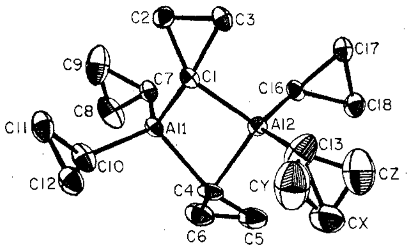
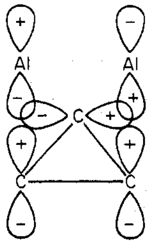


Figure 1. Perspective view of the tricyclopropylaluminum dimer with labeling.

atoms and the subsequent CNDO II calculations which appeared to support this model also predict that the C_α–C_β bond length should increase while the C_β–C_β bond length should decrease with greater double-bond character as indicated in **3**. One also would predict shortening of the Al–C bridge bond lengths, but, as noted earlier, although the trends in the bond lengths are in correct direction, the minimal changes observed are not sufficient to be significant.



3

One might note that similar bond shortening has also been looked for in both cyclopropyl cyanide[21] and cyclopropylacetylene,[22] on the assumption that the C_α–C_x bond should decrease through interaction between the π systems and the p orbitals of the cyclopropyl rings, but was not observed. Thus, one might not expect significant bond shortening in this case either. What does appear to be clear from all of the available data, including the NMR studies cited, the limited CNDO II calculations, and the present structural work, is that the cyclopropyl groups are preferentially located in the bridging positions in the syn configuration and that the Al–C–Al bridge bond appears to be stabilized in some manner by the cyclopropyl ring with the most attractive possibility that of interaction between the p orbitals of the ring carbon and the nonbonding metal orbitals as initially suggested.

Acknowledgment. W.H.T. was a Lubrizol Fellow, 1977–1978. The work was supported in part by NSF Grant No. CHE75-17217.

Registry No. $[Al(c\text{-}Pr)_3]_2$, 21892-05-7.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

---

(21) Friend, J. P.; Dailey, B. P. *J. Chem. Phys.* **1958**, *29*, 577.
(22) Collins, M. J.; Brutt, C. O.; Boggs, J. E. *J. Chem. Phys.* **1972**, *56*, 4262.

Contribution from the Department of Chemistry,
Wayne State University, Detroit, Michigan 48202

Metal–Silicon-Bonded Compounds. 11. Crystal and Molecular Structures of $Li_2Hg(SiMe_2Ph)_4$ and $Li_2Hg(SiMe_3)_4$, Novel Chain and Caged Lithium Metallates

WILLIAM H. ILSLEY, MICHAEL J. ALBRIGHT, THOMAS J. ANDERSON, MILTON D. GLICK,
and JOHN P. OLIVER*

Received March 10, 1980

$Li_2Hg(SiMe_2Ph)_4$ (I) and $Li_2Hg(SiMe_3)_4$ (II) crystallize in the space group $C2/c$ with four molecules per unit cell. The cell dimensions for I are a = 16.269 (5) Å, b = 10.298 (3) Å, c = 22.390 (6) Å, and β = 110.05 (2)° and for II are a = 15.932 (6) Å, b = 15.388 (2) Å, c = 9.494 (4) Å, and β = 93.53 (3)°. Full-matrix least-squares refinement for I gave final discrepancy factors of R_1 = 0.029 and R_2 = 0.034 for 1677 counter data for which $I > 3\sigma(I)$, while for II, R_1 = 0.026 and R_2 = 0.030 for 1395 counter data for which $I > 2.5\sigma(I)$. The structure of molecule I consists of discrete formula units with the mercury on a twofold axis of symmetry and with the lithium cations enclosed in a cage of silicon and carbon atoms. The mercury–silicon distances are 2.549 (2) and 2.493 (2) Å, the lithium–mercury distance is 2.58 (1) Å, and the lithium–silicon and lithium–carbon distances are in the range from 2.90 (1) to 3.04 (1) and 2.42 (2) to 2.61 (2) Å, respectively. The crystal structure of II consists of zigzag chains of $Li_2Hg(SiMe_3)_4$ units. The individual $Li_2Hg(SiMe_3)_4$ units of the chains are held together by the lithium atoms which serve as bridges between the $Hg(SiMe_3)_4$ moieties of the chains. Each $Hg(SiMe_3)_4$ fragment has a distorted tetrahedral arrangement of silicon atoms about the mercury with mercury–silicon distances of 2.539 (2) to 2.548 (2) Å; the mercury is on a twofold axis of symmetry. The mercury–lithium distance is 2.57 (1) Å, and the lithium–silicon and lithium–carbon distances are 2.69 (1)–2.87 (1) and 2.32 (1)–2.63 (1) Å, respectively. The interactions of the lithium atoms with carbon, silicon, mercury, and hydrogen atoms are considered, and the implications of these interactions with regard to the bonding in these systems are discussed.

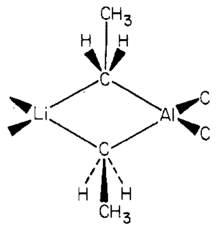
Introduction

The unusual properties of the "ate" derivatives such as $LiBMe_4$, $LiAlMe_4$, and Li_2BeMe_4 have generated interest in their structures and in the bonding interactions present in these complexes. A number of studies have been undertaken in order to gain insight into the nature of the lithium interactions in this class of compounds. These studies have shown that the solid-state structure of $LiAlEt_4$[1] consists of a chain in which the lithium atoms bridge two $AlEt_4$ units as depicted in I. In $LiBMe_4$ a more complex structure is observed with the lithium occurring in two kinds of positions, one described in terms of a "normal" electron-deficient bond and the second as a linear Li–C–B bond with an extremely short Li–C bond distance.[2,3]

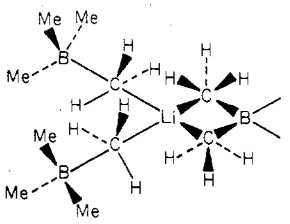
---

(1) Gerteis, R. L.; Dickerson, R. E.; Brown, T. L. *Inorg. Chem.* **1962**, *3*, 872.

0020-1669/80/1319-3577$01.00/0



I



II

These interactions are illustrated in II. In addition, Stucky has suggested that significant interactions occur between the lithium and the hydrogen atoms in these derivatives,[3] similar to those proposed for the lithium alkyls by Craubner,[4] with this interaction playing a role in the determination of the structure and stereochemistry of the complexes. The evidence cited for this is the proximity of the hydrogen atoms to the lithium atoms, as determined from neutron diffraction studies and from the shifts in the infrared bands. Further Li–H–B bridges with a Li–H distance of 2.06 (4) Å have been claimed in the structure of lithium dimesitylborohydride–bis(dimethoxyethane).[5] These and other structures have been reviewed recently.[6]

In other derivatives which have larger cations present or longer Li–C distances, the bonding is best described in terms of the ionic species $M^+,M'R_4^-$, or as $2(M^+),M''R_4^{2-}$. Compounds which appear to have this form of bonding include $MInMe_4$, where M is Li, Na, K, Rb, and Cs,[7] in which the shortest Li–C distance is 2.448 Å, the lithium group 2 metallates Li_2BeMe_4,[8] with the Li–C distance equal to 2.52 Å, and Li_2ZnMe_4,[9] with two Li–C distances of 2.52 and 2.82 Å. Certainly there may be Li–C interactions in these systems, but the rather long distances and the similarities in structure to the heavier alkali metal derivatives mitigate against this type of interaction being of major importance.

In a third class of lithium metallates, $Li_2Hg(SiMe_2Ph)_4$, we recently reported a different structure type in which the lithium atom is trapped within a cage of mercury, silicon, and carbon atoms with possible Li–C bonding[10] in the isolated $Li_2Hg(SiMe_2Ph)_4$ units. We now wish to provide a full report on this structure and the structure of a related compound, $Li_2Hg(SiMe_3)_4$, in which there are no aromatic groups present on the silicon atom.

These structures permit a comparison to be made between systems in which the mercury is approximately tetrahedrally surrounded by silicon and systems which contain linear silicon–mercury–silicon groups.[10-12] Further, they provide an excellent opportunity for the study of Li–C, Li–Si, and possible Li–H interactions in "ate" derivatives. The implications with respect to such interactions are discussed in detail.

Experimental Section

The bis(dimethylphenylsilyl)mercury and bis(trimethylsilyl)mercury were prepared by the method of Eaborn et al.[13] by reaction of Me_3SiCl or $Me_2PhSiCl$ in cyclopentane with 0.3–0.5% Na/Hg. These reactions were carried out in sealed tubes covered with aluminum foil to minimize the photochemically induced decomposition. They were purified either by recrystallization from cyclopentane or by sublimation at 50 °C under vacuum at 10^{-5} mmHg.

