1), P(2), and P(3) are 1·82, 2·59, 2·23, and 2·10 Å^2.

isotropy in the thermal motions. Most interesting, the second most prominent peak of height 0·53 e.Å^{-3} is about 1·5 Å from the Rh in such a position as to complete the trigonal bipyramidal configuration about the Rh. We thought that this might be the peak from the hydrogen atom, but since it could also arise because of the restriction of the heavy atoms to isotropic thermal motion a further refinement was run in which this restriction was removed and the Rh and P atoms allowed to vibrate anisotropically. The weighted R in the course of this refinement went down by a factor of 1·023, an improvement that is significant at less than the 1% level (Hamilton, 1965). The conventional R factor for this refinement is 7·2%.* This refinement led to the parameters given in Tables 1 and 3 and to the structure factors presented in Table 4. Another difference Fourier synthesis was then computed, and what we will term the hydrogen peak was still the second most prominent peak on this somewhat smoother map.

Characterization of the hydrogen position

We have pointed out previously (Ibers & Cromer, 1958) that in principle there is an optimum number of data to use in the location of light atoms in the presence of heavy atoms. In the language of the Fourier series the ratio of the peak height of an atom to the standard deviation of the electron density (signal-to-noise ratio) must go through a maximum as a function of scattering angle. This is easily seen. Consider in the present case the peak height $\varrho_{\rm H}$ of a hydrogen atom that is vibrating isotropically. On the assumption that all the structure factors within a limiting radius s_0 (where $s=4\pi\lambda^{-1}\sin\theta$) are available this peak height is simply

$$\varrho^c_{\rm H}=\frac{1}{2\pi^2}\int_0^{s_0}(1+a^2s^2/4)^{-2}\exp\left(-Bs^2/16\pi^2\right)s^2ds \quad (4)$$

where a is the Bohr radius 0·5292 Å. Clearly $\varrho_{\rm H}$ will approach a constant value as s_0 increases. (For $B=0$, $\varrho_A\to(\pi a^3)^{-1}$.) On the other hand the estimated standard deviation of the electron density $\sigma(\varrho)$ increases with s_0 (*i.e.* with the number of terms in the Fourier series), as is apparent from Cruickshank's (1954) formula

$$\sigma(\varrho)=V^{-1}(\Sigma(F_o-F_c)^2)^{\frac{1}{2}}. \quad (5)$$

Thus $\varrho_{\rm H}/\sigma(\varrho)$ will go through a maximum for some value of $\lambda^{-1}\sin\theta$. In practice this value can be determined by varying the number of terms in the Fourier series. Such a procedure has another important advantage. If the peak ascribed to hydrogen

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* This value, as well as some of the distances, including the Rh–H distance, differs slightly from those given previously (La Placa & Ibers, 1963) owing to slight changes in the data brought about by correction of a few indexing errors and the application of an improved absorption correction.

Table 4. *Observed and calculated structure amplitudes* (Cu $K\alpha$) *for* $HRh(CO)(P(C_6H_5)_3)_3$

