tact shifts for the equatorially situated protons are generally small compared with the pseudo-contact shifts. Despite these sources of error, the simple analysis presented here demonstrates that the benzoylacetonate proton shifts in the cobalt complex are predominantly dipolar in nature.

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sym-Diisocyanatotetraorganodisilanes[1]

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The synthesis and characterization of two representatives of a new class of organofunctional disilanes, the *sym*-diisocyanatotetraorganodisilanes, $\mathrm{OCN(R)_2SiSi(R)_2NCO}$, wherein R = CH_3 or C_6H_5 is reported. Compounds containing the silicon isocyanate linkage (Si–NCO) have been known for some time and studies on the addition of amines to this isocyanate linkage have been reported.[3] Goubeau and Henbach[4] have shown that this addition reaction leads to the formation of silylureas. Furthermore, Neville and McGee[3] illustrated these ureas to be easily hydrolyzed by moisture to yield a substituted urea.

$$\mathrm{4RR'NH + Si(NCO)_4 \longrightarrow Si(NHCONRR')_4 \xrightarrow{2H_2O} 4H_2NCONRR' + SiO_2}$$

These workers used this reaction as a means of preparing N-mono- and N,N-disubstitured ureas. To our knowledge, the only isocyanatodisilane previously reported was pentamethyldisilanyl isocyanate, $\mathrm{(CH_3)_3SiSi(CH_3)_2NCO}$, prepared by Urenovitch and MacDiarmid.[5] The synthesis of the *sym*-diisocyanatotetraorganodisilanes reported in the present work offers an advantage of difunctionality. Thus, the incorporation of the disilane linkage into various polymeric systems through addition reactions to the isocyanate units should be possible.

The diisocyanatotetraorganodisilanes were prepared from the corresponding *sym*-dichlorotetraorganodisilane derivatives. The tetramethyl-[6] and tetraphenyldisilanes,[7] $\mathrm{Cl(R)_2SiSi(R)_2Cl}$, where R = CH_3 or C_6H_5, were obtained through known routes. These disilanes were shown to be free of siloxane (Si–O–Si) impurities by infrared analysis. Treatment of these intermediates with silver isocyanate led to the formation of the desired compounds.

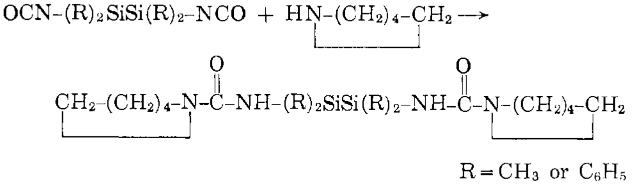
$$\mathrm{Cl(R)_2SiSi(R)_2Cl \xrightarrow{AgNCO} OCN(R)_2SiSi(R)_2NCO} \qquad \mathrm{R = CH_3\ or\ C_6H_5}$$

These new materials are very sensitive to moisture and oxygen. Consequently, all work was carried out under a deoxygenated, anhydrous nitrogen atmosphere.

It was of interest to determine (a) whether or not the $\equiv$Si—N= linkage is as unstable in a *sym*-diuredotetraorganodisilane derivative as are the silylureas of Neville and McGee[3] and (b) whether or not a nucleophilic species could be added to the isocyanate function without cleavage of the disilane linkage.

The first problem was solved by an analytical technique used to determine the Si–Si linkage,[7] *i.e.*, the determination of the hydrogen value of the materials. A weighed amount of the compound was decomposed in moist piperidine and the resulting hydrogen gas collected and measured. Analysis of the reaction mixture for both the diisocyanatotetramethyl- and -tetraphenyldisilanes gave a solid product shown to be piperidine carboxamide. This result indicates that the Si–N linkage in these compounds is susceptible to hydrolylic cleavage.