Table I. Physical Constant and Experimental Crystal Data for $Li_2Hg(SiMe_2Ph)_4$ and $Li_2Hg(SiMe_3)_4$

	$Li_2Hg(SiMe_2Ph)_4$	$Li_2Hg(SiMe_3)_4$
cryst system	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*
molecules/unit cell	4	4
a, Å	16.269 (5)	15.932 (6)
b, Å	10.298 (3)	15.388 (5)
c, Å	22.390 (6)	9.494 (4)
β, deg	110.05 (2)	93.95 (3)
V, Å^3	3523.8	2322.0
D(calcd), g/cm^3	1.42	1.45
2θ scan range, deg	$K\alpha_1$ −0.9 to $K\alpha_2$ +0.9	$K\alpha_1$ −1.0 to $K\alpha_2$ +1.0
max dev of stands during data collectn, %	14	6
no. of unique data collected	2160	1636
no. of data used	1677	1395
min for obsd data (*I*/σ(*I*))	3	2.5
$2\theta_{\text{Mo K}\alpha(\text{max})}$, deg	45	45
linear abs coeff (μ), cm^{-1}	45.2	68.1
range of abs correction factors	1.6–1.8 (estimated)	3.2–6.8

$Li_2Hg(SiMe_2Ph)_4$ was obtained from Hovland.[15] It was prepared by the direct reaction of Li metal with $Hg(SiMe_2Ph)_2$ in cyclopentane. After approximately 3 weeks of shaking a solution of $Hg(SiMe_2Ph)_2$ with excess Li metal at room temperature, the low-temperature NMR spectra revealed the presence of at least two compounds thought to be $LiSiMe_2Ph$ or $LiHg(SiMe_2Ph)_3$ and $Li_2Hg(SiMe_2Ph)_4$. Cooling this solution in a refrigerator gave yellow-green crystals of $Li_2Hg(SiMe_2Ph)_4$ which were separated and used for the X-ray structure determination.

$(LiSiMe_3)_6$ was prepared by the direct reaction of lithium metal with bis(trimethylsilyl)mercury in a hydrocarbon solvent as previously described.[14] This reaction proceeds to completion in the presence of excess Li metal with shaking at room temperature in approximately 1 week. $Li_2Hg(SiMe_3)_4$ was prepared by adding 0.342 g (0.986 mmol) of $Hg(SiMe_3)_2$ in 3 mL of benzene to 0.079 g (0.164 mmol) of $(LiSiMe_3)_6$ dissolved in 3 mL of benzene. A white solid immediately crystallized from the greenish solution. The reaction mixture was then concentrated to about 2 mL and warmed in a water bath at 30 °C until all the solid dissolved. Cooling of the water bath overnight yielded clear, single crystals of $Li_2Hg(SiMe_3)_4$ which were suitable for X-ray analysis.

X-ray Data Collection for $Li_2Hg(SiMe_2Ph)_4$ and $Li_2Hg(SiMe_3)_4$. A summary of data collection and crystal parameters for both compounds is given in Table I. Crystals were cut to a suitable size and sealed in thin-walled glass capillaries under an argon atmosphere; data were taken as previously described.[11]

Structure Determination of $Li_2Hg(SiMe_2Ph)_4$. The crystal chosen for data collection was approximately a cube with edges of 0.15 mm. The lack of clear view of the crystal inside the capillary as well as the decomposition of the crystal prevented exact measurement of the crystal dimensions. Rotation and oscillation photographs indicated the monoclinic crystal system. Lattice constants were obtained by least-squares refinement of 12 reflections with 2θ between 6.7 and 15.5° centered by using Mo Kα radiation (λ = 0.710 69 Å) with a programmed centering routine. Systematic absences in a preliminary data set indicated the monoclinic space group *C*2/*c* or *Cc*. A variable scan rate between 4 and 24°/min with the scan time inversely proportional to the peak intensity was used to reduce the effects of decomposition. During data collection the intensities of three standard reflections were measured every 50 reflections as a check on crystal and electronic stability. The standards showed an overall decrease in intensity of 14%, attributed to crystal decomposition. The data

---

(2) Groves, D.; Rhine, W.; Stucky, G. D. *J. Am. Chem. Soc.* **1971**, *93*, 1553.
(3) Rhine, W. E.; Stucky, G. D.; Peterson, S. W. *J. Am. Chem. Soc.* **1975**, *97*, 6401.
(4) Craubner, I. *Z. Phys. Chem.* **1966**, *51*, 225.
(5) Hooz, J.; Akiyama, S.; Cedar, F. J.; Bennett, M.; Tuggle, R. M. *J. Am. Chem. Soc.* **1974**, *96*, 274.
(6) Oliver, J. P. *Adv. Organomet. Chem.* **1977**, *15*, 235.
(7) Hoffman, K.; Weiss, E. *J. Organomet. Chem.* **1972**, *37*, 1.
(8) Weiss, E.; Wolfrum, R. *J. Organomet. Chem.* **1968**, *12*, 257.
(9) Weiss, E.; Wolfrum, R. *Chem. Ber.* **1968**, *101*, 35.
(10) Albright, M. J.; Schaaf, T. F.; Butler, W. M.; Hovland, A. K.; Glick, M. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1975**, *97*, 6261.
(11) Ilsley, W. H.; Schaaf, T. F.; Albright, M. J.; Sadurski, E. A.; Anderson, T. J.; Glick, M. D.; Oliver, J. P. *J. Organomet. Chem.* **1980**, *190*, 257.
(12) Bleckman, P.; Soliman, M.; Reuter, K.; Neumann, W. P. *J. Organomet. Chem.* **1976**, *108*, C18.
(13) Eaborn, C.; Jackson, R. A.; Walsingham, R. W. *J. Chem. Soc. C* **1967**, 2188.
(14) Schaaf, T. F.; Oliver, J. P. *J. Am. Chem. Soc.* **1969**, *91*, 4327.
(15) Hovland, A. K. Ph.D. Dissertation, Wayne State University, Detroit, 1975.

Table II. Atomic Coordinates and Anisotropic Thermal Parameters for $Li_2[Hg(SiMe_2Ph)_4]$[a,b]

atoms	*x*	*y*	*z*	atoms	*x*	*y*	*z*
Hg	0.0	−0.28950 (4)	−0.25	H(1)	−0.237 (7)	−0.306 (9)	−0.259 (5)
Si(1)	−0.1269 (1)	−0.1522 (2)	−0.2432 (1)	H(2)	−0.206 (7)	−0.288 (9)	−0.198 (5)
Si(2)	0.0499 (2)	−0.4310 (2)	−0.1538 (1)	H(3)	−0.280 (8)	−0.195 (8)	−0.249 (5)
C(1)	−0.2207 (7)	−0.2491 (12)	−0.2376 (6)	H(4)	−0.156 (6)	0.016 (10)	−0.180 (4)
C(2)	−0.1026 (8)	−0.0301 (9)	−0.1747 (4)	H(5)	−0.072 (6)	−0.076 (9)	−0.130 (4)
C(3)	−0.1714 (5)	−0.0484 (7)	−0.3175 (3)	H(6)	−0.061 (7)	0.038 (10)	−0.178 (4)
C(4)	−0.2464 (6)	−0.0844 (9)	−0.3690 (4)	H(7)	−0.285 (7)	−0.162 (10)	−0.362 (4)
C(5)	−0.2726 (7)	−0.0146 (11)	−0.4252 (4)	H(8)	−0.321 (6)	−0.045 (9)	−0.458 (5)
C(6)	−0.2256 (8)	0.0884 (10)	−0.4339 (4)	H(9)	−0.251 (6)	0.144 (10)	−0.472 (5)
C(7)	−0.1529 (7)	0.1274 (9)	−0.3849 (5)	H(10)	−0.111 (7)	0.189 (9)	−0.400 (5)
C(8)	−0.1260 (6)	0.0578 (8)	−0.3279 (4)	H(11)	−0.081 (6)	0.102 (9)	−0.296 (4)
C(9)	0.1642 (7)	−0.4967 (11)	−0.1301 (5)	H(12)	0.203 (6)	−0.416 (10)	−0.121 (4)
C(10)	−0.0238 (8)	−0.5743 (10)	−0.1612 (5)	H(13)	0.165 (7)	−0.554 (10)	−0.161 (4)
C(11)	0.0463 (6)	−0.3362 (7)	−0.0824 (3)	H(14)	0.183 (6)	−0.538 (9)	−0.083 (4)
C(12)	0.1130 (7)	−0.2494 (9)	−0.0494 (4)	H(15)	−0.011 (7)	−0.615 (10)	−0.129 (4)
C(13)	0.1058 (10)	−0.1677 (10)	−0.0007 (5)	H(16)	−0.079 (7)	−0.550 (10)	−0.167 (5)
C(14)	0.0333 (12)	−0.1759 (11)	0.0154 (5)	H(17)	−0.035 (6)	−0.637 (10)	−0.201 (4)
C(15)	−0.0333 (10)	−0.2575 (13)	−0.0152 (5)	H(18)	0.166 (8)	−0.248 (9)	−0.058 (5)
C(16)	−0.0267 (8)	−0.3348 (10)	−0.0636 (4)	H(19)	0.155 (7)	−0.099 (10)	−0.011 (4)
Li	0.0493 (10)	−0.1415 (15)	−0.1510 (5)	H(20)	0.018 (7)	−0.116 (10)	0.038 (4)
				H(21)	−0.084 (7)	−0.284 (8)	0.005 (5)
				H(22)	−0.080 (6)	−0.402 (9)	−0.087 (4)