K	L	OBS	CALC
••••••H=0••••••			
0	0	0	1887
4	0	128	122
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1	-5	49	39
4	-5	75	81
5	-5	36	38
6	-5	85	86
7	-5	91	84
8	-5	107	104
9	-5	55	60
10	-5	97	95
11	-5	100	98
12	-5	84	82
13	-5	53	44
14	-5	88	99
16	-5	74	66
18	-5	85	92
22	-5	101	108
1	-6	39	37
2	-6	68	70
4	-6	48	38
5	-6	49	51
6	-6	103	109
7	-6	58	52
8	-6	66	56
9	-6	108	106
10	-6	97	106
12	-6	101	100
13	-6	92	76
14	-6	47	41
15	-6	59	59
16	-6	49	45
17	-6	50	44
19	-6	64	50
20	-6	53	47
1	-7	61	56
7	-7	84	82
8	-7	85	95
9	-7	65	56
10	-7	57	51
11	-7	58	60
12	-7	59	60
15	-7	72	69
9	-8	79	66
10	-8	94	94
8	-9	53	63
10	-9	54	52
12	-9	55	70
1	-10	75	81
3	-10	67	70
••••••H=4••••••			
3	0	25	24
4	0	133	141
5	0	122	120
6	0	113	100
7	0	29	26
8	0	69	62
9	0	69	67
10	0	121	113
12	0	57	55
13	0	64	64
14	0	67	68
15	0	61	57
16	0	37	40
18	0	84	81
22	0	96	108
24	0	58	49
2	1	114	124
3	1	135	139
5	1	70	56
6	1	108	113
7	1	63	59
8	1	122	111
9	1	78	77
10	1	72	80
12	1	143	134
13	1	101	97
15	1	57	57
16	1	79	83
17	1	61	65
18	1	40	30
20	1	106	112
21	1	54	54
24	1	68	66
0	2	91	93
1	2	73	81
3	2	75	77
4	2	65	58
6	2	36	21
7	2	114	116
9	2	52	54
10	2	95	96
11	2	96	96
12	2	70	76
13	2	59	65
14	2	62	66
15	2	137	156
17	2	49	43
18	2	65	58
19	2	95	113
21	2	64	58
23	2	58	55
1	3	105	112
3	3	45	36
4	3	87	84
5	3	70	71
6	3	63	62
7	3	91	87
9	3	55	52
10	3	40	37
11	3	34	32
13	3	106	113
15	3	96	90
17	3	106	101
0	4	53	46
1	4	89	89
2	4	50	47
3	4	86	82
5	4	87	86
7	4	53	67
8	4	62	56
10	4	61	61
15	4	100	88
19	4	72	66
1	5	142	143
4	5	58	53
5	5	107	108
12	5	63	61
13	5	71	69
16	5	76	67
17	5	110	112
0	6	51	44
1	6	63	59
3	6	136	150
4	6	46	43
7	6	82	75
11	6	72	69
14	6	70	59
15	6	90	94
18	6	47	36
19	6	90	93
1	7	85	92
2	7	40	32
3	7	41	51
4	7	41	42
5	7	105	120
9	7	96	91
13	7	85	82
1	8	76	70
3	8	88	92
7	8	71	60
8	8	85	80
11	8	66	69
6	9	67	64
9	9	90	83
1	-1	20	11
2	-1	156	167
3	-1	129	116

Table 4 (*cont.*)

