eight steps from 4-cumyloxy-2-cyclopentenone (**5**) to (+)-PGF$_{2\alpha}$ and the enantioner of its 15-epimer in 17% overall yield.[11,12]

References and Notes

(1) G. Stork and M. Isobe, *J. Am. Chem. Soc.*, **97**, 4745 (1975).
(2) (a) C. J. Sih, P. Prince, R. Sood, R. G. Salomon, G. Peruzzotti, and M. Casey, *J. Am. Chem. Soc.*, **94**, 3643 (1973); (b) A. F. Kluge, K. G. Untch, and J. H. Fried, *ibid.*, **94**, 7827 (1972); (c) early experiments with 1,4 addition of vinyl cuprates to 4-acetoxy-2-(6-carbomethoxyhexyl)-2-cyclopentenone were carried out by Dr. K. Hattori at Columbia in 1967.
(3) Cf. footnote 10, ref 1; this is a special problem with the 4-oxygenated 2-cyclopentenones, largely because of the much greater acidity of the 5-methylene group caused by the inductive effect of the 4-alkoxy group (cf. A. A. Bothner-By and C. Sun, *J. Org. Chem.*, **32**, 492 (1967)).
(4) Cf. G. Stork, Q. Branca, H. W. Pinnick, J. Quick, and T. Takahashi, manuscript in preparation.
(5) This simplification of the method reported in ref 4 was initially studied by A. Mitra in this laboratory (cf. H. Haubenstock, P. G. Mennitt, and P. E. Butler, *J. Org. Chem.*, **35**, 3208 (1970).
(6) From Polysciences, Inc.
(7) The removal of the acetate can be carried out more cleanly, though less conveniently, with lithium aluminum hydride as described by Haubenstock et al. in a related case.
(8) The (±) form of this iodooctenol was first made by Dr. K. Hattori (ref 2c). The reactions described here with the optically active 1-iodo-1-octen-3-ol have also been carried out with the racemic substance, thus leading to (±)-PGE$_{2\alpha}$ and its 15-epimer.
(9) There appears to be some retroaldol loss of formaldehyde from **7** during work-up. This is minimized by repeated washing with the buffer (10 × 50 ml).
(10) The only (minor) differences involved the use of triethylamine in the elimination of the mesylate of **7** and the use of 2:1 (v/v) acetic acid–water at room temperature for 5 hr to hydrolyze the terminal ethoxyethyl protecting group. The spectra of the intermediates were very similar to those previously reported, with the replacement of the benzylic hydrogens signals of the previous series by the gem dimethyl 6 H singlet of the cumyloxy group at $\delta \sim 1.52$.
(11) Approximately 9% overall of pure (+)-PGF$_{2\alpha}$ and 7% of the 15-epi enantiomer from **5**.

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The Structure of Compounds Containing Linear and Tetrahedral Silicon–Mercury Bonds, a Uniquely Caged Lithium Ion

Sir:

We wish to report the first single-crystal X-ray diffraction studies of compounds containing silicon to mercury bonds. The cyclic compound 2,2,4,4,6,6,8,8-octamethyl-2,4,6,8-tetrasila-1,5-mercuracyclooctane (I) is a centrosymmetric molecule containing two linear Si-Hg-Si moieties joined by methylene groups. The lithium tetrakis(dimethylphenylsilyl)mercurate (II) may be described as an isolated contact ion pair of crystallographic symmetry $2\text{-}C_2$, in which the anion comprises a mercury tetrahedrally coordinated by four dimethylphenylsilyl groups with the two lithium cations entrapped in symmetry related cages comprised of the mercury, three silicon atoms, and five carbon atoms. The crystallographically required twofold axis passes through the mercury.

The structures of I and II are shown in Figures 1 and 2. One may contrast silicon-mercury bonds in the linear configuration and in the tetrahedral system. The Hg-Si distances are equivalent in the cyclic compound with a linear Si-Hg-Si system (178.7°) with an average distance of 2.503 Å, whereas in the tetrahedral system two clearly discernible distances are present at 2.493 and 2.549 Å with an average 2.521 Å distance. The distinctly different Hg-Si distances observed in $Li_2Hg(SiMe_2Ph)_4$ are a manifestation of the distortion caused by the lithium ion and may be accounted for by noting Si(1) interacts with two lithium cations, whereas Si(2) only interacts with a single lithium cation.