atoms	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hg	0.00367 (2)	0.00835 (4)	0.001650 (8)	0.0	0.00087 (1)	0.0
Si(1)	0.0033 (1)	0.0100 (2)	0.00216 (5)	0.0002 (1)	0.0011 (1)	−0.0002 (1)
Si(2)	0.0042 (1)	0.0089 (2)	0.00189 (5)	−0.0002 (1)	0.0009 (1)	0.0004 (1)
C(1)	0.0043 (7)	0.0189 (17)	0.0040 (3)	−0.0018 (7)	0.0015 (4)	0.0000 (5)
C(2)	0.0069 (7)	0.0119 (12)	0.0028 (2)	0.0019 (7)	0.0014 (3)	−0.0010 (4)
C(3)	0.0035 (5)	0.0093 (9)	0.0023 (2)	0.0005 (5)	0.0008 (2)	−0.0006 (3)
C(4)	0.0052 (6)	0.0111 (10)	0.0028 (2)	0.0010 (6)	0.0005 (3)	−0.0005 (4)
C(5)	0.0057 (7)	0.0147 (13)	0.0027 (3)	0.0022 (8)	−0.0006 (3)	−0.0012 (5)
C(6)	0.0088 (8)	0.0129 (12)	0.0027 (3)	0.0036 (9)	0.0005 (4)	0.0013 (5)
C(7)	0.0075 (7)	0.0119 (11)	0.0037 (3)	0.0007 (8)	0.0015 (4)	0.0020 (5)
C(8)	0.0047 (6)	0.0098 (9)	0.0030 (2)	0.0005 (6)	0.0011 (3)	0.0005 (4)
C(9)	0.0063 (7)	0.0148 (14)	0.0032 (3)	0.0028 (7)	0.0006 (4)	0.0003 (5)
C(10)	0.0080 (8)	0.0115 (12)	0.0032 (3)	−0.0021 (8)	0.0012 (4)	0.0004 (4)
C(11)	0.0043 (5)	0.0100 (9)	0.0020 (2)	−0.0011 (5)	0.0006 (3)	0.0004 (3)
C(12)	0.0063 (7)	0.0130 (11)	0.0025 (2)	−0.0002 (6)	0.0012 (3)	0.0006 (4)
C(13)	0.0096 (9)	0.0126 (13)	0.0028 (3)	−0.0020 (8)	0.0009 (4)	−0.0011 (4)
C(14)	0.0127 (12)	0.0148 (16)	0.0031 (3)	0.0000 (10)	0.0037 (5)	−0.0007 (5)
C(15)	0.0116 (11)	0.0228 (18)	0.0034 (3)	−0.0030 (11)	0.0043 (5)	−0.0021 (6)
C(16)	0.0078 (8)	0.0173 (14)	0.0028 (3)	−0.0025 (8)	0.0026 (4)	−0.0012 (4)
Li	0.0066 (9)	0.0131 (16)	0.0019 (3)	−0.0005 (11)	0.0007 (4)	−0.0004 (6)

[a] Standard deviations from the variance-covariance matrix are given in parentheses for the least significant digit(s) in all tables. [b] The form of the anisotropic temperature factor reported here is $\exp[-(h^2\beta_{12} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

were corrected by standard methods,[16] by assuming a stepwise decomposition curve.

The structure was solved in the centrosymmetric space group $C2/c$ by direct methods with the program MULTAN.[17] Phasing was carried out for 378 E's with magnitudes greater than 1.3. The solution with the highest overall figure of merit was used to calculate an E map which established the mercury position on the twofold axis and the positions of two silicon atoms and the two phenyl rings. Subsequent Fourier and difference syntheses established the remaining nonhydrogen positions.[16] Full-matrix anisotropic least-squares refinement on F of the nonhydrogen atoms yielded the discrepancy factors

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.068$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.088$$

Probable hydrogen positions were taken from a difference Fourier synthesis and ranged in intensity from 0.3 to 0.8 e/A^3. Least-squares refinement of nonhydrogen anisotropic atomic parameters and the positional coordinates of the hydrogen atoms, with isotropic thermal parameters set to 5.0 and with anomalous scattering contributions included for the mercury atom, yielded final values of $R_1 = 0.029$, $R_2 = 0.034$, an error of fit of 1.06, and residual electron density in the final difference synthesis of 0.39 e/Å^3.

Atomic coordinates and anisotropic thermal parameters are given in Table II and bond distances and angles in Table III. A listing of observed and calculated structure factors is available.[18]

Structure Determination of $Li_2Hg(SiMe_3)_4$. A crystal of dimensions 0.31 × 0.19 × 0.34 mm was used for data collection. The structure was initially solved in the triclinic space group $P\bar{1}$ in which the chosen cell had lattice constants a = 14.224 (6) Å, b = 11.076 (5) Å, c = 9.494 (4) Å, α = 92.83 (4)°, β = 128.96 (3)°, and γ = 89.66 (4)°. These lattice constants were obtained by least-squares refinement of 15 reflections with 2θ between 21.5 and 26.6° centered by using Mo Kα radiation (λ = 0.71069 Å) with a programmed centering routine. The data were collected at 2°/min with the intensities of three standard reflections measured every 50 reflections as a check on crystal and electronic stability. The standards showed no significant decrease in intensity throughout data collection.

Solution of the three-dimensional Patterson function gave the position of the mercury atom. Subsequent Fourier difference syntheses established the remaining nonhydrogen positions. Full-matrix anisotropic least-squares refinement on F of the nonhydrogen atoms

---

(16) Local versions of the following programs were used: (1) SYNCOR, W. Schmonsees' program for data reduction; (2) FORDAP, A. Zalkin's Fourier Program; (3) ORFLS and ORFFE, W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function error program; (4) ORTEP, C. K. Johnson's program for drawing crystal models. Scattering factors, including anomalous dispersion corrections for mercury, were taken from: Ibers, J. A.; Hamilton, W. C. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(17) Germain, G.; Main, P.; Wolfson, M. M. *Acta Crystallogr., Sect. B* **1970**, *B26*, 274.

(18) See paragraph at end of paper regarding supplementary material.

Table III. Interatomic Distances and Angles for $Li_2Hg(SiMe_2Ph)_4$[a]

Distances (Å)

Li–Hg	2.58 (1)	Si(2)–C(9)	1.88 (1)	C(4)–H(7)	1.1 (1)	C(12)–H(18)	1.0 (1)
Li–Si(1)	2.90 (1)	Si(2)–C(10)	1.87 (1)	C(5)–H(8)	0.93 (9)	C(13)–H(19)	1.0 (1)
Li–Si(2)	2.98 (1)	Si(2)–C(11)	1.890 (8)	C(6)–H(9)	1.0 (1)	C(14)–H(20)	0.9 (1)
Li–Si(1′)	3.04 (1)	C(3)–C(4)	1.41 (1)	C(7)–H(10)	1.1 (1)	C(15)–H(21)	1.0 (1)
Li–C(2)	2.61 (2)	C(4)–C(5)	1.38 (1)	C(8)–H(11)	0.96 (9)	C(16)–H(22)	1.09 (9)
Li–C(3′)	2.51 (2)	C(5)–C(6)	1.36 (1)	C(9)–H(12)	1.0 (1)	C(11)–C(12)	1.40 (1)
Li–C(8′)	2.53 (2)	C(6)–C(7)	1.37 (1)	C(9)–H(13)	0.90 (9)	C(12)–C(13)	1.41 (1)
Li–C(11)	2.54 (2)	C(7)–C(8)	1.40 (1)	C(9)–H(14)	1.06 (9)	C(13)–C(14)	1.36 (2)
Li–C(12)	2.42 (2)	C(8)–C(3)	1.38 (1)	C(10)–H(15)	0.80 (9)	C(14)–C(15)	1.35 (2)
Hg–Si(1)	2.549 (2)	C(1)–H(1)	0.92 (9)	C(10)–H(16)	0.9 (1)	C(15)–C(16)	1.38 (1)
Hg–Si(2)	2.493 (2)	C(1)–H(2)	0.9 (1)	C(10)–H(17)	1.08 (9)	C(16)–C(11)	1.39 (1)
Si(1)–C(1)	1.86 (1)	C(1)–H(3)	1.0 (1)			C(2)–H(4)	0.9 (1)
Si(1)–C(1)	1.916 (9)					C(2)–H(5)	1.0 (9)
Si(1)–C(3)	1.897 (7)					C(2)–H(6)	1.0 (1)

Angles (Deg)