K	L	OBS	CALC
******H=4******			
4	-1	97	95
5	-1	31	21
6	-1	50	48
8	-1	75	78
9	-1	46	40
10	-1	121	122
11	-1	55	56
12	-1	31	39
13	-1	61	64
14	-1	63	65
15	-1	61	44
16	-1	45	43
17	-1	38	40
18	-1	40	50
20	-1	74	76
23	-1	57	57
0	-2	189	204
1	-2	56	55
5	-2	55	55
6	-2	63	65
8	-2	72	72
9	-2	120	110
10	-2	46	36
12	-2	55	52
15	-2	68	63
16	-2	59	49
17	-2	39	40
18	-2	49	56
19	-2	51	39
22	-2	85	90
2	-3	59	57
3	-3	101	100
4	-3	53	55
5	-3	61	56
6	-3	76	73
8	-3	98	99
9	-3	52	49
10	-3	44	47
12	-3	34	36
14	-3	77	77
15	-3	37	40
16	-3	55	55
20	-3	93	86
21	-3	55	45
0	-4	171	189
1	-4	60	50
2	-4	90	86
3	-4	49	45
4	-4	117	117
5	-4	51	31
6	-4	104	107
7	-4	53	53
8	-4	133	140
12	-4	80	80
15	-4	39	46
16	-4	66	70
18	-4	105	103
22	-4	120	135
1	-5	56	51
2	-5	135	135
3	-5	32	31
4	-5	61	62
5	-5	66	60
6	-5	85	81
7	-5	48	49
8	-5	85	88
9	-5	62	56
10	-5	115	116
12	-5	81	73
14	-5	86	76
16	-5	74	74
20	-5	87	102
0	-6	51	45
1	-6	51	41
3	-6	51	55
4	-6	81	87
6	-6	69	72
7	-6	80	76
8	-6	66	70
10	-6	74	75
11	-6	90	96
12	-6	71	74
14	-6	52	48
15	-6	54	58
17	-6	64	65
2	-7	49	48
3	-7	56	63
4	-7	40	39
5	-7	75	66
9	-7	79	78
10	-7	80	81
8	-8	63	72
6	-9	82	86
******H=5******			
2	0	60	72
3	0	92	100
4	0	26	32
5	0	43	33
6	0	133	128
7	0	73	65
8	0	62	53
9	0	49	43
10	0	76	76
11	0	39	36
12	0	52	46
13	0	88	81
14	0	63	59
15	0	76	77
16	0	74	67
20	0	64	61
1	1	84	119
2	1	30	26
4	1	98	102
5	1	55	58
7	1	102	99
8	1	155	170
9	1	29	30
10	1	72	78
11	1	94	98
12	1	59	62
14	1	101	97
15	1	82	80
17	1	66	67
18	1	43	42
1	2	125	138
2	2	36	34
3	2	76	75
4	2	50	48
5	2	91	93
6	2	47	37
9	2	110	117
10	2	77	75
12	2	91	90
13	2	133	141
15	2	49	47
16	2	71	74
17	2	100	107
19	2	64	62
21	2	68	59
0	3	61	56
1	3	119	131
3	3	98	98
5	3	55	53
7	3	78	75
8	3	40	32
10	3	50	42
11	3	78	73
15	3	114	124
16	3	61	50
17	3	70	60
19	3	81	82
1	4	96	100
3	4	68	61
5	4	71	67
9	4	69	61
13	4	77	84
17	4	79	97
0	5	74	71
1	5	86	84
2	5	35	36
3	5	76	87
5	5	37	43
7	5	60	62
15	5	45	45
1	6	91	104
2	6	39	35
3	6	40	33
5	6	76	75
9	6	74	57
13	6	65	63
1	7	80	75
3	7	81	87
7	7	89	84
8	7	78	77
11	7	93	98
1	8	57	47
5	8	57	53
6	8	94	81
9	8	102	106
0	-1	49	64
1	-1	47	48
2	-1	28	30
4	-1	31	32
6	-1	85	82
7	-1	35	24
8	-1	101	85
9	-1	35	28
10	-1	56	60
11	-1	59	56
12	-1	78	86
13	-1	35	30
14	-1	45	41
15	-1	89	84
16	-1	39	38
18	-1	52	40
2	-2	45	48
3	-2	131	132
4	-2	87	79
5	-2	35	20
6	-2	121	109
8	-2	70	61
9	-2	64	62
10	-2	74	74
13	-2	80	81
20	-2	85	83
0	-3	138	142
1	-3	58	55
2	-3	58	57
3	-3	83	76
4	-3	109	98
5	-3	34	20
6	-3	102	97
7	-3	52	47
8	-3	66	61
10	-3	82	75
11	-3	60	55
12	-3	63	61
15	-3	57	56
18	-3	82	90
2	-4	126	129
4	-4	132	131
5	-4	39	38
6	-4	126	127
8	-4	116	111
10	-4	120	122
12	-4	61	59
14	-4	71	79
16	-4	53	50
0	-5	117	114
1	-5	35	47
2	-5	81	80
4	-5	93	95
6	-5	95	99
