

As(2) is 2.358 (1) Å; *cf.* the sum of covalent radii of 2.342 Å.<sup>17</sup> The reasons for this are not readily apparent. However, the different lengths are consistent with the distribution of "short" and "long" bonds about Co(3) and Co(4). It is of interest to note that calculation has shown that the lone pair on each arsenic is directed along the cobalt-arsenic vector which rules out explanations involving "bent bonds."

The average carbon-arsenic bond length is 1.942 (7) Å which is close to the average value found in Co<sub>4</sub>(CO)<sub>8</sub>(ffars)<sub>2</sub>,<sup>9</sup> 1.93 Å, individual esd 0.02 Å. Angles of type C-As-C are smaller than the tetrahedral angle whereas those of type M-As-C, M = metal, are larger. This effect is probably due to the carbon-arsenic bonds having more p-orbital character than cobalt-arsenic bonds which have a high s-orbital character, a distribution due to cobalt being more electropositive than carbon.<sup>18</sup>

In the ethylidyne group, the C(18) forms equal bonds to each cobalt atom of lengths 1.907 (7), 1.895 (7), and 1.907 (7) Å to Co(3), Co(4), and Co(5), respectively; *cf.* 1.90 Å in III and 1.91 (2) Å in IV. The angles involving C(18) are also consistent with those with a similar CH<sub>3</sub>CCO<sub>3</sub>-grouping. A normal, single carbon-carbon bond of length 1.50 (1) Å joins C(18) and C(19).

The different environment of Co(5) from Co(3) and Co(4) is reflected in the bridging carbonyl groups. C(22), which spans Co(3) and Co(4), has essentially equal cobalt-carbon bond lengths whereas those bridg-

ing Co(3), Co(5) and Co(4), Co(5) are asymmetric; in each case, the longer cobalt-carbon bond involves Co(5) (see Table II). The values may be compared with the value of 1.92 Å found in Co<sub>2</sub>(CO)<sub>8</sub><sup>15i</sup> where the bridge is symmetrical. Cobalt-carbon bonds involving terminal groups are normal, mean 1.76 (1) Å. It is observed that the carbon-oxygen bond lengths for terminal groups are consistently shorter than those for bridging groups. This trend is also true for Co<sub>6</sub>(CO)<sub>10</sub>-(SC<sub>2</sub>H<sub>5</sub>)<sub>5</sub><sup>15b</sup> and SC<sub>6</sub>(CO)<sub>11</sub>(SC<sub>2</sub>H<sub>5</sub>)<sub>4</sub><sup>15c</sup> whereas the reverse situation is found for Co<sub>3</sub>{(SC<sub>2</sub>H<sub>5</sub>)<sub>5</sub>(CO)}-(CO)<sub>3</sub>.<sup>15a</sup> It is expected that the bridging groups should have the shortest carbon-oxygen bond length but Cotton<sup>19</sup> pointed out that this bond length is very insensitive to bond order change.

The molecule has approximately C<sub>s</sub> symmetry with the largest deviations (~0.04 Å) from the plane (Table III) in the carbonyl groups. However these deviations are not considered to be chemically significant.

Within the ffars ligand, C(10)-C(11) is a double bond (1.36 (1) Å), while other carbon-carbon bonds have the single-bond value. The carbon-fluorine distances are equal, average 1.347 Å, individual esd 0.009 Å, which are near the published value, 1.344 (4) Å.<sup>20</sup>

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(19) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966, p 729.

(20) Reference 12b, p 275.

(17) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960.

(18) C. E. Mellish and J. W. Linnett, *Trans. Faraday Soc.*, **50**, 657 (1954).

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## Structure and Bonding of the Lithium Rhodium Hydrides Li<sub>4</sub>RhH<sub>4</sub> and Li<sub>4</sub>RhH<sub>5</sub><sup>1</sup>

