

Figure 1. View of the complex cation of **1c**. Atoms have been drawn as spheres of arbitrary radius, hydrogen atoms have been omitted. Averaged bond distances (Å) within heterocycles: C1–O, 1.36 (2); O–C3, 1.49 (2); C3–C4, 1.56 (2); C4–N, 1.51 (2); N–C1, 1.33 (2).

particularly, from the appearance of a well-resolved ^{103}Rh – ^{13}C coupling ($J = 36$ Hz) in the case of **4b**. Similar δ (187.2) and J (35 Hz) values have been reported for $[\text{Rh}[\text{C}(\text{NHR})\text{N}(\text{Me})\text{C}(\text{NHR})](\text{Me})(\text{I})(\text{CNR})_2]^+$ ($\text{R} = t\text{-Bu}$).⁷ The UV spectra (e.g., **2a** (H_2O) 295 (2.53), 230 (sh), <190 (>4.7) [CT band] nm (log ϵ)) reflect the expected high ligand field splitting capacity of the carbene ligand which even surpasses that of cyanide in hexacyanocobaltate(III)⁸ and -rhodate(III).⁹

Conclusive evidence for the existence of hexacarbene complexes is finally produced by an X-ray analysis of **1c**.¹⁰ In spite of the poor quality of the data,¹¹ the overall geometry of a central cobalt atom surrounded by six five-membered rings is reliably defined (Figure 1) with the average values of the ring dimensions comparing favorably with those determined recently for tetrakis(oxazolidin-2-ylidene)palladium dichloride.¹ In both cases, the metal to carbene distances ($\text{Co}-\text{C}$, 1.95 (1); $\text{Pd}-\text{C}$, 2.020 (2) Å) are only slightly shorter than the estimated $\text{M}-\text{C}_{\text{sp}^2}$ single-bond lengths ($\text{Co}-\text{C}$, 1.96; $\text{Pd}-\text{C}$, 2.05 Å), precluding any significant metal to carbon π bonding.

In summary, the combination of 2-hydroxyalkyl isocyanides with higher valent metals opens the most efficient route to (particularly homoleptic) carbene complexes^{1,12} of which the hexacarbene species **1–4** represent a new genus. Their syntheses, most surprisingly, are best carried out under rather “non-organometallic”-type reaction conditions. Actually, this exemplifies an interesting trend in modern organometallic chemistry away from inert atmospheres, nonpolar solvents, and low oxidation states of metals which has already led to some rather spectacular results.^{13–16}

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Supplementary Material Available: Table of further crystal data and positional and isotropic equivalent thermal parameters for compound **1c** (4 pages). Ordering information is given on any current masthead page.

An Anomously Long-Wavelength Electronic Transition in Conformationally Locked Organosilane High Polymers

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The first organosilane polymers (i.e., polymers containing only silicon in the backbone) were reported in 1924,¹ but these highly insoluble and intractable materials evoked little scientific interest. Recently, however, the synthesis of soluble substituted polysilane derivatives² has both rekindled considerable scientific interest and has spawned the development of a number of new applications.³

One of the most intriguing properties of catenated substituted silane derivatives is their remarkable electronic absorption spectra.⁴ An intense absorption, described variously as either a $\sigma\sigma^*$ or a $\sigma 3d\pi_{\text{Si-Si}}$ transition,⁵ moves initially to longer wavelengths with increased silicon catenation but rapidly approaches a limiting value with increasing chain length.⁶ For this reason, most simple, alkyl-substituted silane high polymers absorb around 305–320 nm.⁴ We report here the surprising observation that this limiting value apparently applies only to polysilane derivatives either in solution or in the amorphous solid state and that in certain cases where conformational rigidity is enforced, for example, by side-chain crystallization, the electronic absorption of the polysilane backbone occurs at considerably longer wavelengths.

In a continuing study of the photolability of substituted silane high polymers as a function of the substituents, we have prepared a number of symmetrically disubstituted polymers by the condensation of the appropriate silyl dichlorides with sodium as shown below.^{2d} The electronic absorption spectra of **2a** and **2b** were as expected,⁴ showing a strong absorption in the 310–320-nm region both in solution or as solid films. The absorption spectrum of poly(di-*n*-hexylsilane) (PDHS) in the solid state was, however, most unusual.

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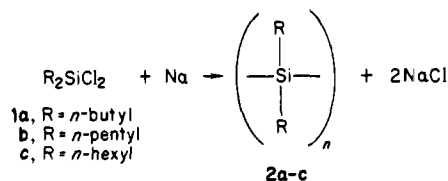
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In solution, **2c** exhibited a typical polysilane absorption appearing as a broad featureless band with a maximum at 317 nm. This was, however, not the case for films of **2c**. Films of PDHS $\sim 0.25 \mu\text{m}$ thick, spun from solution displayed an additional intense and anomalously long-wavelength absorption at 374 nm (see Figure 1). When the film was heated (100 °C, 1 min) the anticipated polysilane absorption reappeared at 317 nm. This absorption was, however, unstable upon cooling to room temperature, and the long-wavelength absorption returned upon standing. The process was thus totally reversible. This behavior was independent of the casting solvent or the molecular weight of the sample (\bar{M}_w range (4×10^4) – (2×10^6)), although the kinetics for reformation of the 374 nm absorption in a baked sample were somewhat molecular weight dependent. Thermal analysis (DSC) of samples of **2c** revealed a strong endothermic transition ($\sim 84 \text{ J/g}$) around 41 °C. This thermal transition was reversible upon cooling, although considerable supercooling (15–25 °C) was observed. It was demonstrated that the onset of this phase transition is associated with the described change in the electronic absorption spectrum.