8	-5	114	110
9	-5	66	63
10	-5	62	44
11	-5	80	79
12	-5	96	89
16	-5	55	49
17	-5	46	51
18	-5	88	93
2	-6	72	67
3	-6	55	46
7	-6	49	45
8	-6	41	49
9	-6	88	93
10	-6	79	80
13	-6	54	56
15	-6	46	49
5	-7	43	46
6	-7	43	42
8	-7	70	69
6	-8	66	59
8	-8	47	49
******H=6******			
2	0	22	32
3	0	21	16
4	0	40	42
5	0	65	57
6	0	60	53
7	0	50	44
8	0	64	70
10	0	69	61
11	0	73	63
12	0	76	72
13	0	38	31
14	0	68	53
15	0	65	51
17	0	54	56
18	0	71	73
1	1	39	60
2	1	54	61
3	1	71	73
5	1	81	71
6	1	81	85
7	1	49	43
8	1	47	46
9	1	107	97
10	1	67	72
12	1	78	67
13	1	94	100
15	1	51	49
16	1	74	72
17	1	77	82
0	2	43	45
1	2	121	129
3	2	89	93
4	2	27	20
5	2	70	61
7	2	119	112
8	2	65	62
10	2	36	36
11	2	83	92
15	2	100	105
1	3	114	119
3	3	68	66
4	3	39	39
5	3	69	69
8	3	36	37
9	3	78	80
10	3	38	36
13	3	79	83
17	3	88	94
1	4	98	103
3	4	69	79
7	4	54	44
9	4	49	42
15	4	73	77
1	5	80	81
3	5	55	53
5	5	49	51
6	5	40	36
1	6	79	72
3	6	91	100
8	6	63	52
11	6	74	62
1	7	91	100
3	7	73	81
5	7	57	60
6	7	57	51
2	-1	31	30
3	-1	46	45
4	-1	40	43
5	-1	50	51
6	-1	51	52
7	-1	55	51
8	-1	55	53
10	-1	95	86
12	-1	44	45
13	-1	92	102
15	-1	65	45
0	-2	56	68
3	-2	54	57
4	-2	67	67
5	-2	46	41
6	-2	49	47
7	-2	55	48
8	-2	114	106
10	-2	34	39
11	-2	56	54
12	-2	79	79
15	-2	72	80
16	-2	43	30
17	-2	44	45
18	-2	46	66
2	-3	99	107
3	-3	50	49
4	-3	51	52
5	-3	57	51
6	-3	80	73
8	-3	96	80
9	-3	82	83
10	-3	93	90
13	-3	75	74
14	-3	42	42
15	-3	43	45
16	-3	70	61
0	-4	94	91
2	-4	33	34
4	-4	90	96
6	-4	106	120
7	-4	62	59
8	-4	98	99
9	-4	66	60
10	-4	83	84
12	-4	77	73
14	-4	44	50
16	-4	46	58
2	-5	106	112
4	-5	71	75
6	-5	83	81
8	-5	75	68
10	-5	73	76
0	-6	78	74
4	-6	42	46
5	-6	85	86
6	-6	43	52
6	-7	46	62
******H=7******			
3	0	37	46
4	0	40	53
5	0	48	47
6	0	65	72
8	0	53	50
9	0	57	57
10	0	85	83
12	0	47	37
13	0	56	52
1	1	44	69
3	1	66	84
4	1	69	76
5	1	42	33
7	1	88	78
8	1	94	94
10	1	62	58
11	1	75	80
12	1	68	76
15	1	69	69
1	2	113	132
3	2	79	76
5	2	113	117
6	2	68	65
8	2	43	41
9	2	63	46
10	2	54	56
13	2	73	87
0	3	78	84
1	3	103	108
3	3	98	96
4	3	41	33
7	3	83	82
11	3	73	76
1	4	105	112
2	4	73	62
3	4	37	30
5	4	39	41
7	4	40	
1	5	81	77
2	5	41	46
3	5	50	58
1	6	70	75
3	6	84	91
0	-1	28	39
1	-1	33	35
2	-1	27	29
3	-1	33	37
4	-1	23	22
5	-1	59	54
6	-1	47	30
7	-1	59	57
8	-1	63	53
10	-1	43	42
11	-1	58	53
12	-1	66	60
13	-1	40	28
15	-1	68	66
2	-2	44	43
3	-2	49	45
4	-2	33	28
5	-2	64	58
6	-2	37	32
7	-2	45	47
8	-2	33	32
9	-2	102	107
10	-2	68	60
13	-2	76	85
0	-3	78	86
1	-3	30	25
2	-3	53	48
3	-3	38	32
4	-3	67	66
6	-3	72	66
7	-3	89	75
8	-3	67	69
9	-3	46	40
10	-3	47	42
11	-3	69	63
12	-3	65	52
13	-3	52	40
1	-4	43	53
2	-4	120	125
3	-4	44	39
4	-4	77	71
5	-4	37	33
6	-4	70	65
7	-4	38	27
8	-4	88	89
9	-4	70	74
10	-4	50	51
0	-5	120	133
2	-5	49	58
4	-5	90	104
6	-5	71	66
8	-5	60	58
2	-6	76	79