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The structure and bonding of the lithium rhodium hydrides Li<sub>4</sub>RhH<sub>4</sub> and Li<sub>4</sub>RhH<sub>5</sub> have been studied using single-crystal X-ray diffraction and magnetic susceptibility techniques. X-Ray intensities were measured with a scintillation counter. Li<sub>4</sub>RhH<sub>4</sub> has *a* = 6.338 (5) and *c* = 4.113 (8) Å, probable space group *I4/m*, *Z* = 2, and calculated density 2.707 g/cm<sup>3</sup>. The rhodium atom is surrounded by four lithium atoms at 2.83 (2) Å, eight lithium atoms at 2.84 (3) Å, and four hydrogen atoms at about 1.9 Å. The final values for *R<sub>w</sub>* are 0.0625 with hydrogen and 0.0718 without hydrogen. Li<sub>4</sub>RhH<sub>5</sub> has *a* = 3.880 (3), *b* = 9.020 (5), and *c* = 8.895 (6) Å, probable space group *Cmcm*, *Z* = 4, and calculated density 2.895 g/cm<sup>3</sup>. The rhodium atom position was derived from the X-ray data. The remainder of the structure was inferred from packing considerations and from its relation to the structure of Li<sub>4</sub>RhH<sub>4</sub>. For the refinement with rhodium alone, *R<sub>w</sub>* = 0.126; with all atoms in their presumed positions, but without further refinement, *R<sub>w</sub>* = 0.145. In the proposed structure of Li<sub>4</sub>RhH<sub>5</sub>, Rh-Li distances are 2.55 and 2.79 Å, Li-Li distances range from 2.46 to 2.75 Å, Rh-H distances are 1.81-1.96 Å, and Li-H distances range from 1.82 to 1.97 Å. Both lithium rhodium hydrides were found to possess weak, temperature-independent paramagnetism over the temperature range 51-297°K. The molar susceptibilities, in cgs units, were determined to be 1.2 × 10<sup>-6</sup> for Li<sub>4</sub>RhH<sub>4</sub> and 2.1 × 10<sup>-6</sup> for Li<sub>4</sub>RhH<sub>5</sub>. These data indicate that the spins of the electrons are paired in both compounds. Both compounds appear to be related to LiH, suggesting ionic bonding between hydrogen and both of the metals. There is also some indication of metallic bonding between lithium and rhodium. The structure rules out the presence of localized rhodium-rhodium bonding.

### Introduction

When lithium hydride and rhodium metal are heated

(1) Work performed under the auspices of the U. S. Atomic Energy Commission, presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, and based on a dissertation submitted by L. B. Lundberg in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Denver, May 1968.

together to approximately 600° in an inert atmosphere, a black liquid forms which changes to a brittle black solid upon cooling to room temperature. Farr's<sup>2</sup> original work on this reaction established the existence of two compounds, Li<sub>4</sub>RhH<sub>4</sub> and Li<sub>4</sub>RhH<sub>5</sub>. These formu-

(2) J. D. Farr, *J. Inorg. Nucl. Chem.*, **14**, 202 (1960).

las were later confirmed by Magee.<sup>8</sup> From a structural standpoint, these early studies established only that  $\text{Li}_4\text{RhH}_4$  is tetragonal.

The present work was undertaken in an attempt to determine the crystal structures of these compounds and to learn as much as possible about the nature of the bonding. We had hoped to use both X-ray and neutron diffraction for the structure studies but the neutron diffraction work was unsuccessful. Large single crystals were not obtained, and bulk specimens for powder neutron diffraction were too impure to produce useful patterns. We were able to locate the rhodium atoms in both compounds from single-crystal X-ray diffraction data. For  $\text{Li}_4\text{RhH}_4$ , the location of the lithium atom was clearly evident from X-ray data, and some indication of the hydrogen atom position was also obtained. We postulate reasonable positions for lithium and hydrogen in  $\text{Li}_4\text{RhH}_5$ .

Magnetic susceptibility data were obtained and were used along with our proposed structures to make inferences regarding the bonding.

### Experimental Section

Samples of  $\text{Li}_4\text{RhH}_4$  were prepared in essentially the manner described by Farr<sup>2</sup> and Magee.<sup>3</sup>  $\text{Li}_4\text{RhH}_5$  was prepared by adding hydrogen directly to molten  $\text{Li}_4\text{RhH}_4$  contained in a molybdenum cup. The hydrogen pressure was maintained at 550 Torr over the product as it was slowly cooled to room temperature.

Samples were fractured under dry *n*-hexadecane with a mortar and pestle, and promising looking fragments were sealed in thin-walled glass capillaries under a helium atmosphere. Suitable crystals of both compounds were obtained, although the  $\text{Li}_4\text{RhH}_5$  crystals were eventually found to be twinned. Precession, cone axis, and Laue photographs were used to determine approximate unit cells and possible space groups. More accurate lattice constants were obtained from least-squares analyses of several high-order reflections measured at room temperature ( $\sim 25^\circ$ ) with a General Electric Co. single-crystal orienter on an XRD-5 using Mo  $K\alpha_1$  radiation ( $\lambda 0.70926 \text{ \AA}$ ).

