Fig. 1.—N.m.r. spectrum of dilithium *as*-indacenide in THF.

line solid insoluble in DME, but soluble in tetrahydrofuran (THF). It reacts with deuterium oxide to give dideuterated dihydro-*as*-indacene. *Anal.* Calcd. atom % excess D for $C_{12}H_8D_2$: 20.00. Found: 19.85. That the deuterium atoms are in the allylic positions is shown by the decrease by a factor of two, relative to the other n.m.r. peaks, of the peaks at τ 6.95 and 7.22. The n.m.r. spectrum of dilithium *as*-indacenide, determined in THF solution at an n.m.r. frequency of 100 Mc., is shown in Fig. 1.[4] The spectrum, analyzed in Table I, consists of an ABX pattern[5] and a singlet.

TABLE I

N.M.R. SPECTRUM OF DILITHIUM *as*-INDACENIDE IN THF

Proton	Observed chemical shift (in τ-units)	Relative intensity	Position assignment[a]	Charge density[b]
ϕ	3.155 ± 0.005	2.0	4, 5	−0.10
A	4.076 ± 0.006		1, 8	−0.24
B	4.158 ± 0.006	6.4	3, 6	−0.23
X	3.944 ± 0.003		2, 7	−0.18
			(Av. 9,10,11,12	−0.13)[c]

$J_{AX} = J_{BX} = \pm(3.12 \pm 0.13)$ c.p.s.

$|J_{AB}| = 2.06 \pm 0.17$ c.p.s.

[a] The position assignments for the protons A and B may be reversed. The assignment of the X protons as the ones attached to carbon atoms 2 and 7 is based on the presumption that the lowest negative charge density in the five-membered ring resides on those carbons (*cf.* ref. 3 and 6). [b] The charge density associated with carbon atoms 4 and 5 is given as $\rho = -a/10.7$, where ρ is the charge density and a is the proton chemical shift relative to benzene, corrected for differential ring-current effects. For the carbons 1, 2, 3, 6, 7, and 8 the density is given as $-(0.2 + a/10.7)$, where a is the proton chemical shift relative to lithium cyclopentadienide in THF (τ 4.472),[7] corrected for differential ring-current effects. [c] The average charge density of positions 9, 10, 11, and 12 is given as

$$- \frac{1}{4}\left(2 + \sum_{i=1}^{8} \rho_i\right)$$

The negative charge densities associated with each carbon atom of I were estimated (Table I) by a procedure similar, with one exception, to that used by Schaeffer and Schneider for other hydrocarbon anions.[6] The chemical shifts of the protons 1, 2, 3, 6, 7, and 8, after correcting for the ring-current effects of the other rings, were compared, not with the chemical shift of benzene, but with the chemical shift of lithium cyclo-

(4) The n.m.r. spectrum was determined with the help of Mr. T. K. Wu.
(5) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw–Hill Book Co., Inc., New York, N. Y., 1959, p. 132.
(6) T. Schaeffer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

pentadienide in THF,[7] and the difference was evaluated as proportional to the difference in charge density. The charge densities at carbon atoms 4 and 5 were evaluated by comparing the corrected chemical shift with that of benzene.

Dilithium *as*-indacenide in THF reacts with a suspension of ferrous chloride to give in 10% yield, after chromatography on silica gel and crystallization from a mixture of ethanol and methylene chloride, bis(*as*-indacenyliron). *Anal.* Calcd. for $C_{12}H_8Fe$: C, 69.28; H, 3.88; Fe, 26.84; mol. wt., 416. Found: C, 68.94; H, 3.96; Fe, 26.95; mol. wt., 434 (vapor pressure osmometry). The compound is a rust colored crystalline solid that does not melt, but darkens between 250 and 300°. The ultraviolet spectrum in methylene chloride[8] has a maximum at 509 mμ (log ϵ 2.51) and an inflection at 395 mμ (log ϵ 2.92).

No polymeric material in which metal atoms and ligand molecules alternate has yet been identified.