Piperidine was selected as the initial nucleophilic species. Treatment of the two isocyanate derivatives with this amine under anhydrous conditions led to the formation of the corresponding ureas; *i.e.*, cleavage of either the Si–N or Si–Si linkages did not occur.



$$\mathrm{OCN{-}(R)_2SiSi(R)_2{-}NCO + \underbrace{HN{-}(CH_2)_4{-}CH_2}} \longrightarrow$$

$$\mathrm{\underbrace{CH_2{-}(CH_2)_4{-}N}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH{-}(R)_2SiSi(R)_2{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underbrace{N{-}(CH_2)_4{-}CH_2}}$$

$$\mathrm{R = CH_3\ or\ C_6H_5}$$

This result establishes that these materials react as difunctional isocyanates under anhydrous conditions. It therefore should be possible to incorporate the tetraorganodisilane unit into polymeric systems by reaction through these isocyanate linkages. Investigations are under way to explore this possibility.

Experimental Section

Reagents.—(a) The nitrogen used was first bubbled through an alkaline solution of pyrogallol (15 g of pyrogallol dissolved in 100 ml of 50% sodium hydroxide solution) and then through concentrated sulfuric acid followed by passage through a solid sodium hydroxide–Drierite trap.

(b) The piperidine was stored over potassium hydroxide for at least 2 days before distillation from fresh potassium hydroxide.

(c) The solvents were placed over an appropriate drying agent (calcium chloride was used in most cases) and distilled from fresh drying agent. The solvents were then deoxygenated by allowing deoxygenated anhydrous nitrogen gas to bubble through them for at least 1 hr.

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[1] Abstracted in part from the M.S. Thesis of E. B. Moynahan, Lowell Technological Institute, 1965.

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(d) The silver cyanate was freshly prepared as commercially available material was shown to be unreactive.

Diisocyanatotetramethyldisilane.—To a solution of 5 g (0.0267 mole) of *sym*-dichlorotetramethyldisilane (bp 147.5–149.5°) in 35 ml of anhydrous diethyl ether, contained in a 100-ml three-necked flask, to which was attached a reflux condenser, thermometer, and solid addition flask, was added silver cyanate (9.3 g, 0.0621 mole, a slight excess). The addition of the solid silver cyanate, at room temperature and over a 30-min period, was accompanied with a very slight rise in temperature. The reaction mixture was stirred for 10–12 hr at room temperature under a deoxygenated anhydrous nitrogen atmosphere and then filtered. The precipitate (8.7 g) was washed with several small portions of anhydrous ether. The filtrate and the washings were combined and the ether was removed by distillation (under nitrogen). The product was obtained by distillation under reduced pressure giving the desired *sym*-diisocyanatotetramethyldisilane (bp 105.5–106.5° (30 mm)); yield: 2.19 g, 54%.

Anal. Calcd for $C_6H_{12}N_2O_2Si_2$: N, 13.98; Si, 28.1; hydrogen value for one Si–Si bond per molecule, 111.8. Found: N, 13.9; Si, 27.7; hydrogen value, 112.5.

The infrared spectrum was compatible with the assigned structure. A strong band at 2280 cm^{-1} was attributed to the isocyanate grouping.

Diisocyanatotetraphenyldisilane.—Using a procedure similar to that described for the preparation of diisocyanatotetramethyldisilane, a solution of *sym*-dichlorotetraphenyldisilane (4.0 g, 0.0092 mole) in 75 ml of anhydrous diethyl ether was treated with silver cyanate (2.8 g, 0.0183 mole, a slight excess). The precipitate (3.2 g) obtained by filtration was washed with several small portions of anhydrous diethyl ether and the washings were combined with the filtrate. The ether was removed by distillation under nitrogen, leaving a white solid which was recrystallized once from a 1:1 benzene–petroleum ether (bp range 30–60°) mixture, giving 3.5 g (84%) of the desired material (mp 123–124°).

Anal. Calcd for $C_{26}H_{20}N_2O_2Si_2$: N, 6.25; Si, 12.5; hydrogen value for one Si–Si bond per molecule, 50.1. Found: N, 5.93; Si, 12.7; hydrogen value, 53.8.

The infrared spectrum of this material was compatible with the assigned structure. The strong NCO band appeared at 2280 cm^{-1}.