$\text{Li}_4\text{RhH}_4$  was found to be tetragonal with  $a = 6.338$  (5) and  $c = 4.113$  (8)  $\text{\AA}$ . All reflections with  $h + k + l \neq 2n$  were absent. The Laue symmetry is  $4/m$  so possible space groups are  $I4$ ,  $I\bar{4}$ , and  $I4/m$ . We describe the structure in space group  $I4/m$  but small puckering of the lithium or hydrogen layers would change the symmetry to  $I\bar{4}$ . Similarly, if the  $z$  coordinates of the lithium and hydrogen atoms were slightly different from each other or from that of the rhodium atom, the symmetry would be  $I\bar{4}$ . Using X-ray data, we cannot hope to detect small departures from  $I4/m$ . With two formula units per unit cell the calculated density is  $2.707 \text{ g/cm}^3$ . Attempts to measure densities were unsuccessful because the compounds reacted with trace amounts of water in the immersion liquids. Magee<sup>3</sup> reported measured densities of  $2.05$  and  $2.14 \text{ g/cm}^3$ , but he also had difficulty because of reaction with the immersion liquid.

$\text{Li}_4\text{RhH}_5$  was found to have an orthorhombic cell with  $a = 3.880$  (3),  $b = 9.020$  (5), and  $c = 8.895$  (6)  $\text{\AA}$ . Some difficulty was encountered in assigning the proper space group to this compound because of twinning. Examination of several fragments which were originally thought to be single crystals showed that interchange of the  $b$  and  $c$  axes resulted in every fragment being twinned. After properly indexing reflections from half of a twin, we found that for  $hkl$  reflections those with  $h + k \neq 2n$  were absent as were  $h0l$  reflections with  $l \neq 2n$ . The space group is thus  $Cmcm$ , if centric. We cannot rule out the acentric subgroup of this space group except on the grounds that the structure we propose in  $Cmcm$  is reasonable.

With four formula units the calculated density is  $2.895 \text{ g/cm}^3$ . Because of high reactivity the density could not be measured experimentally. This unit cell is a simple distortion of the tetragonal cell of  $\text{Li}_4\text{RhH}_4$ . The  $a$  axis is a shortened tetragonal  $c$  axis, while  $b$  and  $c$  are, respectively, slightly lengthened and shortened base diagonals of the tetragonal cell.

(3) C. B. Magee, Report DRI-2189, Denver Research Institute, Denver, Colo., 1964.

X-Ray intensities were measured on the XRD-5 using Zr-filtered Mo radiation and a scintillation counter with pulse height analyzer. Counts were accumulated during a  $\theta$ - $2\theta$  scan of  $4^\circ$   $2\theta$  centered on the computed  $2\theta$  value. Background was measured by a similar scan with a balanced yttrium filter. An additional contribution to the background, caused primarily by the glass capillary, was obtained by taking fixed time counts with each filter near each reflection at nondiffracting  $\varphi$  settings. An approximate absorption correction was made by applying empirical corrections based on the measured variation of intensity  $\varphi$  at  $\chi = 90^\circ$  and applying spherical absorption corrections ( $\mu r = 0.4$ ) based on the average radius of the fragments.

An additional background was subtracted from specific reflections of the  $\text{Li}_4\text{RhH}_5$  crystal because of the twinning. The nature of the twinning caused certain reflections to overlap while others were separated. Those  $hkl$  reflections with  $h + k = 2n$  and  $h + l = 2n$  were the sum of reflections from both halves of the twin. All other reflections were nonoverlapping. Those  $hkl$  reflections with  $h + k = 2n$  and  $h + l \neq 2n$  originated from the larger half of the twin, while, in terms of the indices of the larger half, those  $hkl$  reflections with  $h + k \neq 2n$  and  $h + l = 2n$  originated from the smaller half. A correction factor was derived from the ratio of the intensities of matched pairs of reflections. These matched pairs consisted of  $h_1k_1l_1$  reflections from the larger half of the twin and  $h_2k_2l_2$  reflections from the smaller half of the twin for which  $h_1 = h_2$  and  $k_1 = l_2$ . The correction factor used is a weighted average of all these ratios and is defined by the expression

$$m = \frac{\sum_i w_i (I_{h_1k_1l_1} / I_{h_2k_2l_2})_i}{\sum_i w_i} \quad (1)$$

where

$$w_i = \frac{1}{\sqrt{I_{h_1k_1l_1} + I_{h_2k_2l_2}}} \quad (1a)$$

The correction was applied to the measured total background,  $b$ , for overlapping reflections according to the relation

$$b' = m(I_{hkl} - b) + b \quad (2)$$

The new background,  $b'$ , was then applied to the intensity data. For the crystal measured,  $m = 0.125$ . The correction for overlapping reflections was applied to the background rather than to the intensity so that these points would have less weight in the least-squares refinement of the structure.