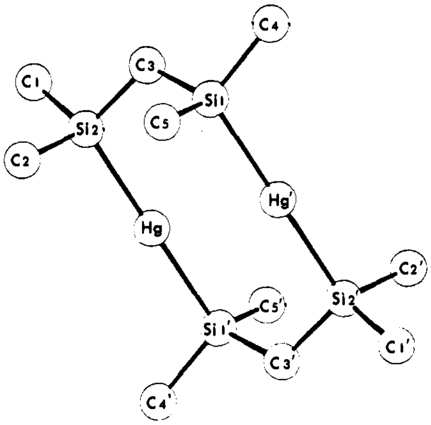


Figure 1. The skeletal structure of octamethyl-2,4,6,8-tetrasila-1,5-mercuracyclooctane.

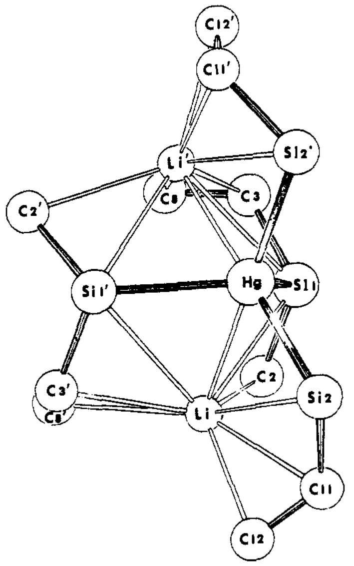


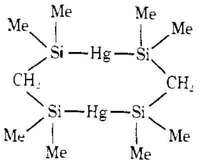
Figure 2. A partial structure of tetrakis(dimethylphenylsilyl)mercurate which shows the coordination of the lithium ions. Only the carbon atoms forming the cages around the lithium ions have been included for the sake of clarity. The C2 and C2′ carbons are methyl carbon atoms while all other carbons are phenyl carbon atoms.

These data, in conjunction with the earlier data reported on $^{3}J_{\mathrm{Hg-H}}$ coupling,[1] support the relationship which has been proposed between the geometry surrounding mercury and $^{3}J_{\mathrm{Hg-H}}$ which show a decrease from 43.5 to 27.0 to 19.0 Hz going from the linear sp hybridized mercury, to sp^2, to the sp^3 hybridized tetrahedral complex. This strongly supports the proposed trigonal coordination for the mercury atom in $Li[Hg(SiR_3)_3]$ species. Data for $^{3}J_{\mathrm{Hg-H}}$ in the Me_2PhSi series of derivatives are given in Table I.

Figure 2 shows that the lithium ion is novelly encompassed in a cage composed of carbon, silicon, and mercury atoms. The lithium-carbon distances are in the range of 2.4–2.6 Å, slightly longer than lithium-carbon bonds in alkyl-lithium derivatives (2.18–2.30),[2] but similar to those observed in lithium-hydrocarbon ion pairs.[3] The silicon-lithium distances are 2.9–3.0 Å, again longer than the corresponding silicon-lithium bond distance observed in silyllithium derivatives (2.68 Å).[4] The lithium-mercury distance is 2.58 Å.

The most interesting feature of this system is the entrapment of the lithium ion by the silicon-carbon moieties of the anion which results in a "bare" lithium ion unlike those

Table I. Proton Magnetic Resonance Parameters for Some Silymercurials

Compound	Solvent[a]	δ (ppm)[b]	$^3J_{\mathrm{Hg-H}}$ (Hz)[c]
$Hg(SiMe_3)_2$	CP	1.23	40.8
	CP	1.22	40.0
$Hg(SiMe_2Ph)_2$	CP	1.03	42.5
	THF	1.08	43.5
$Li[Hg(SiMe_2Ph)_3]$	THF	1.08[d]	27.0[d]
$K[Hg(SiMe_2Ph)_3]$	THF	1.08[d]	27.2[d]
$Li_2[Hg(SiMe_2Ph)_4]$	CP	1.07	21.5
	THF	1.35[e]	19.0[e]

[a] Key: CP, cyclopentane; THF, tetrahydrofuran. [b] Methyl resonance reported ppm upfield from internal cyclopentane. [c] Mercury to methyl proton coupling. [d] At −10°C. [e] At −30°C.

observed in other organometallic ion pairs which are usually coordinated with a base. It appears that this entrapment is not restricted to species containing aromatic groups since $Li_2Hg(SiMe_3)_4$ has properties similar to II forming unsolvated, hydrocarbon soluble crystals.

Addition of a coordinating solvent such as THF or DME (1,2-dimethoxyethane) leads to the formation of coordinated derivatives such as $LiHg(SiR_3)_3{\cdot}mL$ and $Li_2Hg(SiR_3)_4{\cdot}nL$ which give rise to well-defined crystalline materials.[1] In these derivatives it appears that the lithium ions are abstracted from the cage and coordinated by the ether in an effectively irreversible step, since the ether cannot be removed easily from these species and on removal does not give rise to the hydrocarbon-soluble starting material.