is an artifact, arising for example from improper treatment of the Rh scattering or vibrations, then it should disappear or shift markedly as the number of terms in the series is varied. If the peak is genuine, then its position should stay approximately constant and its height should change in accordance with equation (4), as the number of terms is varied.

Fourier maps were calculated for cut-offs in $\lambda^{-1}\sin\theta$ of 0·20, 0·25, 0·30, 0·35, and 0·416 Å^{-1} (complete data set). Table 5 lists the number of independent terms in these series, the derived peak height ϱ^E of the hydrogen peak, $\sigma(\varrho)$ calculated in accordance with equation (5), $\varrho^E/\sigma(\varrho)$, the derived Rh–H distance, and ϱ^C for a hydrogen atom with a B of 3 Å^2. Note that $\sigma(\varrho)$ varies smoothly with the square root of the number of independent terms, as is expected if errors in F_o are independent of scattering angle. The 0·20 Fourier map is definitely inferior to the others as judged both visually and by the lower value of $\varrho^E/\sigma(\varrho)$. Presumably this is because of the greater relative effects of ripple from termination and because of the greater relative errors that result from the missing low-order terms. The values of $\varrho^E/\sigma(\varrho)$ in Table 5 cannot be interpreted in the ideal way suggested above, for a careful examination of the maps shows that an interfering peak begins to grow in the vicinity of the hydrogen peak on the 0·35 map and that the interference is serious on the 0·416 map. Thus at the high cut-offs there is greater uncertainty in the peak height and in position of the hydrogen peak. Because of this interference ϱ^E does not vary smoothly with cut-off as can be seen when it is compared with ϱ^C (Table 5). The particular values of ϱ^C are included in Table 5 for illustrative purposes, rather than because a zero charge on the hydrogen and a B of 3 Å^2 are favored. In fact the general agreement between ϱ^E and ϱ^C (for a variety of assumptions about charge and thermal motion) is very good indeed. This, together with the fact that this peak is the only constant feature on the various maps, convinces us that this peak is in fact from hydrogen scattering. There is no apparent interference on the 0·25 and 0·30 maps and from these we derive an Rh–H distance of 1·60 Å. The standard deviation, as estimated from Cruickshank's (1954) formula is 0·12 Å. In view of this large, but reasonable, standard deviation it did not seem worthwhile to attempt to refine the hydrogen position.

Since one does not ordinarily expect to detect hydrogen in the presence of an atom as heavy as rhodium, it is worthwhile speculating on why it was possible here. First, the data are obviously of good quality, or else the very smooth difference map and the very low R factor would not have been obtained. Second, because of the very large cell there are a considerable number of low-order terms to which the hydrogen atom contributes, and from which its position can be derived. Third, the structure exhibits

Table 5. *Hydrogen peak heights and related quantities*

Cut-off (Å^{-1})	Number of terms	ϱ^E (e.Å^{-3})	$\sigma(\varrho)$ (e.Å^{-3})	$\varrho^E/\sigma(\varrho)$	ϱ^C (e.Å^{-3})	Rh–H (Å)
0·20	240	0·16	0·025	6·3	0·16	1·95
0·25	461	0·27	0·033	8·1	0·25	1·63
0·30	762	0·34	0·043	7·9	0·34	1·57
0·35	1088	0·51	0·052	9·9	0·42	1·5
0·416	1480	0·53	0·061	8·7	0·53	1·4

little thermal motion because the bulky phenyl rings interlock tightly. Fourth, as mentioned above, the scattering of the Rh and P atoms is not overbearing. Finally, fifth, the group refinement prevents the loss of detail (some of which can be spurious) by eliminating extra, physically unnecessary parameters.