All the X-ray intensity data were corrected for Lorentz-polarization effects, absorption, and background through use of a computer program prepared by Larson, *et al.*,<sup>4</sup> called DATA-FREP. Reflections were considered observed if  $(I_{hkl} - b) \geq 2.0(I_{hkl} + b)^{1/2}$ . The observed reflections were weighted according to the counting statistics by the factor given by Evans,<sup>5</sup> while the unobserved reflections were given zero weight. Extinction effects were not considered because the rather poor quality of the crystals made the effect unimportant.

The positive quadrant was measured for both crystals within the range  $2\theta \leq 50^\circ$ . For  $\text{Li}_4\text{RhH}_4$ , 98 nonspace-group extinct reflections were measured and all were observed. For  $\text{Li}_4\text{RhH}_5$ , 167 nonextinct reflections were measured and 152 were observed.

### Determination of the Structures

For the least-squares refinement, the quantity minimized was  $\sum w(F_o - KF_c)^2$  where  $K$  is a scale factor. Relativistic Hartree-Fock form factors were used for rhodium<sup>6a</sup> and lithium,<sup>6b</sup> and that of Stewart, Davidson, and Simpson<sup>6c</sup> was used for hydrogen. Isotropic thermal parameters were used.  $R$  indices quoted are  $R = \sum |F_o| - |KF_c| / \sum |F_o|$  and  $R_w = [\sum w(|F_o| - |KF_c|)^2 / \sum w F_o^2]^{1/2}$ . The calculations were done on a CDC-6600 computer using a program written by Larson.<sup>7</sup>

With two formula units present, the rhodium atom must be

(4) A. C. Larson, D. T. Cromer, and R. B. Roof, Jr., Report LA-3043, Los Alamos Scientific Laboratory, Los Alamos, N. M., 1964.

(5) H. T. Evans, Jr., *Acta Crystallogr.*, **14**, 689 (1961).

(6) (a) D. T. Cromer and J. T. Waber, unpublished work, 1968; (b) P. A. Doyle and P. S. Turner, *Acta Crystallogr., Sect. A*, **24**, 390 (1968); (c) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(7) A. C. Larson, unpublished work, 1970.

placed at the origin of  $I4/m$ . After a few least-squares cycles to fix the scale factor and the thermal parameter of the rhodium atom, a difference Fourier map was computed. The  $z = 0$  section is shown in Figure 1. The lithium atom is quite prom-

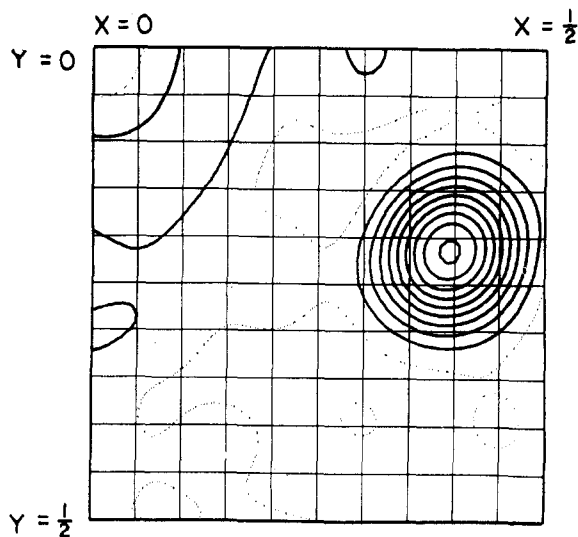


Figure 1.—One-quarter of the  $z = 0$  section of the difference Fourier map of  $\text{Li}_4\text{RhH}_4$  with the origin rhodium removed. Contours are at  $0.707 \text{ e}/\text{\AA}^3$  and the zero contour is dotted.

inently shown in an eightfold special position  $xy0$ . The only other features in this map are diffraction ripples around the origin and a small peak at approximately  $0.30, 0.30, 0$ . This small peak we believe to be the hydrogen atom. With the rhodium atom only,  $R = 0.860$  and  $R_w = 0.1294$ .

The model obtained from the difference Fourier map was refined by least squares. When the hydrogen atom was allowed to move freely, it went to  $x = 0.056$ ,  $y = 0.214$ ,  $z = 0$  and its thermal parameter became about  $-2 \text{ \AA}^2$ . This position is only  $1.4 \text{ \AA}$  from the rhodium atom at the origin. It appears that this least-squares refinement is seeking to place the hydrogen atom in a positive region of the diffraction ripples near the origin. The hydrogen atom was then constrained so that it would remain at  $1.90 \text{ \AA}$  from the rhodium atom, the approximate distance from the origin to the small peak in Figure 1, although it could move anywhere on this radius. This refinement led to  $R = 0.0408$  and  $R_w = 0.0625$ . The parameters are given in Table I and observed and calculated structure factors are in Table II.<sup>8</sup>