Si(1)–Hg–Si(1′)	112.6 (1)	C(9)–Si(2)–Li	111.4 (5)	C(4)–C(3)–Si(1)	122.1 (6)	H(4)–C(2)–H(5)	118 (7)
Si(2)–Hg–Si(2′)	108.5 (1)	C(10)–Si(2)–Li	141.6 (5)	C(8)–C(3)–Si(1)	121.9 (6)	H(4)–C(2)–H(6)	105 (8)
Si(1)–Hg–Si(2)	107.64 (7)	C(11)–Si(2)–Li	57.6 (3)	C(4)–C(3)–C(8)	115.5 (7)	H(5)–C(2)–H(6)	107 (8)
Si(1′)–Hg–Si(2)	110.19 (7)	Si(1)–Li–C(2)	40.2 (3)	C(3)–C(4)–C(5)	121.3 (9)	H(7)–C(4)–C(3)	118 (5)
Si(1)–Hg–Li	69.0 (3)	Si(2)–Li–C(2)	116.4 (6)	C(4)–C(5)–C(6)	121.5 (9)	H(7)–C(4)–C(5)	121 (5)
Si(1)–Hg–Li′	72.8 (3)	C(3)–Li′–C(8)	31.8 (3)	C(5)–C(6)–C(7)	119.1 (9)	H(8)–C(5)–C(4)	117 (6)
Si(2)–Hg–Li	71.9 (3)	C(3)–C(8)–Li′	73.5 (6)	C(7)–C(8)–C(3)	122.8 (8)	H(8)–C(5)–C(6)	121 (6)
Si(2)–Hg–Li′	179.2 (3)	C(8)–C(3)–Li′	74.7 (6)	C(12)–C(11)–Si(2)	122.2 (7)	H(9)–C(6)–C(5)	120 (6)
Li–Hg–Li′	107.6 (6)	C(11)–Li–C(12)	32.8 (3)	C(16)–C(11)–Si(2)	122.6 (6)	H(9)–C(6)–C(7)	120 (6)
Li–Si(1)–Li′	88.9 (3)	C(11)–C(12)–Li	78.0 (6)	C(12)–C(11)–C(16)	114.7 (8)	H(10)–C(7)–C(6)	114 (5)
C(1)–Si(1)–C(2)	104.5 (5)	C(12)–C(11)–Li	69.2 (6)	C(11)–C(12)–C(13)	122 (1)	H(10)–C(7)–C(8)	123 (5)
C(1)–Si(1)–C(3)	106.6 (5)	H(12)–C(9)–Si(2)	103 (6)	C(12)–C(13)–C(14)	119 (1)	H(11)–C(8)–C(7)	111 (6)
C(2)–Si(1)–C(3)	104.0 (4)	H(13)–C(9)–Si(2)	105 (7)	C(13)–C(14)–C(15)	121 (1)	H(11)–C(8)–C(3)	125 (6)
C(1)–Si(1)–Li	127.1 (5)	H(14)–C(9)–Si(2)	110 (5)	C(14)–C(15)–C(16)	120 (1)	H(18)–C(12)–C(11)	119 (7)
C(1)–Si(1)–Li′	129.6 (5)	H(12)–C(9)–H(13)	123 (9)	C(15)–C(16)–C(11)	123 (1)	H(18)–C(12)–C(12)	119 (7)
C(2)–Si(1)–Li	61.5 (4)	H(12)–C(9)–H(14)	100 (7)	H(1)–C(1)–Si(1)	110 (7)	H(19)–C(13)–C(12)	109 (5)
C(2)–Si(1)–Li′	124.8 (5)	H(13)–C(9)–H(14)	115 (8)	H(2)–C(1)–Si(1)	111 (7)	H(19)–C(13)–C(14)	131 (5)
C(3)–Si(1)–Li	126.0 (4)	H(15)–C(10)–Si(2)	111 (8)	H(3)–C(1)–Si(1)	113 (6)	H(20)–C(14)–C(13)	124 (7)
C(3)–Si(1)–Li′	55.5 (3)	H(16)–C(10)–Si(2)	112 (7)	H(1)–C(1)–H(2)	112 (9)	H(20)–C(14)–C(15)	113 (7)
C(9)–Si(2)–C(10)	106.4 (5)	H(17)–C(10)–Si(2)	118 (5)	H(1)–C(1)–H(3)	101 (9)	H(21)–C(15)–C(14)	122 (5)
C(9)–Si(2)–C(11)	105.1 (4)	H(15)–C(10)–H(16)	104 (11)	H(2)–C(1)–H(3)	110 (9)	H(21)–C(15)–C(16)	117 (5)
C(10)–Si(2)–C(11)	106.1 (5)	H(15)–C(10)–H(17)	112 (9)	H(4)–C(2)–Si(1)	107 (6)	H(22)–C(16)–C(15)	120 (5)
		H(16)–C(10)–H(17)	100 (8)	H(5)–C(2)–Si(1)	109 (5)	H(22)–C(16)–C(11)	116 (5)
				H(6)–C(2)–Si(1)	111 (6)		

[a] The primed atoms correspond to those atoms generated by the 2-C_2 axis of symmetry.

yielded discrepancy factors $R_1 = 0.042$ and $R_2 = 0.054$. The data were then corrected for absorption and transformed to the monoclinic space group $C2/c$ for which the unit cell parameters are $a = 15.932$ (6) Å, $b = 15.388$ (5) Å, $c = 9.494$ (4) Å, and $\beta = 93.95$ (3)°.[19] Relative to the triclinic lattice, the base vectors of the monoclinic cell are $(1\bar{1}1)$, $(\bar{1}\bar{1}\bar{1})$ and $(00\bar{1})$. Atomic coordinates were transformed by the matrix

$$\begin{bmatrix} 0.5 & -0.5 & 0 \\ -0.5 & -0.5 & 0 \\ 1 & 0 & -1 \end{bmatrix}$$

Full-matrix anisotropic least-squares refinement on the nonhydrogen atoms yielded discrepancy factors $R_1 = 0.030$ and $R_2 = 0.038$. Probable hydrogen positions were obtained from subsequent difference maps where they were found to be the highest peaks not readily identified with the mercury atoms and ranged in intensity 0.3 to 0.8 e/Å^3. Subsequent full-matrix anisotropic least-squares refinement on the nonhydrogen atoms using fixed contributions for the hydrogen atoms, which were assigned isotropic thermal parameters 10% higher than the thermal parameter for the carbon atom to which they were attached, yielded final discrepancy factors of $R_1 = 0.026$ and $R_2 = 0.030$ and an error of fit of 0.61. The maximum residual electron density was 1.5 e/Å^3 and was within 0.10 Å of the mercury atom. Other residual electron density was less than 0.35 e/Å^3. The maximum

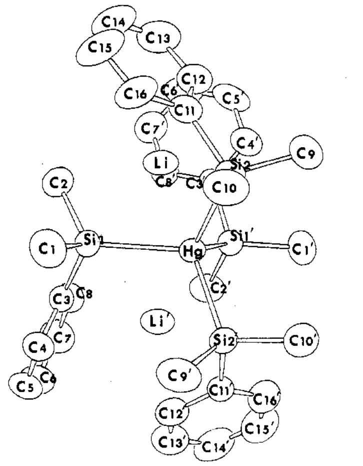


Figure 1. View of the $Li_2Hg(SiMe_2Ph)_4$ molecule with the labeling scheme. The atoms are represented by 50% probability thermal ellipsoids. Hydrogens are omitted for clarity. Primed atoms correspond to C_2-related atoms.

---

(19) We wish to thank the reviewer who discovered that the structure was not of the triclinic space group $P1$ but was monoclinic with space group $C2/c$. This error in the choice of the appropriate crystal class was a result of the use of unrefined axial lengths and an unrealistically low error limit in the initial cell reduction. The original axial solutions used in the cell reduction (with use of the program TRACER) were $a = 14.166$ (13) Å, $b = 11.088$ (5) Å, $c = 9.480$ (7) Å, $\alpha = 93.25$ (5)°, $\beta = 128.94$ (6)°, and $\gamma = 89.72$ (6)°. Based upon a DEL = 0.50 only the triclinic cell used for the original solution of the structure was obtained. The correct cell is obtained from the unrefined lattice constants with a DEL = ~1.5. Use of the refined triclinic lattice constants $a = 14.224$ (6) Å, $b = 11.076$ (5) Å, $c = 9.494$ (4) Å, $\alpha = 92.83$ (4)°, $\beta = 128.96$ (3)°, and $\gamma = 89.66$ (4)° resulted in the correct identification of the monoclinic cell with DEL = 0.10.

