establish that $FeCl^{2+}$ is produced in the reaction of $CoCl^{2+}$ with Fe^{2+} and that this reaction proceeds *via* an inner-sphere activated complex in which the chloride is bonded directly to both the cobalt and the iron.

It should be noted that the equilibrium constant for the reaction $Co^{3+} + Cl^- \rightleftharpoons CoCl^{2+}$ is about ten times larger than that for the $Fe^{3+} + Cl^- \rightleftharpoons FeCl^{2+}$ reaction.[7] Consequently, when the chloride is added to only the cobalt(III), the amount of $FeCl^{2+}$ produced in the $CoCl^{2+} + Fe^{2+}$ reaction is about forty times its final equilibrium concentration.

In order to minimize the extent of the reaction

$$2Co^{3+} + 2Cl^- \rightleftharpoons 2Co^{2+} + Cl_2$$

the cobalt(III) was generally added to the chloride solution immediately before the runs.[7] On the other hand, when the cobalt(III) chloride solution was allowed to age for about 15 min. prior to mixing it with the iron(II) solution, a reaction which produces $FeCl^{2+}$ at a rate intermediate between that of the $CoCl^{2+} + Fe^{2+}$ and $Fe^{3+} + Cl^-$ reactions could be detected. Apparently this reaction is the oxidation of Fe^{2+} by Cl_2. This was confirmed by mixing a solution of Cl_2 in 3.0 M $HClO_4$ containing 4.0×10^{-3} M (Cl^-) with a solution containing 1.0 M [Fe(II)] and 3.0 M ($HClO_4$); the formation of $FeCl^{2+}$ ($k \approx 50\ M^{-1}$ sec.$^{-1}$) and its subsequent dissociation were observed.

(7) T. J. Conocchioli, G. H. Nancollas, and N. Sutin, submitted to *Proc. Chem. Soc.*

(8) Visiting Scientist from the Chemistry Department, The University, Glasgow, W. 2, Scotland.

CHEMISTRY DEPARTMENT
BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11937

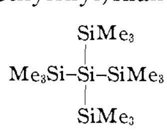
T. J. CONOCCHIOLI
G. H. NANCOLLAS[8]
N. SUTIN

RECEIVED JANUARY 31, 1964

Tetrakis(trimethylsilyl)silane

Sir:

Since the first reported preparation of a branched chain organopolysilane,[1] several efforts have been made to synthesize tetrasilyl-substituted silanes.[1,2] Tris(triphenylsilyl)silane (4.4%) was obtained from the reaction of trichlorosilane with triphenylsilyllithium.[1] The attempted synthesis of tetrakis(triphenylsilyl)silane by the reaction of triphenylsilyllithium and silicon tetrachloride only afforded hexaphenyldisilane (72%) and a yellow oil.[1] We now report the preparation of tetrakis(trimethylsilyl)silane (I).



I

In a typical procedure, 94.18 g. (0.864 mole, 20% molar excess) of chlorotrimethylsilane was dissolved in 200 ml. of sodium-dried tetrahydrofuran, to which 15.13 g. (2.16 g.-atom, 50% g.-atom excess) of lithium wire was added. To this rapidly stirred mixture, 20 ml. of a solution of 30 g. (0.18 mole) of silicon tetrachloride dissolved in 150 ml. of sodium-dried tetrahydrofuran was added at room temperature.[3] After stirring at room temperature for 4 hr., the reaction mixture became dark brown and heat was evolved. At this stage, dropwise addition of the silicon tetrachloride solution was continued. Upon completed addition, the mixture was stirred overnight at room temperature. Unreacted lithium metal, some salts, and a brown polymer[4] were separated by filtration of the reaction mixture prior to hydrolysis with 200 ml. of 15% hydrochloric acid. The organic layer was separated, dried over anhydrous sodium sulfate, and the organic solvents were distilled under reduced pressure. To the yellow semisolid residue was added a few milliliters of 95% ethanol. The solids were filtered from the ethanolic solution and purified by sublimation at 75° (0.01 mm.) giving 40.5 g. (70%) of I, m.p. 261–263.[5] Gas phase chromatography on a Dow Corning silicone grease column at 200° gave a single peak indicative of its purity. *Anal.* Calcd. for $C_{12}H_{36}Si_5$: C, 44.91; H, 11.31; mol. wt., 321. Found: C, 45.76; H, 11.22; mol. wt., 319 (by osmometry in benzene). The infrared spectrum of I showed no peaks indicative of Si–H, Si–OH, or Si–O–Si. N.m.r. exhibits a sharp singlet at τ 9.79, consistent with the highly symmetrical structure. Also, it is of interest that its high melting point[6] and ease of sublimation are presumably associated with its symmetry. Other related group IVB types are being investigated.

Acknowledgment.—This research was supported by The United States Air Force under Contract AF-33(657)-10288 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio. The authors are grateful to G. Schwebke and W. Atwell for helpful suggestions and Dr. Roy King for the n.m.r. spectral determination.

(1) D. Wittenberg, M. V. George, and H. Gilman, *J. Am. Chem. Soc.*, **81**, 4812 (1959).

(2) G. Schwebke and P. K. Sen, unpublished studies.

(3) Silicon tetrachloride reacts with refluxing tetrahydrofuran giving a mixture of chlorobutoxysilanes [M. Kratochvil and J. Frejka, *Chem. Listy*, **52**, 151 (1958); *Chem. Abstr.*, **52**, 16, 329*e* (1958)].

(4) Possibly mixtures of siloxanes.

(5) Melting points were taken in a sealed tube completely immersed in the heating unit of a Mel-Temp melting point apparatus.

(6) With the straight chain analogs of the type $Me_3Si(SiMe_2)_nSiMe_3$, only $n = 6$, b.p. 194–198° (3 mm.), m.p. 60–61, and $n = 8$, b.p. 244° (3 mm.), m.p. 113–114°, are low melting solids; whereas $n = 0$ through 5 are liquids. [M. Kumada, private communication; also see M. Kumada and M. Ishikawa, *J. Organometal. Chem.*, **1**, 153 (1963)].

DEPARTMENT OF CHEMISTRY
IOWA STATE UNIVERSITY
AMES, IOWA

HENRY GILMAN
CLIFFORD L. SMITH

RECEIVED FEBRUARY 7, 1964

Conversion of Hexasubstituted Benzenes to Cyclohexadienones

Sir:

In a recent communication[1] the use of peroxytrifluoroacetic acid in the presence of boron fluoride to effect hydroxylation of aromatic hydrocarbons was reported. For example, mesitylene was converted to mesitol in good yield with efficient use of the peracid. In the oxidation of prehnitene (I) a cyclohexadienone (II) was isolated in small quantities, and its formation was attributed to attack by a positive species (here referred to, for simplicity, as OH^+), followed by methyl

(1) C. A. Buehler and H. Hart, *J. Am. Chem. Soc.*, **85**, 2177 (1963).