TABLE I  
LEAST-SQUARES PARAMETERS FOR  $\text{Li}_4\text{RhH}_4$

Atom	$x$	$y$	$z$	$B, \text{\AA}^2$
Rh	0	0	0	1.22 (8)
Li	0.395 (5)	0.211 (5)	0	0.99 (52)
H	0.066 (21)	0.292 (5)	0	-0.58 (290)

The hydrogen temperature factor has the physically impossible value of  $-0.58 \text{ \AA}^2$ . Although this negative value is far less, in magnitude, than its standard deviation, it might be an indication that the hydrogen exists as a hydride ion. If the hydrogen  $B$  is held at the more reasonable value of  $1.22 \text{ \AA}^2$  (the same as that of the rhodium atom),  $R = 0.0400$  and  $R_w = 0.0627$ . If the hydrogen atom is omitted,  $R = 0.0416$  and  $R_w = 0.0718$ .

We cannot claim to have located the hydrogen atom with any great precision, particularly because of the constraint placed on it. Nevertheless it is in a reasonable location with respect to the other atoms. Also, one may use Hamilton's<sup>9</sup>  $R$  ratio to

(8) Tables II and IV, listing observed and calculated structure factors for  $\text{Li}_4\text{RhH}_4$  and  $\text{Li}_4\text{RhH}_5$ , respectively, will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for \$3.00 for photocopy of \$2.00 for microfiche.

(9) W. H. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

test the hypothesis that hydrogen does not contribute to the experimental intensities. The number of parameters with hydrogen is 8 and without hydrogen is 5; thus the dimension of the hypothesis is 3. The number of degrees of freedom is  $98 - 8 = 90$ . Interpolation in Hamilton's tables gives  $R_{3,90,0.01} = 1.062$ . The observed  $R_w$  ratio is 1.146, so that at the 99% confidence level we must reject the hypothesis that hydrogen does not contribute to the intensities.

A Patterson map of  $\text{Li}_4\text{RhH}_5$  showed that the rhodium atom is in set  $4c$  ( $0, y, 1/4$ ) with  $y \approx 0.205$ . After least-squares refinement of the rhodium position, isotropic temperature factor, and the scale factor,  $y_{\text{Rh}} = 0.2043$  (8),  $B_{\text{Rh}} = 1.93$  (5),  $R = 0.145$ , and  $R_w = 0.126$ . A difference Fourier map with the rhodium atom removed was calculated. One eightfold  $0, y, z$  peak appeared which refined as a lithium atom. Other peaks occurred in the  $x = 0$  section but were either too close to other atoms or would not refine at all. This crystal, besides being twinned, was of poorer quality than the one of  $\text{Li}_4\text{RhH}_4$ . The diffraction data were not good enough to locate the lithium atoms, much less the hydrogen atoms. Attempts to determine further details of the structure from the diffraction data were abandoned.

We propose the following arrangement of light atoms based on packing considerations and on the relation between the unit cells of the two compounds. In Figure 2(a) the basal plane of the

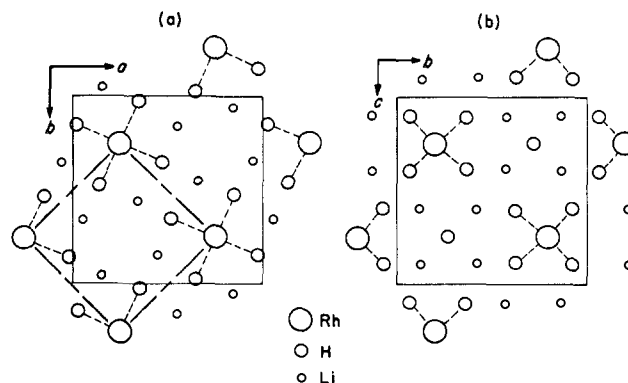


Figure 2.—Basal plane of the face-centered tetragonal (—) and the body-centered tetragonal (---) representations of  $\text{Li}_4\text{RhH}_4$  (a) and the  $0, y, z$  plane of  $\text{Li}_4\text{RhH}_5$  (b).