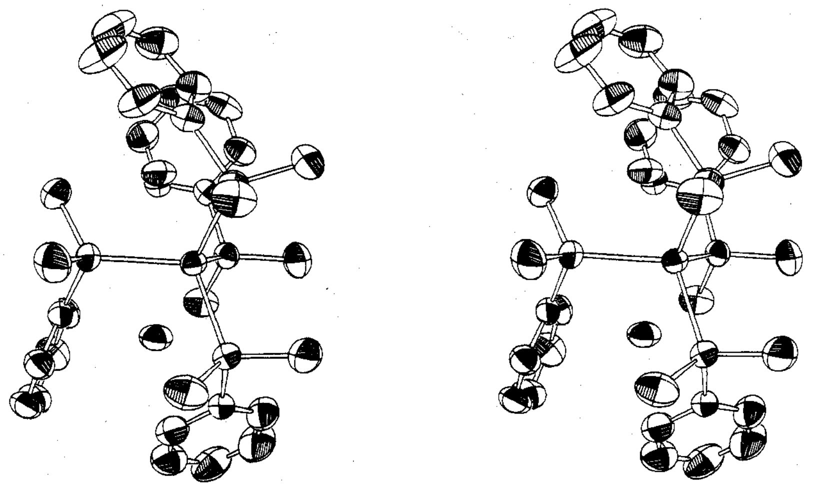


Figure 2. Stereoscopic view of the $Li_2Hg(SiMe_2Ph)_4$ molecule with hydrogen atoms omitted for clarity. The atoms are represented by 50% probability thermal ellipsoids.

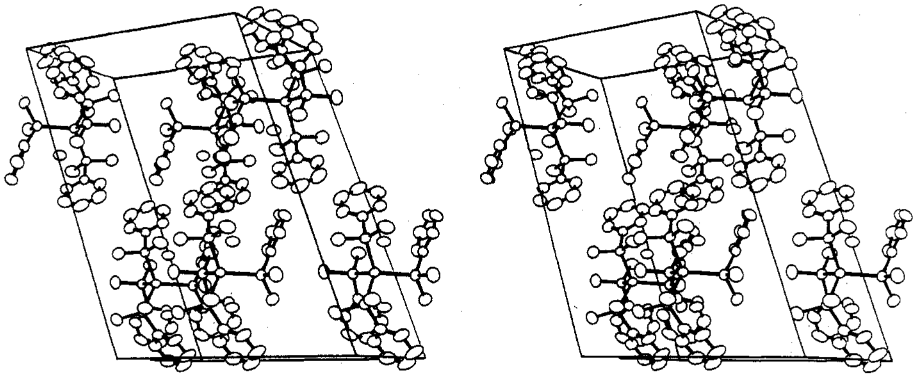


Figure 3. Stereoscopic packing diagram of the $Li_2Hg(SiMe_2Ph)_4$ molecule with hydrogens omitted for clarity. The atoms are represented by 50% probability thermal ellipsoids.

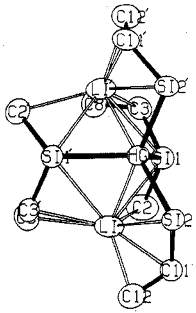


Figure 4. Partial structure of $Li_2Hg(SiMe_2Ph)_4$ showing the cage of atoms surrounding the lithium cations.

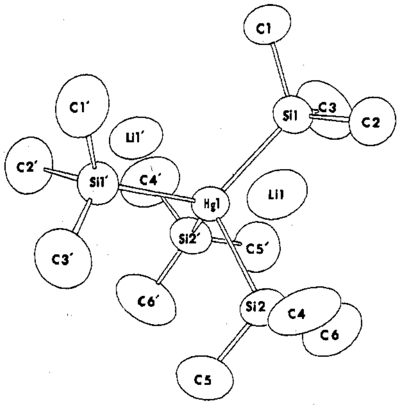


Figure 5. View of the $Li_2Hg(SiMe_3)_4$ molecule with the labeling scheme. The atoms are represented by 50% probability thermal ellipsoids, and hydrogen atoms are omitted for clarity.

residual electron density associated with the hydrogens was 0.28 e/Å^3.

Atomic coordinates and anisotropic thermal parameters are given in Table IV and bond distances and angles in Table V. A listing of observed and calculated structure factors is available.[18]

Results

Structure of $Li_2Hg(SiMe_2Ph)_4$. The crystal structure of $Li_2Hg(SiMe_2Ph)_4$ consists of discrete molecular units in which the lithium cations are enclosed in a cage of silicon and carbon atoms. A view of the molecule, including the atom labeling scheme, is shown in Figure 1. A stereoscopic view and a crystal packing diagram of the molecule are shown in Figures 2 and 3. Figure 4 shows only the lithium ions and the cage of nearest-neighbor atoms that surround them but does not necessarily imply bonding between the lithium and the nine surrounding atoms. The mercury atom is on a twofold axis which bisects the Si(1)–Hg–Si(1′) fragment. The mercury atom is surrounded by a slightly distorted tetrahedral arrangement of silicon atoms. Each lithium atom is near a mercury atom, three silicon atoms, and five carbon atoms. Si(2) and Si(2′) are each adjacent to only one lithium, and Si(1) and Si(1′) are each adjacent to two lithium atoms. All distances and angles are given in Table III.

Structure of $Li_2Hg(SiMe_3)_4$. The crystal structure of $Li_2Hg(SiMe_3)_4$ consists of tetrahedral $Hg(SiMe_3)_4$ units with the lithium atoms embedded in two of the faces. The lithium atoms serve as bridges between the $Hg(SiMe_3)_4$ units which join along an edge of the tetrahedron giving rise to a zigzag chain. The individual $Li_2Hg(SiMe_3)_4$ unit is shown in Figure

Table IV. Atomic Coordinates and Anisotropic Thermal Parameters for $Li_2Hg(SiMe_3)_4$ [a]

atom	x	y	z	B_{iso}, Å^2	atom	x	y	z	B_{iso}, Å^2
Hg(1)	0.0	−0.30334 (2)	0.2500		H(5)	0.256	−0.434	0.315	6.09
Si(1)	0.1217 (1)	−0.3884 (1)	0.3714 (2)		H(6)	0.243	−0.332	0.247	6.09
Si(2)	0.0543 (1)	−0.1956 (1)	0.0752 (2)		H(7)	0.195	−0.278	0.525	7.61
C(1)	0.1064 (4)	−0.5083 (5)	0.4183 (9)		H(8)	0.101	−0.353	0.605	7.61
C(2)	0.2203 (4)	−0.3943 (5)	0.2663 (9)		H(9)	0.215	−0.373	0.577	7.61
C(3)	0.1609 (6)	−0.3430 (7)	0.5469 (9)		H(10)	0.120	−0.198	−0.126	6.76
C(4)	0.1130 (6)	−0.2469 (5)	−0.0773 (9)		H(11)	0.165	−0.285	−0.046	6.76
C(5)	−0.0307 (5)	−0.1297 (5)	−0.0226 (10)		H(12)	0.066	−0.294	−0.124	6.76
C(6)	0.1337 (6)	−0.1169 (6)	0.1524 (10)		H(13)	0.0	−0.099	−0.083	7.10
Li(1)	0.0984 (9)	−0.3646 (7)	0.0715 (15)		H(14)	−0.062	−0.094	0.041	7.10
H(1)	0.167	−0.539	0.455	5.64	H(15)	−0.073	−0.165	−0.090	7.10
H(2)	0.062	−0.521	0.490	5.64	H(16)	0.184	−0.145	0.187	8.20
H(3)	0.068	−0.543	0.359	5.64	H(17)	0.107	−0.086	0.212	8.20
H(4)	0.215	−0.437	0.187	6.09	H(18)	0.148	−0.087	0.090	8.20

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hg(1)	0.00334 (2)	0.00286 (2)	0.00852 (4)	−0.0	0.00028 (2)	0.0
Si(1)	0.0035 (1)	0.0038 (1)	0.0101 (2)	0.0003 (1)	−0.0002 (1)	0.0006 (1)
Si(2)	0.0048 (1)	0.0034 (1)	0.0119 (2)	−0.0007 (1)	0.0002 (1)	0.0010 (1)
C(1)	0.0046 (3)	0.0046 (3)	0.0251 (14)	0.0000 (3)	0.0027 (6)	0.0048 (6)
C(2)	0.0044 (3)	0.0060 (4)	0.0210 (13)	0.0001 (3)	0.0022 (5)	0.0026 (6)
C(3)	0.0074 (5)	0.0096 (5)	0.0170 (13)	0.0019 (5)	−0.0042 (7)	−0.0027 (8)
C(4)	0.0100 (5)	0.0058 (4)	0.0184 (13)	−0.0001 (5)	0.0070 (7)	0.0034 (7)
C(5)	0.0067 (4)	0.0062 (4)	0.0209 (14)	0.0008 (4)	−0.0002 (6)	0.0035 (6)
C(6)	0.0090 (5)	0.0079 (5)	0.0217 (15)	−0.0038 (5)	−0.0013 (8)	0.0017 (8)
Li(1)	0.0068 (6)	0.0042 (5)	0.0184 (19)	−0.0001 (5)	0.0033 (10)	−0.0001 (8)

[a] The form of the anisotropic temperature factor reported here is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