(7) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960). *Cf.* ref. 6. The chemical shift of benzene was taken to be τ 2.734.
(8) The compound is only slightly soluble in methylene chloride and insoluble in saturated hydrocarbons or ethanol. Chlorinated hydrocarbon solvents, however, are known to produce marked changes in the ultraviolet spectrum of ferrocene [J. C. D. Brand and W. Sneeden, *Trans. Faraday Soc.*, **53**, 894 (1957)].
(9) National Science Foundation Predoctoral Fellow, 1960–1963, National Science Foundation Cooperative Fellow, 1963–1964.

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Pentacoordinate Silicon Derivatives. II.[1] Salts of Bis(*o*-arylenedioxy)organosiliconic Acids

Sir:

Finely divided silica was reported by Rosenheim[2] to react with catechol in the presence of various bases to yield crystalline salts containing the dibasic *hexa*-coordinate silicate anion, $[Si(C_6H_4O_2)_3]^{-2}$. We have confirmed and extended this little known work to include examples containing carbon–silicon bonds. These organosilicon salts are believed to possess anions in which the silicon atom is *penta*-coordinate (I).
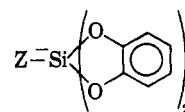

I, Z = alkyl or aryl

We have found these compounds to be prepared most conveniently from alkoxysilanes,[3] *i.e.*

(1) Paper I: C. L. Frye, G. E. Vogel, and J. A. Hall, *J. Am. Chem. Soc.*, **83**, 996 (1961).
(2) A. Rosenheim, B. Raibmann, and G. Schendel, *Z. Anorg. Allgem. Chem.*, **196**, 160 (1931).
(3) In like manner, the *tris*(*o*-arylenedioxy)siliconates described by Rosenheim are also easily prepared from ethyl silicate; *i.e.*

$(EtO)_4Si + 3C_6H_4(OH)_2 + 2R_3N \longrightarrow$
$[R_3NH]_2^+[Si(C_6H_4O_2)_3]^{-2} + 4EtOH$
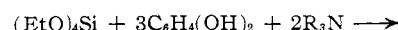
The use of alkoxysilanes rather than aqueous reactants conveniently avoids the uncertainty associated with the *hydrated* products encountered in earlier work:
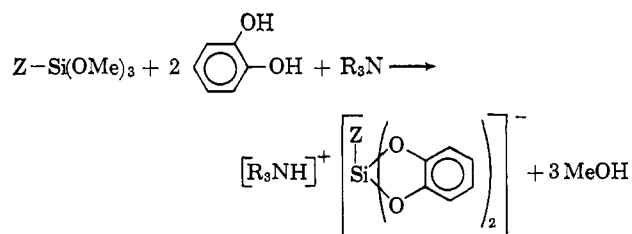
These salts are prepared by merely warming the appropriate reactants in a suitable solvent (usually methanol). As an example, triethylammonium bis(o-phenylenedioxy)phenylsiliconate, i.e., $[Et_3NH]^+[Ph-Si(C_6H_4O_2)_2]^-$, deposited in 78% yield from a methanol solution of $PhSi(OMe)_3$, catechol, and Et_3N; m.p. 220–230° dec. Anal. Calcd. for $C_{24}H_{29}O_4NSi$: C, 68.1; H, 6.86; N, 3.31; Si, 6.64. Found: C, 68.6; H, 7.04; N, 3.29; Si, 6.57. In related fashion we have prepared analogous pentacoordinate organosilicon catecholates of many other bases ranging in strength from pyridine to quaternary ammonium hydroxides.[4] The infrared spectrum of each of these salts (obtained from mineral oil mulls) exhibited a strong band at 12.1–12.3 λ which is believed to be the silicon–oxygen stretching frequency. This is considerably displaced from the usual position of this band $(10.2–10.9 \lambda)$[5] and is a reasonable consequence of the somewhat longer Si–O bond lengths expected in such pentacoordinate species. To date we have been unable to isolate extracoordinate silicon catecholates bearing more than one carbon–silicon bond. An attempt to prepare such a derivative from diphenyldimethoxysilane resulted in an unusually facile Ph–Si bond cleavage.