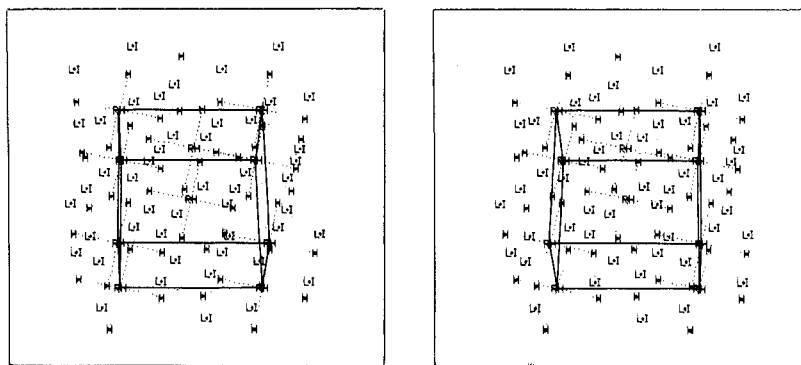
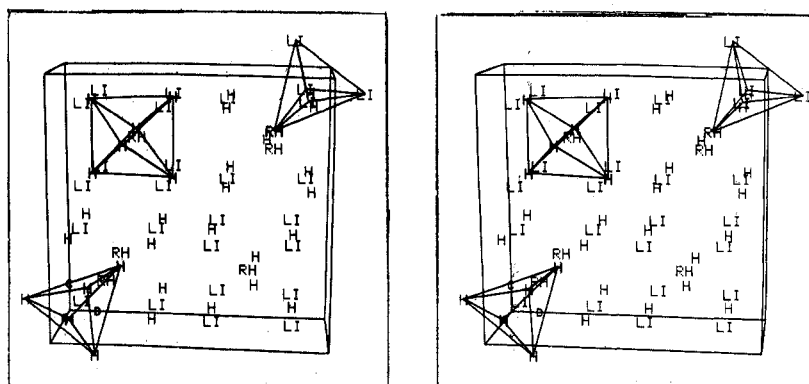
body-centered  $\text{Li}_4\text{RhH}_4$  structure is shown along with the face-centered representation of this cell but with the origin shifted to correspond to the orthorhombic cell of  $\text{Li}_4\text{RhH}_5$ . The orthorhombic cell, Figure 2(b), is a slight distortion of the face-centered tetragonal cell. Starting with the rhodium position determined from the X-ray data, two lithium atoms and two hydrogen atoms were placed in eightfold  $0, y, z$  positions and an additional fourfold hydrogen was placed in a  $0, y, 1/4$  position between the rhodium atoms. With these positions as starting parameters, a least-squares program written by Larson<sup>10</sup> was used to find the best positions. This program minimized the function  $\sum_{ij} [1.0 - \exp\{5(1 - d_{ij}/D_{ij})\}]^2$  in which  $D_{ij}$  is the desired distance from atom  $i$  to atom  $j$ , and  $d_{ij}$  is the actual distance in the model. The  $D_{ij}$  values used were comparable to distances in  $\text{Li}_4\text{RhH}_4$ , and the rhodium position was held constant. This program worked very well and led to the parameters listed in Table III.

TABLE III  
PROPOSED ATOM POSITIONS IN  $\text{Li}_4\text{RhH}_5$

Atom	$x$	$y$	$z$	Atom	$x$	$y$	$z$
Rh	0	0.204	$1/4$	H(1)	0	0.072	0.097
Li(1)	0	0.585	0.108	H(2)	0	0.369	0.109
Li(2)	0	0.869	0.100	H(3)	0	0.731	$1/4$

In Figure 2(b) the rhodium atoms have been shifted from  $y = 1/4$  to  $y = 0.204$ , a distance of  $0.41 \text{ \AA}$ . The extra hydrogen is inserted in the hole near the rhodium and completes an octahedral sixfold coordination of hydrogen about the rhodium. This process is accompanied with small shifts of the original lithium and hydrogen atoms.

(10) A. C. Larson, unpublished work, 1965.

Figure 3.—Stereogram of the proposed  $\text{Li}_4\text{RhH}_4$  crystal structure.Figure 4.—Stereogram of the proposed  $\text{Li}_4\text{RhH}_5$  crystal structure.

The structure factors, calculated with the positions of Table III, the scale factor from the rhodium-only refinement, and an isotropic  $B$  of  $2.0 \text{ \AA}^2$  for all atoms, are given in Table IV.<sup>8</sup> For this parameter set  $R = 0.168$  and  $R_w = 0.145$ , an agreement worse than with rhodium only. Further least-squares refinement was unsuccessful; thermal parameters for most atoms either became very large or negative.

### Magnetic Susceptibility

The static magnetic susceptibilities of both hydrides were measured by the Gouy method at 51, 75, and  $297^\circ\text{K}$  in the field range 4–10 kG. Both compounds exhibited weak, temperature-independent paramagnetism. The molar susceptibilities, in cgs units, were determined to be  $1.2 \times 10^{-6}$  for  $\text{Li}_4\text{RhH}_4$  and  $2.1 \times 10^{-6}$  for  $\text{Li}_4\text{RhH}_5$ . These data indicate that the spins of the electrons are paired in both compounds.