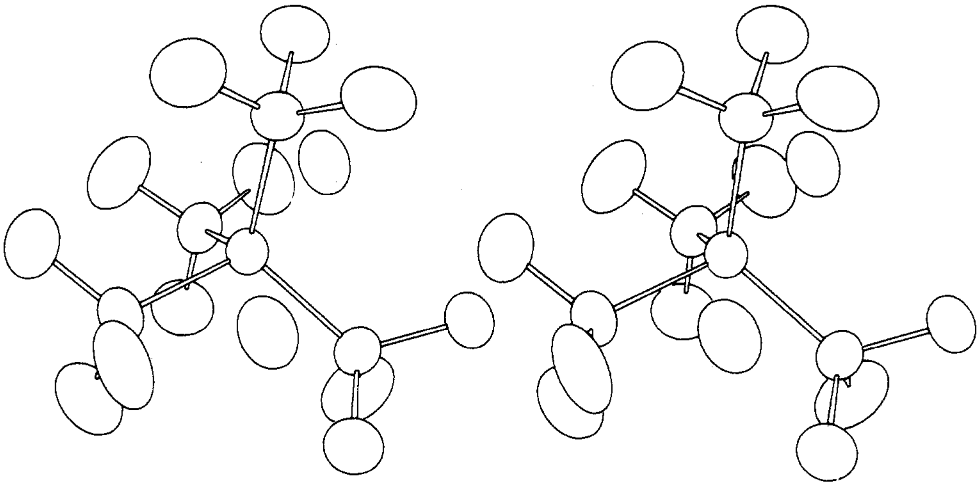


Figure 6. Stereoscopic view of the $Li_2Hg(SiMe_3)_4$ molecule with hydrogen atoms omitted for clarity. The atoms are represented by 50% probability thermal ellipsoids.

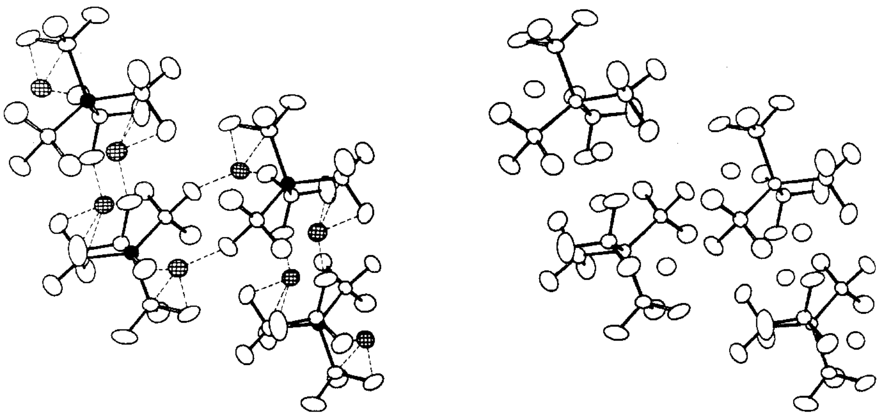


Figure 7. Stereoscopic packing diagram of the $Li_2Hg(SiMe_3)_4$ molecule with hydrogen atoms omitted for clarity. The atoms are represented by 50% probability thermal ellipsoids.

Table V. Interatomic Distances and Angles for $Li_2Hg(SiMe_3)_4$[a]

Distances (Å)			
Hg(1)–Si(1)	2.548 (2)	C(1)–H(3)	0.964
Hg(1)–Si(2)	2.539 (2)	C(2)–H(4)	0.999
Hg(1)–Li(1)	2.566 (13)	C(2)–H(5)	0.935
Si(1)–C(1)	1.917 (7)	C(2)–H(6)	1.045
Si(1)–C(2)	1.920 (7)	C(3)–H(7)	1.16
Si(1)–C(3)	1.875 (8)	C(3)–H(8)	1.14
Si(2)–C(4)	1.945 (8)	C(3)–H(9)	1.00
Si(2)–C(5)	1.885 (8)	C(4)–H(10)	0.89
Si(2)–C(6)	1.865 (8)	C(4)–H(11)	1.04
C(4)–Li(1)	2.318 (15)	C(4)–H(12)	1.11
C(2)–Li(1)	2.628 (16)	C(5)–H(13)	0.91
Si(1)–Li(1)	2.869 (14)	C(5)–H(14)	0.98
Si(2)–Li(1)	2.694 (11)	C(5)–H(15)	1.05
Li(1)–C(1″)	2.446 (14)	C(6)–H(16)	0.95
Si(1)–Li(1′)	3.604 (13)	C(6)–H(17)	0.87
C(1)–H(1)	1.109	C(6)–H(18)	0.79
C(1)–H(2)	1.034		
Angles (Deg)			
Si(1)–Hg(1)–Si(1′)	118.16 (8)	Si(1)–C(3)–H(9)	108
Si(1)–Hg(1)–Si(2)	110.37 (6)	Si(2)–C(4)–H(10)	97
Si(2)–Hg(1)–Si(2′)	98.48 (9)	Si(2)–C(4)–H(11)	116
Si(2)–Hg(1)–Si(1′)	108.83 (6)	Si(2)–C(4)–H(12)	103
Si(1)–Hg(1)–Li(1)	68.2 (3)	Si(2)–C(5)–H(13)	101
Si(1′)–Hg(1)–Li(1)	89.6 (3)	Si(2)–C(5)–H(14)	112
Si(2)–Hg(1)–Li(1)	63.7 (3)	Si(2)–C(5)–H(15)	116
Si(2)–Hg(1)–Li(1′)	157.3 (3)	Si(2)–C(6)–H(16)	112
C(1)–Si(1)–Hg(1)	119.6 (2)	Si(2)–C(6)–H(17)	105
C(2)–Si(1)–Hg(1)	114.4 (2)	Si(2)–C(6)–H(18)	108
C(3)–Si(1)–Hg(1)	114.0 (3)	H(1)–C(1)–H(2)	109
C(1)–Si(1)–C(2)	101.4 (3)	H(1)–C(1)–H(3)	117
C(1)–Si(1)–C(3)	101.1 (4)	H(2)–C(1)–H(3)	81
C(2)–Si(1)–C(3)	104.2 (4)	H(4)–C(2)–H(5)	88
C(4)–Si(2)–Hg(1)	115.1 (2)	H(4)–C(2)–H(6)	119
C(5)–Si(2)–Hg(1)	114.1 (3)	H(5)–C(2)–H(6)	119
C(6)–Si(2)–Hg(1)	114.8 (3)	H(7)–C(3)–H(8)	128
C(4)–Si(2)–C(5)	102.6 (4)	H(7)–C(3)–H(9)	93
C(4)–Si(2)–C(6)	102.0 (4)	H(8)–C(3)–H(9)	122
C(5)–Si(2)–C(6)	106.8 (4)	H(10)–C(4)–H(11)	120
Si(1)–C(1)–H(1)	111	H(10)–C(4)–H(12)	117
Si(1)–C(1)–H(2)	116	H(11)–C(4)–H(12)	104
Si(1)–C(1)–H(3)	119	H(13)–C(5)–H(14)	115
Si(1)–C(2)–H(4)	113	H(13)–C(5)–H(15)	104
Si(1)–C(2)–H(5)	105	H(14)–C(5)–H(15)	110
Si(1)–C(2)–H(6)	111	H(16)–C(6)–H(17)	118
Si(1)–C(3)–H(7)	107	H(16)–C(6)–H(18)	104
Si(1)–C(3)–H(8)	98	H(17)–C(6)–H(18)	110

[a] The distribution of C–H distances is consistent with an average esd of ~0.10 Å for the hydrogen position.

5 with labeling and in Figure 6 as a stereoscopic projection. Figure 7 shows the chain structure with parallel chains which are isolated except for van der Waals interactions.

The mercury atom in $Li_2Hg(SiMe_3)_4$ is on a twofold axis of symmetry and is surrounded by a distorted tetrahedral arrangement of silicon atoms at distances of 2.549 (2) and 2.493 (2) Å. The coordination sphere of the mercury atom is completed by two lithium atoms at 2.57 (1) Å. Each of the silicon atoms is bonded, in addition to the mercury atom, to three methyl carbon atoms which are at typical distances (1.865 (8)–1.945 (8) Å) from the silicon atom.[20] Si(1) and Si(1′) are 2.87 (1) and 3.60 (1) Å away from Li(1), respectively, while Si(2) is only 2.69 (1) Å away from Li(1). All of these interactions are intramolecular with all distances and angles summarized in Table V. Consideration of the coordination about the lithium atoms becomes more complex since there are both intramolecular and intermolecular interactions which lead to the formation of the chains of $Li_2Hg(SiMe_3)_4$ units which are fused along edges of the tetrahedral $Hg(SiMe_3)_4$ units by lithium–carbon and possibly lithium–hydrogen atom interactions. The environment around each lithium atom consists of three carbon atoms, two silicon atoms, and a mercury atom (Figure 8). As shown in Table V, there are three distinct classes of lithium–carbon atom distances which range from 2.32 (2) to 2.63 (2) Å and include interactions with two adjacent $Hg(SiMe_3)_4$ units. The mercury–lithium atom distance is 2.57 (1) Å. Each lithium atom also may interact with two silicon atoms as previously noted. This is in contrast to what has been observed for $Li_2Hg(SiPhMe_2)_4$ where each lithium atom is nearly equidistant from three silicon atoms.