Final parameters and errors

The errors on the group parameters (Table 1) are those derived from the inverse matrix. From this matrix the errors in the coordinates of individual group atoms can be derived. The coordinates and errors of the carbon atoms (but not the hydrogen atoms) are given in Table 2. These coordinate errors can be applied to an error analysis of distances not involved in the same ring. The intra-ring distances are, of course, fixed.

The tabulation of structure factors (Table 4) does not include unobserved reflections, for no value of F_c exceeded our estimate of $F_{\min}$ for any of the weak reflections accessible on the films.

In Table 6 we list the principal values of the root-mean-square amplitudes of vibration of the Rh and three P atoms. The orientations of these vibrational ellipsoids in space are not given, because they do not appear to conform to any simple picture of the vibrations of the molecule as whole. The orientations can, of course, be derived from the data of Table 3.

Table 6. *Root-mean-square amplitudes of vibration* (Å)

Atom	Min.	Int.	Max.
Rh	0·139(4)	0·153(4)	0·162(4)
P(1)	0·142(15)	0·170(14)	0·222(11)
P(2)	0·095(21)	0·173(13)	0·214(12)
P(3)	0·122(16)	0·161(15)	0·198(12)

Description of the structure

The parameters of Tables 1 and 3 and the symmetry elements and cell dimensions define a molecular configuration for tris-triphenylphosphine rhodium carbonyl hydride that is essentially a trigonal bipyramid. A perspective drawing of the molecule is shown in Fig. 1. Selected intramolecular distances and angles are tabulated in Table 7.

Table 7. *Selected intramolecular distances and angles*

Rh–H	1·60(12) Å	OC–Rh–H	170(5)°
Rh–P(1)	2·336(8)	O–C–Rh	179(2)
Rh–P(2)	2·316(9)	P(1)–Rh–CO	94·8(8)
Rh–P(3)	2·315(8)	P(2)–Rh–CO	104·0(8)
Rh–C	1·829(28)	P(3)–Rh–CO	97·8(8)
Rh–O	3·002(20)	P(1)–Rh–P(2)	115·8(2)
P(1)–P(2)	3·942(11)	P(1)–Rh–P(3)	120·5(3)
P(1)–P(3)	4·039(12)	P(2)–Rh–P(3)	116·7(3)
P(2)–P(3)	3·943(13)	P(1)–P(2)–P(3)	61·6(2)
		P(2)–P(3)–P(1)	59·2(2)

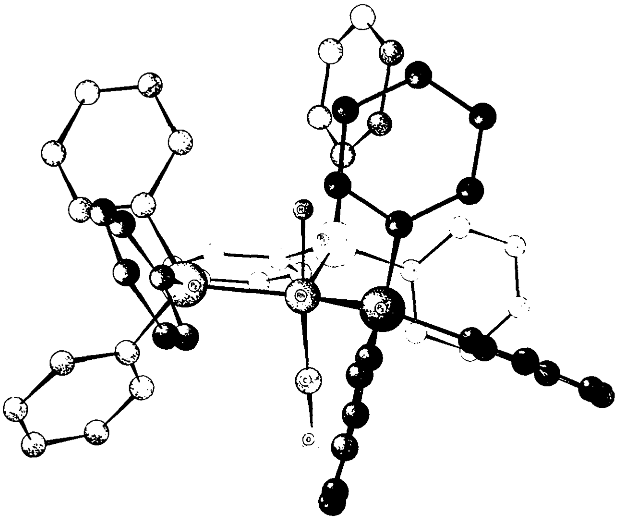

Fig. 1. A perspective drawing of one molecule of $RhH(CO)(P(C_6H_5)_3)_3$. Ring hydrogen atoms are not shown.