### Discussion

There is a striking resemblance between the structures proposed here for  $\text{Li}_4\text{RhH}_4$  and  $\text{Li}_4\text{RhH}_5$  (see Figures 3 and 4) and the LiH structure.<sup>11</sup> The structure of the latter is of the NaCl type with each ion coordinated octahedrally by six ions of opposite charge. The Li–H interionic distance in LiH is  $2.04 \text{ \AA}$ . If every fifth LiH group in lithium hydride is replaced by a rhodium atom at the position vacated by the lithium ion, the  $\text{Li}_4\text{RhH}_4$  structure is obtained. This substitution results in fourfold coordination of the rhodium atom by hydrogen atoms in the basal plane and vacant sites along the  $c$  axis above and below the basal plane. The rhodium atom also has 12 nearly equidistant lithium neighbors. The lithium atoms are coordinated in a nearly octahedral manner by five hydrogen atoms and one vacant site, and the hydrogen atoms by five lithium atoms and one rhodium atom. The average of

TABLE V  
INTERATOMIC DISTANCES ( $\text{\AA}$ ) IN  $\text{Li}_4\text{RhH}_4$

Rh–4 Li	2.83 (2)	Li–2 Rh	2.83 (2)
–8 Li	2.84 (3)	–Rh	2.84 (3)
–4 H	1.90 <sup>a</sup>	–2 Li	2.75 (4)
		–2 Li	2.80 (4)
H–Rh	1.90 <sup>a</sup>	–4 Li	2.95 (3)
–Li	1.88	–Li	2.99 (6)
–2 Li	2.07	–H	1.88 <sup>a</sup>
–Li	2.14	–2 H	2.07
–Li	2.18	–H	2.14
–2 H	2.69	–H	2.18
–H	2.77		
–4 H	2.84		

<sup>a</sup> Because of the constraint, standard deviations on distances involving hydrogen atoms are meaningless.

the Li–H distances ( $2.07 \text{ \AA}$ ) in  $\text{Li}_4\text{RhH}_4$  (Table V) is comparable with that in LiH. Some of the Li–Li and H–H distances are shorter than those in LiH ( $2.88 \text{ \AA}$ ) because of distortions of the LiH lattice by rhodium.

In  $\text{Li}_4\text{RhH}_5$  the additional hydrogen atom completes the octahedral hydrogen coordination of rhodium. The additional hydrogen, H(3), is also octahedrally surrounded by two rhodium and four lithium atoms. However, the distortion is such that now the lithium atoms and H(1) and H(2) each have five close neighbors forming distorted trigonal pyramids. The coordination polyhedra for Li(1), H(1), and rhodium are shown in the stereogram of Figure 4.

It is interesting to note that the addition of the fifth hydrogen causes a 6% shrinkage of the volume of the face-centered tetragonal cell of  $\text{Li}_4\text{RhH}_4$ . The Li–H distances in  $\text{Li}_4\text{RhH}_5$  (Table VI) are also comparable to that in LiH. The Rh–H distances in  $\text{Li}_4\text{RhH}_5$  are somewhat shorter than those in  $\text{Li}_4\text{RhH}_4$ , but none is as short as the covalent Rh–H bond length of  $1.60 \text{ \AA}$

(11) E. Zintl and A. Harder, *Z. Phys. Chem., Abt. B*, **28**, 478 (1935).

TABLE VI  
INTERATOMIC DISTANCES (Å) IN  $\text{Li}_4\text{RhH}_5$ 

Rh-Rh	3.88	Li(2)-2 Rh	2.79
-4 Li(1)	2.55	-Li(1)	2.56
-4 Li(2)	2.79	-2 Li(1)	2.71
-2 H(1)	1.81	-2 Li(1)	2.75
-2 H(2)	1.95	-Li(2)	2.67
-2 H(3)	1.96	-2 H(1)	1.83
Li(1)-2 Rh	2.55	-2 H(2)	1.94
-Li(1)	2.46	-H(3)	1.82
-Li(1)	2.53	H(1)-Rh	1.81
-Li(2)	2.56	-2 Li(1)	1.95
-2 Li(2)	2.71	-2 Li(2)	1.83
-Li(2)	2.75	-H(1)	2.16
-2 H(1)	1.95	H(2)-Rh	1.95
-H(2)	1.95	-Li(1)	1.95
-H(2)	1.97	-Li(1)	1.97
-H(3)	1.82	-2 Li(2)	1.94
		H(3)-2 Rh	1.96
		-2 Li(1)	1.82
		-2 Li(2)	1.82

found in tris(triphenylphosphine)rhodium carbonyl hydride.<sup>12</sup>

The similarities between the proposed structures and Li-H distances for the lithium-rhodium hydrides and those of lithium hydride, along with other similarities such as brittleness and reaction with water to yield hydrogen gas, lead to the conclusion that the bonding of these compounds is predominantly ionic.