$$Ph_2Si(OMe)_2 + 2C_6H_4(OH)_2 + Et_3N \xrightarrow[\Delta]{MeOH}$$
$$[Et_3NH]^+[PhSi(C_6H_4O_2)_2]^- + C_6H_6 + 2\ MeOH$$
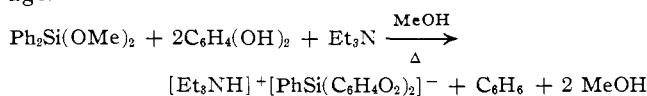
The observation that amines as weakly basic as pyridine may be used suggests that a species such as II would be a relatively strong acid, presumably due to the stability of the anion, I.
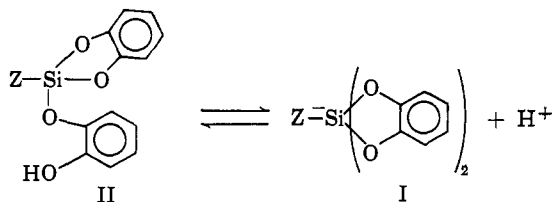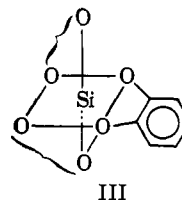

The stability of such extracoordinate species is further underscored by their formation in high yield even when alcohols are used as solvents, despite the ostensibly excellent opportunity for solvolytic reversal of reaction. This stability is perhaps not too surprising in view of the extensive charge delocalization presumably possible in the above anion; i.e., numerous canonical forms may be drawn in which the negative charge is distributed to the arylene rings.[6]

(4) When a strong base is used, the products form rapidly and often deposit quickly from solution without any heating at all being necessary. If, however, the base is weak, correspondingly longer reaction times and/or higher reaction temperatures are required.

(5) A. L. Smith, Spectrochim. Acta, **16**, 87 (1960).

(6) That the stability of these pentacoordinate silanes is not entirely dependent upon the charge delocalizing arylene rings is demonstrated, however, by the existence of a related series of aliphatic 1,2-diol derivatives which we will describe in the near future.

Rosenheim's assignment of a monomeric hexacoordinate dinegative silicate ion has recently been criticized by Weiss, et al.,[7] who argued that such structures are precluded by the highly strained (sic) five-membered rings (III) containing compressed O–Si–O bond angles.

III

From an examination of Stuart–Brieglieb models we have concluded that the compressive strain admittedly present in tetrahedral formulations[8] is virtually absent in extracoordinate silicon species because of the availability of much smaller silicon valence bond angles (approximately 90°). The essentially complete release from such strain resulting upon rehybridization is presumably part of the driving force leading to stable extracoordinate silicon catecholates. The unnecessarily more complicated dimeric quadrinegatively charged species suggested by Weiss also fails to account for the ortho-diol structural requirement. Structural formulations depicting these materials as mere salts of tetrahedral silanes (IV) are likewise completely inconsistent with the observable facts; i.e., the strained ring in this sp[3] silicon species would certainly not resist alcoholysis, nor would we expect such strikingly stable ammonium salts. Their high melting points[2,7] are

IV
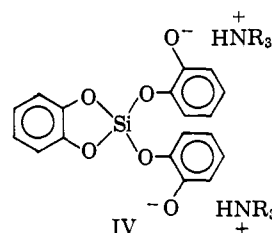
also more consistent with Rosenheim's highly symmetrical structure.

We cannot answer at this time the subtle question of whether the pentacoordinate catecholates involve trigonal bipyramidal or square tetragonal hybridization of the silicon valences.

(7) Ar. Weiss, G. Reiff ,and Al. Weiss, Z. Anorg. Allgem. Chem., **311**, 151 (1961).

(8) It is significant that even tetracoordinate silicon catecholates have been reported.[9]

(9) (a) M. Jacovic, Z. Anorg. Allgem. Chem., **288**, 324 (1956); (b) J. J. Zuckerman, J. Chem. Soc., 873 (1962).

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Calculation of the Magnitude of the Rotation of the Components of a Racemic Modification, by way of Two Partial, Consecutive Resolutions in Homogeneous Medium

Sir:

When two racemic compounds A and B, each composed of two enantiomers (the enantiomers present in A are designated A_D and A_L, and the enantiomers