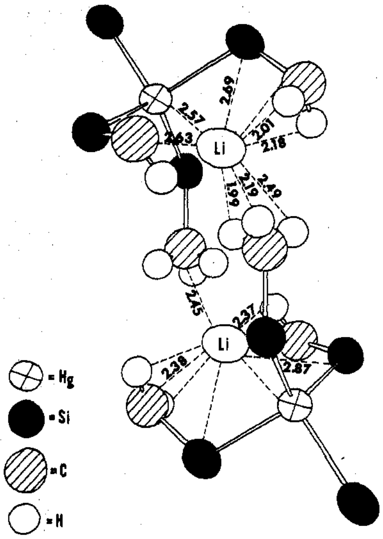


Figure 8. Partial view of $Li_2Hg(SiMe_3)_4$ showing the interaction between the lithium atoms and the $Hg(SiMe_3)_4$ units. All nonhydrogen atoms are represented by 50% probability thermal ellipsoids and hydrogen atoms by 10% probability thermal ellipsoids.

Discussion

As indicated in the Introduction, the structure and bonding present in the alkali metallate complexes, $MM'R_4$ and $M_2M''R_4$, have been of interest for some time. The bonding in these systems has been considered to be normal around the central metal atom with the unusual properties of the lithium derivatives ascribed to the interactions between the lithium ions and the R groups associated with the metal complex.

The crystal structures of $Li_2Hg(SiMe_2Ph)_4$ and $Li_2Hg(SiMe_3)_4$ provide evidence for the mode of interaction of the lithium ion with the $Hg(SiMe_2Ph)_4^{2-}$ and $Hg(SiMe_3)_4^{2-}$ metallate anions and show the influence upon the structure caused by the substitution of a methyl group by a phenyl group.

The compounds $Li_2Hg(SiMe_2Ph)_4$ (Figure 1) and $Li_2Hg(SiMe_3)_4$ (Figure 5) have normal Si–C distances. The C–Si–C angles are somewhat compressed from the ideal tetrahedral values to an average of 105.1 (5)° in $Li_2Hg(SiMe_2Ph)_4$ and 103.0 (4)° in $Li_2Hg(SiMe_3)_4$. Concomitant with the compression of the C–Si–C angles, there is a corresponding increase in the C–Si–Hg angle.

The Hg–Si distances in $Li_2Hg(SiMe_2Ph)_4$ are 2.493 (2) and 2.549 (2) Å with an average value of 2.521 Å. The Hg–Si distances in $Li_2Hg(SiMe_3)_4$ are 2.539 (2) and 2.548 (2) Å with an average value of 2.544 Å. The average values for these Hg–Si distances are slightly greater than the observed values in linear Si–Hg–Si systems[9–12] as expected from the increased nonbonded repulsions in the tetrahedral case. They are significantly less than the value predicted by using Grdenic's[21] value for the tetrahedral radius (1.48 Å) for mercury and suggest that the value established for digonal compounds of

---

[20] See ref 10 for a summary of Si–C and Si–Hg distances.

[21] Grdenic, D. *Q. Rev., Chem. Soc.* **1965**, *19*, 303.

Table VI. Comparison of Distances (Å) for $Li_2Hg(SiMe_2Ph)_4$ and $Li_2Hg(SiMe_3)_4$

	$Li_2Hg(SiMe_2Ph)_4$	$Li_2Hg(SiMe_3)_4$
Hg–Si(1)	2.549 (2)	2.548 (2)
Hg–Si(2)	2.493 (2)	2.539 (2)
Hg–Li(1)	2.58 (1)	2.57 (1)
Li(1)–Si(1)	2.90 (1)	2.87 (1)
Li(1)–Si(2)	2.98 (1)	2.69 (1)
Li(1)–Si(1′)	3.04 (1)	3.60 (1)
Li(1)–C(2)	2.61 (2)	2.63 (2)
Li(1)–C(4)		2.32 (2)
Li(1)–C(1″)		2.45 (1)
Li(1)–C(3′)	2.51 (2)	
Li(1)–C(8′)	2.53 (2)	
Li(1)–C(11)	2.54 (2)	
Li(1)–C(12)	2.42 (2)	

1.3 Å does not increase significantly on formation of four-coordinate derivatives. The 0.04–0.05 Å difference between Si(1)–Hg and Si(2)–Hg distances in the two compounds may result from the fact that Si(1) is adjacent to two lithium atoms while Si(2) is close only to a single lithium atom. In any event, these values lie in the observed range for all other Si–Hg bond distances,[20] as do the Si–C bond distances; thus both the Si–C and Si–Hg bonds may be considered normal with only minor perturbation of these by the lithium atoms present.

The most significant feature of this study concerns the coordination and bonding of the lithium atoms to the complex, since these interactions determine the properties of the compounds both in solution and in the solid state. Further understanding of the lithium–metallate interactions in these species should aid in understanding the general problem of lithium interactions in organometallic species. Examination of the packing diagrams (Figures 3 and 7) and the coordination about the lithium atoms (Figures 4 and 8) shows that $Li_2Hg(SiMe_2Ph)_4$ comprises discrete units in which the lithium atoms are entrapped in a cage formed by the mercury and silicon atoms, one methyl group, and two phenyl groups. $Li_2Hg(SiMe_3)_4$ is composed of chains in which the lithium atoms lie between the $Hg(SiMe_3)_4$ units and serve as bridges between them. Thus, in $Li_2Hg(SiMe_2Ph)_4$, the interactions with the lithium atoms are all of an intramolecular nature while in $Li_2Hg(SiMe_3)_4$ both intra- and intermolecular interactions occur.

As described above, the lithium atom in the phenyldimethylsilyl derivative has nine nearest neighbors. The Li–Hg distance of 2.58 (1) Å is the same as that observed in $Li_2Hg(SiMe_3)_4$. This distance lies between the sum of the covalent radii (2.64 Å) and the contact distance (1.99 Å) obtained by addition of the ionic radius of lithium (0.68 Å) to the covalent radius of mercury (1.30 Å). Lithium–silicon distances range from 2.90 (1)–3.04 (1) Å and are all greater then the average Li–Si distances (2.64 (1), 2.77 (1) Å) observed in hexameric $(LiSiMe_3)_6$.[22,23] They appear to be too long for significant Li–Si bonding but still serve to protect the lithium atom from interaction with other species.

Turning to the Li–C distances we find that two carbon atoms from each of two phenyl groups are close to the lithium atom with distances ranging from 2.42 (2)–2.54 (2) Å. The lithium atom is located over the edge of the ring, which is oriented so that a line dropped from the lithium atom to the C–C bond nearly bisects the bond and is approximately perpendicular to the ring. These results resemble those found in a variety of lithium–aromatic ion pairs[24–26] (Table VII).

Table VII. Comparison of Distances (Å) for Selected Organo- and Silyllithium Compounds

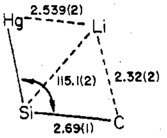
compd	Li–C
[Li  ·TMEDA]$_2$[a]	2.23 (5)
$LiMe_4$[b]	2.31 (5) 2.36 (5)
$(LiEt)_4$[c]	2.188 (4) 2.252 (6)
$(Li\text{-}c\text{-}C_6H_{11})_6\cdot 2Bz$[d]	av 2.184 (3) 2.300 (4)
$(LiSiMe_3)_6$[e]	2.64 (1) (Li–Si) 2.77 (1) (Li–Si)
$(Ph_3C)LiTMEDA$[f]	2.23 C(1) 2.49 C(14) 2.54 C(15) 2.51 C(2)
$(TMEDA)_2Li(nap)$[g]	2.32 C(1) 2.27 C(2) 2.26 C(3) 2.33 C(4) 2.66 C(5) 2.66 C(5′)

[a] Reference 31. [b] References 28 and 29. [c] Reference 27. [d] Reference 30. [e] References 22 and 23. [f] Reference 25. [g] Reference 26.

Further, this orientation of the phenyl rings protects the lithium atom from the surrounding molecules. The only remaining open area near the lithium atom is occupied by a methyl carbon attached to a third silicon atom. This lithium–carbon distance (2.61 (2) Å) is greater than the observed Li–C distance in alkyl derivatives[27–31] (Table VII) and is greater than most of the distances observed for lithium–aromatic ion pairs.[24] Therefore it appears not to have much effect on the stability of the species other than to block access to the lithium atom. Moreover, the orientations of all of the groups, except the methyl group surrounding the lithium atom, preclude Li–H interactions.