The fact that  $\text{Li}_4\text{RhH}_5$  exhibits temperature-independent paramagnetism is consistent with an ionic model. The temperature-independent paramagnetism of  $\text{Li}_4\text{RhH}_4$  is suggestive of rhodium metallic bonding along the *c* axis of the crystal. Preliminary room-temperature electrical resistivity measurements on polycrystalline samples (resistivities of about 0.5 ohm cm for  $\text{Li}_4\text{RhH}_4$  and about 1.5 ohm cm for  $\text{Li}_4\text{RhH}_5$ )

(12) S. J. La Placa and J. H. Ibers, *Acta Crystallogr.*, **13**, 511 (1965).

are inconclusive on this point, but the relatively large Rh-Rh distance (4.11 Å) along the *c* axis argues against delocalized metallic bonding between rhodium atoms. On the other hand, intermetallic bonding between rhodium and lithium is quite possible. The Li-Rh interatomic distances in both compounds are similar to that found in the intermetallic compound  $\text{LiRh}$  (2.663 Å).<sup>13</sup> This type of bonding may account for the apparent absence of an unpaired electron in the four-hydrogen compound.

In conclusion it should be noted that the lithium rhodium hydrides are not unique. We are currently studying the Li-Pd-H and Li-Ir-H systems and find evidence of ternary hydrides.<sup>14,15</sup> Graefe and Robeson<sup>16</sup> have observed reactions between lithium hydride and several metals. Moyer, *et al.*,<sup>17</sup> have prepared and studied  $\text{Sr}_2\text{IrH}_4$  and in addition have observed ternary phases in other alkaline earth-transition metal-hydrogen systems. Reilly and Wiswall<sup>18</sup> have studied the properties of  $\text{Mg}_2\text{NiH}_4$ , which they prepared by hydriding  $\text{Mg}_2\text{Ni}$ . There are obvious similarities between these compounds, and one naturally seeks a unifying concept to account for their bonding and structures. We hope that the structures proposed here for the lithium rhodium hydrides and the ionic model deduced therefrom will help in attaining that goal.

(13) S. S. Sidhu, K. D. Anderson, and D. D. Zaubers, *ibid.*, **18**, 906 (1965).

(14) F. C. Chang and C. B. Magee, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, No. M-144.

(15) J. Liu and C. B. Magee, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, No. INOR-25.

(16) A. F. Graefe and R. K. Robeson, *J. Inorg. Nucl. Chem.*, **29**, 2917 (1967).

(17) R. O. Moyer, R. Ward, L. Katz, and J. Tanaka, *Inorg. Chem.*, **8**, 1010 (1969).

(18) J. J. Reilly and R. H. Wiswall, Jr., *ibid.*, **7**, 2254 (1968).

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## The Use of Phosphorus Pentafluoride as a Fluorinating Agent in Organosilicon Chemistry. III.<sup>1</sup> Synthesis and Characterization of Some New Fluorosiloxanes<sup>2</sup>

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Although the silicon-oxygen bond of siloxanes and alkoxysilanes is readily cleaved by phosphorus pentafluoride, the silicon-hydrogen bond of hydrosiloxanes can be easily fluorinated at low temperatures by this reagent thus providing a convenient source of fluorosiloxanes. The synthesis and characterization of  $\text{FSiH}_2\text{OSiH}_3$ ,  $(\text{FSiH}_2)_2\text{O}$ ,  $\text{F}(\text{CH}_3)\text{HSiOSiH}_2\text{CH}_3$ , and  $[\text{F}(\text{CH}_3)\text{HSi}]_2\text{O}$  are described.

### Introduction

In the course of investigating the cleavage of the silicon-oxygen bond of siloxanes by phosphorus pentafluoride, we observed an interesting fluorination reaction occurring with siloxanes that contained silicon-

hydrogen bonds.<sup>1a</sup> Fluorosiloxanes were produced in the reaction together with the expected cleavage products. Since methods of preparing partially fluorinated siloxanes are practically nonexistent, we undertook a study into the general feasibility of preparing these types of compounds by the interaction of hydrosiloxanes with phosphorus pentafluoride.

### Experimental Section

**Apparatus.**—A conventional Pyrex-glass high-vacuum system

(1) Papers I and II in this series: (a) E. W. Kifer and C. H. Van Dyke, *Chem. Commun.*, 1330 (1969); (b) M. A. Finch, L. H. Marcus, C. Smirnoff, C. H. Van Dyke, and N. Viswanathan, *Syn. Inorg. Metal-Org. Chem.*, **1**, 103 (1971).

(2) Presented, in part, at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968.