Further studies are in progress on these and related species to determine the spectroscopic, chemical, and structural properties.

2,2,4,4,6,6,8,8-Octamethyl-2,4,6,8-tetrasila-1,5-mercuracyclooctane was prepared by the method of Bettler and Urry.[5] Greenish yellow single crystals were recrystallized from hot cyclohexane in a sealed tube in the absence of oxygen. The compound crystallizes in the triclinic space group, $P\bar{1}$, with unit cell parameters, $a = 6.277$ (3) Å, $b = 8.408$ (3) Å, $c = 9.274$ (4) Å, $\alpha = 92.74$ (3)°, $\beta = 94.79$ (3)°, $\gamma = 100.14$ (2)°, with one molecule of the cyclic $Hg_2Si_4C_{10}H_{28}$ per unit cell. Intensity data were collected with monochromatized Mo Kα radiation by the θ–2θ scan technique on a Syntex P2$_1$ diffractometer. The instability of the crystal required the use of a 4°/min scan rate and the application of a 15% decay factor. Conventional heavy atom techniques followed by full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms resulted in $R = 0.062$ and $R_w = 0.072$ for 1809 data for which $I > 3\sigma(I)$.

Lithium tetrakis(dimethylphenylsilyl)mercurate was prepared in a similar manner to previously reported mercurates by the reaction of lithium with bis(dimethylphenylsilyl)-mercury in cyclopentane.[1] The lithium tetrakis(dimethylphenylsilyl)mercurate was isolated through its decreased solubility. Recrystallization from cyclopentane in a sealed tube in the absence of oxygen gave one large single crystal which had to be cut. The crystal was found to be monoclinic, space group $C2/c$, with unit cell dimensions, $a = 16.268$ (5) Å, $b = 10.297$ (3) Å, $c = 22.389$ (6) Å, $\beta = 69.95$ (2)°, and with four molecules of $Li_2[Hg(SiMe_2Ph)_4]$ per unit cell. A 4°/min θ–2θ scan gave 1677 data $I > 3\sigma(I)$ consistent with the systematic absences for $C2/c$. The high scan rate was used to reduce decomposition which still required application of a 14% decay factor to account for the loss in intensity due to decomposition. Direct methods were used to solve the structure.[6] Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms and constrained isotropic thermal parameters for hydrogen atoms yielded $R = 0.029$ and $R_w = 0.034$.

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Evidence for Carbocation–Arenesulfonate Ion Pairs in Reactions with Hydroxide and Borohydride Ion

Sir:

Ion pairing is important in S$_N$ reactions,[1-3] and we present evidence for ion pairing with arenesulfonate ions in carbocation recombinations with OH^- and BH_4^- in water (cf. ref 4–7). Anionic nucleophilic attack upon both the tri-p-anisylmethyl cation, R^+,[6,7] and Malachite Green (bis(p-dimethylaminophenyl)phenylmethyl cation, MG^+) is inhibited by salts having bulky anions; some examples are shown in Figure 1. These salts also increase both $-H_R$[8] and A-1 reaction rates in water suggesting a role for solvent structure induced ion pairing.[9]

We find difference spectra for mixtures of MG^+ or R^+ and arenesulfonate ions in water with good isosbestic points, showing that there is an interionic interaction. Some examples are shown in Figure 2. Most of these data were obtained with a Cary 118 spectrometer, but the few obtained with a Cary 15 spectrometer agreed with the others. On the assumptions that a 1:1 complex is formed, and that Beer's law is obeyed, we estimate dissociation constants, K_S (Tables I and II), from the difference spectra using eq 1a,b shown for MG^+:

$$\frac{1}{[S^-]} = \frac{(1 - \epsilon_{MG^+S^-}/\epsilon_{MG^+})A_0}{K_s\Delta} - \frac{1}{K_s} \qquad (1a)$$

Where Δ is the difference absorbance, A_0 is the absorbance in the absence of S^-, and K_S is computed using a least-squares fit. Each set of difference spectra was obtained using five–seven different concentrations of the aromatic solute. There was reasonable agreement between independent experiments.

Similar values of K_s (in parentheses) were obtained using the rearranged eq 1b.

$$-\Delta/A_0[S^-] = \epsilon_{MG^+S^-}/\epsilon_{MG^+}K_s - (A_0 - \Delta)/K_sA_0 \qquad (1b)$$

The values of K_s were calculated using a least-squares plot with 95% confidence limits.

Added 2 M sodium perchlorate decreases absorbance of MG^+ by 25%, but only slightly changes λ_{max}. In all experiments MG^+ was present wholly as the monocation, and the difference spectra are identical in pH 4 and 4.5. The difference spectra of R^+ were obtained in 3 M HCl where the