Thus, the structure can be described in terms of a simple ion pair with lithium trapped within a cage composed of carbon, silicon, and mercury atoms with interactions between the lithium and the two adjacent phenyl groups similar to those described by Stucky for lithium–aromatic ion pair systems.[24–26]

The structure of $Li_2Hg(SiMe_3)_4$ is shown in Figures 5–8 with the coordination about the lithium illustrated specifically in Figure 8. The lithium atoms lie between two adjacent $Hg(SiMe_3)_4$ units and serve to bridge them. As previously noted, the Li–Hg distance (2.57 (2) Å) is similar to that observed in $Li_2Hg(SiMe_2Ph)_4$. The lithium atom lies above two Si–C bonds which arise from adjacent $SiMe_3$ groups. The distances to the closest silicon and carbon atoms of the first group are 2.69 (1) and 2.32 (2) Å, respectively. These distances are within the observed values for formation of electron-deficient Li–Si and Li–C bonds (Table VII), suggesting that significant bonding occurs between these two atoms and the lithium atom as shown in III. In the next closest Si–C



III

---

(22) Schaaf, T. F.; Butler, W.; Glick, M. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 7593.

(23) Ilsley, W. H.; Schaaf, T.; Glick, M. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 3769.

(24) Stucky, G. *Adv. Chem. Ser.* **1974**, *No. 130*, 56.

(25) Brooks, J. J.; Stucky, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 7333.

(26) Brooks, J. J.; Rhine, W.; Stucky, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 7339.

(27) Dietrich, H. *Acta Crystallogr.* **1963**, *16*, 681.

(28) Weiss, E.; Lucken, A. C. *J. Organomet. Chem.* **1964**, *2*, 197.

(29) Weiss, E.; Hencken, G. *J. Organomet. Chem.* **1970**, *21*, 265.

(30) Zerger, R.; Rhine, W.; Stucky, G. *J. Am. Chem. Soc.* **1974**, *96*, 6048.

(31) Zerger, R. P.; Stucky, G. D. *J. Chem. Soc., Chem. Commun.* **1973**, 44.

Table VIII. Small Calculated Li-H Distances (Å) in $Li_2Hg(SiMe_2Ph)_4$ and in $Li_2Hg(SiMe_3)_4$

	$Li_2Hg(SiMe_2Ph)_4$		
C(7)-H(10)···Li′	3.62	C(2′)-H(5′)···Li′	2.28
C(8)-H(11)···Li′	2.89	C(2′)-H(6′)···Li′	2.50
C(9′)-H(12′)···Li′	3.68	C(14′)-H(18′)···Li′	2.53
C(2′)-H(4′)···Li′	3.57	C(13′)-H(19′)···Li′	3.45
	$Li_2Hg(SiMe_3)_4$		
C(2)-H(4)···Li(1)	2.37	C(1′)-H(1′)···Li	2.19
C(2)-H(5)···Li(1)	3.46	C(1′)-H(2′)···Li	1.99
C(2)-H(6)···Li(1)	2.79	C(1′)-H(3′)···Li	2.49
C(4)-H(10)···Li	3.20		
C(4)-H(11)···Li	2.01		
C(4)-H(12)···Li	2.18		

bond, the Si and C atoms lie at distances of 2.87 (1) and 2.63 (2) Å from the lithium atom, respectively. These distances are greater than any known bond distances between these atoms, suggesting that no significant interaction occurs. In addition a carbon atom from an adjacent $Hg(SiMe_3)_4$ unit lies 2.45 (1) Å away. This distance is somewhat greater than one might expect for bonding (see Table VII), but the very low solubility of the compound in hydrocarbon solvents supports the proposed interaction between these atoms with the resulting increase in the stability of the chain structure.

Finally consideration should be given to possible Li-H interactions in $Li_2Hg(SiMe_3)_4$ since this type of interaction has been invoked by other authors to account for the structures and properties observed in other lithium metallates. Several of the calculated hydrogen atom positions are within the proposed interaction distance of the lithium atoms. These calculated distances are summarized in Table VIII and include both intra- and intermolecular metal-hydrogen distances with values ranging from 1.99 to 3.46 Å. The smaller values are similar to the observed Li-H distance in lithium hydride,[32] in lithium dimesitylborohydride,[5] in $(Li\text{-}c\text{-}C_6H_{11})_6$,[30] and in $LiBMe_4$.[2,3]

The orientation of the lithium atoms with respect to the calculated hydrogen atom positions on various methyl groups is depicted in IV–VI with all of the interactions shown in

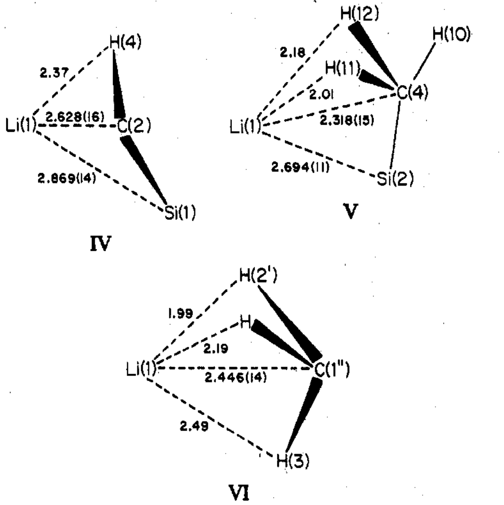


Figure 8. These diagrams show that the lithium atoms may be considered to interact with hydrogen atoms to form a monohydrogen bridge in IV and dihydrogen bridges in V and VI in a manner similar to that suggested by Stucky.[3]

One should be cautious in interpreting these distances in terms of stabilizing interactions since the hydrogen positions are often fixed by the positions of the groups to which they are bound. For example, in V, the lithium atom position seems fixed by its interaction with the mercury, silicon, and carbon atoms, and the hydrogen atoms are located at nearly the maximum distances they can achieve from the lithium atoms. Similarly in VI, if there is significant Li–C interaction, then the Li–H distances are fixed near the values observed. Furthermore, in compounds with known metal–hydrogen bridge bonds, the observed distances are 1.33 Å in boron hydrides,[33] 1.53 and 1.62 Å in $Be(BH_4)_2$,[34] and 1.67 Å in dimethylaluminum hydride[35] and vary from 1.6–1.8 Å in a variety of transition-metal hydrides.[36] In all of these species the effective hydrogen radius is of the order of 0.4–0.5 Å. The fact that there is a strong C–H bond in the alkyl metallates suggests that the effective radius of the hydrogen will be further reduced. On the basis of this and the known lithium radius of 1.34 Å, or the effective radius of 1.5 Å proposed for lithium in electron-deficient bridge bonding,[23] one may conclude that significant Li–H interactions will only occur in systems with Li–H distances of approximately 2 Å or less.

From the above considerations we may conclude that the bonding of the lithium atoms in $Li_2Hg(SiMe_3)_4$ can best be described in terms of a strong interaction between the lithium atom and the close C–Si bond with an additional weaker intermolecular interaction with the methyl carbon on the adjacent $Hg(SiMe_3)_4^{2-}$ unit. No other carbon– or silicon–lithium interactions are of major importance, but the positions of these groups serve to protect the lithium atoms from further interaction.

The question of lithium–hydrogen interactions in these species has not been fully resolved, but in $Li_2Hg(SiPhMe_2)_4$ it clearly is unimportant. In $Li_2Hg(SiMe_3)_4$ there are both intra- and intermolecular Li–H atom distances calculated to be within the range proposed for strong interactions, but no conclusive evidence for these interactions has been found; however, the very low solubility of the compound supports a relatively strong intermolecular interaction of some form which may arise from either Li–C or Li–H interactions or some combination of these. Separation of these two effects cannot be made on the basis of the available data. A final determination of their relative importance must await further studies including both additional neutron diffraction studies which will permit precise location of hydrogen atoms and spectroscopic data which will give evidence regarding direct Li–H interactions.

Acknowledgment. This work was supported in part by NSF Grant No. CHE75-127217. M.J.A. was a Wayne State University Graduate Fellow (1975–1976). W.H.I. was a Lubrizol Foundation Fellow (1977–1978).

Registry No. I, 57528-86-6; II, 25929-76-4; $Hg(SiMe_2Ph)_2$, 59612-26-9; $Hg(SiMe_3)_2$, 4656-04-6; $(LiSiMe_3)_6$, 54170-72-8; Li, 7439-93-2.

Supplementary Material Available: Listings of observed and calculated structure amplitudes (×10) and stereoscopic views of the molecules (15 pages). Ordering information is given on any current masthead page.

---

[32] Zintl, E.; Harder, A. *Z. Phys. Chem., Abt. B* **1935**, *28*, 478.

[33] Lipscomb, W. N., Jr. "Boron Hydrides"; W. A. Benjamin: New York, 1963; Chapter 1.

[34] Marynick, D. S.; Lipscomb, W. N. *Inorg. Chem.* **1972**, *11*, 820.

[35] Anderson, G. A.; Almennigen, A.; Forgaard, F. R.; Haaland, A. *Chem. Commun.* **1970**, 480.

[36] Wilson, R. D.; Koetzle, T. F.; Hart, D. W.; Tipton, D. L.; Bau, R. *J. Am. Chem. Soc.* **1977**, *99*, 1775 and references therein.