Hydrolysis of *sym*-Diisocyanatotetramethyldisilane.—In a 50-ml flask connected to a condenser was placed 0.5 g (0.0025 mole) of 1,2-diisocyanatotetramethyldisilane, and 10 ml of a 10% water–piperidine solution was added. The resulting solution was then heated at reflux temperature for a period of 24 hr. The cooled solution was then diluted with 25 ml of water and extracted with three 20-ml portions of ether. The water phase was then concentrated to dryness under reduced pressure giving a white solid which was recrystallized from benzene–petroleum ether (1:1). Piperidine carboxamide (0.15 g) was isolated having an infrared spectrum identical with that isolated from the hydrolysis of 1,2-diisocyanatotetraphenyldisilane.

Anal. Calcd for $C_6H_{12}ON_2$: N, 21.85. Found: N, 21.60.

Hydrolysis of *sym*-Diisocyanatotetraphenyldisilane.—The products remaining in the moist piperidine solution from three runs in the determination of the hydrogen value of *sym*-diisocyanatotetraphenyldisilane were combined and treated as described above for the hydrolysis of the tetramethyl derivative. The isolated material, piperidine carboxamide, melted at 105–106° (lit.[8] 105–106°). The infrared spectrum was compatible with the assignment.

***sym*-Dipiperidinecarboxamidyltetramethyldisilane.**—In a 100-ml flask attached to a condenser and under a nitrogen atmosphere was placed piperidine (0.52 g, 0.006 mole) in 5 ml of benzene. To this was added dropwise 1,2-diisocyanatotetramethyldisilane (0.59 g, 0.0029 mole) dissolved in 2 ml of benzene. A clear solution resulted. It was warmed to 50° and maintained at that temperature for 1 hr. On cooling, long slender needles formed. Petroleum ether (10 ml) was added to the mixture and the contents of the flask allowed to stand overnight at 10°. Filtration under suction to remove the crystalline solid gave 0.75 g of a material melting at 108–112°. The material recrystallized from a benzene–petroleum ether mixture (3:1) melted at 109–111°.

Anal. Calcd for $C_{16}H_{34}O_2N_4Si_2$: N, 15.11; Si–Si, 60.6 ml/g; Si, 15.17. Found: N, 15.28; Si–Si, 60.7 ml/g; Si, 14.81.

The assigned structure was compatible with the infrared spectrum of the material.

***sym*-Dipiperidinecarboxamidyltetraphenyldisilane.**—In a 100-ml flask attached to a reflux condenser and under an atmosphere of nitrogen was placed piperidine (0.18 g, 0.002 mole) dissolved in 8.0 ml of benzene. To this was added 1,2-diisocyanatotetraphenyldisilane (0.45 g, 0.001 mole) dissolved in 5.0 ml of benzene. The resulting solution was heated at 60° for a period of 4 hr. To the cooled solution was added 15 ml of *n*-hexane and the solution was allowed to stand at 10° overnight. The white crystalline solid (0.43 g) removed by filtration melted at 134–136° after drying.

Anal. Calcd for $C_{36}H_{42}N_4O_2Si_2$: N, 9.05; Si, 9.06. Found: N, 8.75; Si, 9.14.

The assigned structure was compatible with the infrared spectrum of the compound.

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Stereochemical Studies of Metal Chelates. I. Cobalt(III) Complexes Containing an Optically Active Tetramine

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Remarkable progress has been recently made in stereochemical studies of triethylenetetramine–cobalt(III) complexes,[1-3] which were prepared by Basolo for the first time.[4] Recently, Asperger and Liu[5] have synthesized a new optically active ligand, 2,9-dimethyltriethylenetetramine, a C-substituted derivative of trien, and prepared its cobalt(III) complexes. They conclude that nmr spectra could be used in distinguishing the three geometrical isomers and that the complexes having the absolute configuration D(+)-α, and L(−)-β predominate for the *l* ligand by the stereospecific coordination.

Independently we also synthesized two other new optically active derivatives of trien, 5-methyltriethylenetetramine (5-Metrien) and 3,8-dimethyltriethylenetetramine (3,8-Dimetrien), and some novel observations in the stereochemistry of their cobalt(III) complexes are briefly reported here.

The ligand 5-Metrien was synthesized as follows

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