No tabulation of the numerous intramolecular and intermolecular distances involving the phenyl rings is given. There are no unusual intermolecular interactions. The phenyl rings obviously dominate the packing of the molecules, as is evident from their bulk and from the fact that the volume per triphenylphosphine in this structure is only about 3% higher than in triphenylphosphine itself (Daly, 1963). According to Daly's (1963) preliminary report on the structure of triphenylphosphine, the molecule has a pyramidal configuration. The triphenylphosphine ligands in the present structure are also pyramidal. The nine P–C(1) distances range between 1·79 and 1·87 Å, a distribution on the basis of the errors of Table 2 that is consistent with equivalence. The mean P–C(1) distance is accordingly 1·83 ± 0·01 Å. The C(1)–P–C(1′) angles range from 97 to 104° and on the assumption of equivalence average 101 ± 1°. The C(1)–P–C(4) angles range from 173 to 179° and average 176 ± 1°. The mean P–C distance and mean pyramidal angle are in reasonable agreement with those found in the simpler trialkylphosphines, such as $P(CH_3)_3$ (Springall & Brockway, 1938). There has been much interest in the equilibrium conformations of the triaryl- and trialkylphosphines and borons. Our results here for the triphenylphosphine ligand indicate that the phenyls rotate easily about the P–phenyl bonds and adopt a geometry that minimizes the energy of the entire crystal. Thus the dihedral angles between phenyl rings found here are 62, 90, 85°; 99, 82, 84°; 112, 76, 83°, and no particular trend is evident. There are spectroscopic differences between triaryl- and trialkylphosphines as molecules and as ligands (Jaffé, 1954), and it may be that in the triphenylphosphine molecule this ease of rotation is not present and a more regular configuration is adopted. Moreover, the mean P–C(1)–C(4) angle here of $177 \pm 1°$ gives no indication of bending about the P–phenyl bond.

The trigonal bipyramid about the rhodium atom consists of three phosphorus atoms in the basal plane, a carbonyl at one apex, and the hydrogen at the other. The basal plane is slightly distorted from a perfect triangle, presumably as a result of packing effects. The Rh atom lies 0·355 Å from the basal plane toward the carbon atom of the carbonyl, perhaps because the CO group is far bulkier than the H and the P–CO distances must be correspondingly longer. The Rh–P and Rh–C distances appear to be normal, as judged by the usual radii sum rules, although there are few structures in the literature with which these distances can be compared. Dahl, Martell & Wampler (1961) found Rh–CO distances of 1·85 and 1·77 in $[Rh(CO)_2Cl]_2$.

The Rh–H distance of $1·60 \pm 0·12$ Å found here is about what one would predict from the usual sum rules for a normal covalent bond. Subsequent to this work Abrahams, Ginsberg & Knox (1964) in a neutron diffraction study have found that the average Re–H distance in K_2ReH_9 is $1·68 \pm 0·01$ Å. As far as is known these two determinations are the only documented ones of metal–hydrogen bond lengths in transition-metal hydrides. Both of these compounds exhibit the abnormally high chemical shift and other spectroscopic peculiarities that are characteristic of the simpler transition-metal hydrides such as $HCo(CO)_4$. If one is willing to extrapolate from these two examples, then it appears that the M–H bond in transition-metal hydrides is a normal one. This is consistent with the calculations of Lohr & Lipscomb (1964) who have accounted for the chemical shift on the basis of a normal M–H bond. It is probable that the arguments of Cotton and others that have led to the description of the M–H bond as abnormally short need re-examination.

The calculations performed here made use of our local versions of Burnham's GNABS absorption program, Zalkin's FORDAP Fourier program, and Busing & Levy's ORFLS least-squares program, all for the IBM 7090 computer. We are indebted to these programmers for their original versions and to S. C. Abrahams for calling our attention to Burnham's work.

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