We feel that the long-wavelength absorption of **2c** in the solid state is the result of conformational locking of the polysilane backbone into a specific configuration (perhaps planar zigzag) that is different from that normally observed in solution or in amorphous films and that this locking is caused by the crystallization of the *n*-hexyl substituent groups into a paraffin-like matrix. In this regard, the specific side-chain crystallization of long-chain *n*-alkyl substituent groups of stereoregular, isotactic, monosubstituted polyethylenes has been reported previously.⁷

Since it is generally agreed that the highest occupied orbital of catenated polysilane derivatives is a delocalized σ type,^{5d} changes in the backbone conformation would be expected to affect the orbital energies and hence the spectral properties. In this regard, $\sigma_{\text{Si-Si}}$ orbital shifts as a function of the dihedral angle between interacting σ bonds have been predicted theoretically and demonstrated experimentally for smaller substituted silane catenates.⁸

Further insight into of the structural changes that occur upon heating **2c** comes from examination of the temperature-dependent IR spectra⁹ shown in Figure 2. The molecular vibrations of PDHS can be roughly divided into two groups. Those above 700 cm^{-1} are attributable mainly to vibrations involving the *n*-hexyl side groups while those below 700 cm^{-1} involve silicon. This was confirmed by Raman measurements in which the lower frequency vibrations are more intense because of the larger change in polarizability associated with the silicon vibrations.¹⁰ Above 41 °C, the bands due to the *n*-hexyl vibrations become broad and weak as is characteristic of the IR spectra of *n*-alkanes in the melt phase.¹¹ As shown in Figure 2b, the effect of increasing the temperature is to disorder the *n*-hexyl groups as would be expected for a structure whose side groups were responsible for crystallization. Furthermore, the vibrations involving silicon in the infrared and Raman also broaden and weaken above 41 °C, indicating that

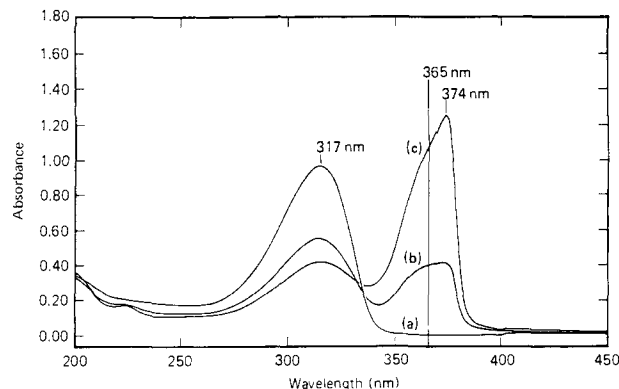


Figure 1. UV spectrum of a thin film ($\sim 0.25 \mu\text{m}$) of fractionated poly(di-*n*-hexylsilane) (**2c**) ($\bar{M}_w = 1.62 \times 10^6$, $\bar{M}_w/\bar{M}_n = 1.45$) deposited on a quartz wafer. (a) Film was baked for 2 min at 100 °C and the spectrum recorded immediately; (b) 90 min at 30 °C; (c) 120 min at 30 °C.

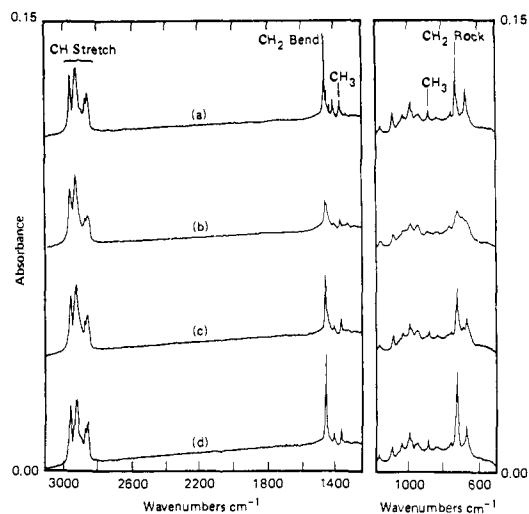


Figure 2. IR spectrum of a thin film ($\sim 0.25 \mu\text{m}$) of poly(di-*n*-hexylsilane) (**2c**) (bimodal molecular weight distribution, $\bar{M}_w = 4 \times 10^4$ and $\bar{M}_w = 2 \times 10^6$). (a) Initial sample, 30 °C, (b) sample heated to 100 °C and run immediately; (c) 50 min after cooling from 100 °C, (d) 75 min after cooling from 100 °C.

the ordered conformation of the silicon chain resulting from side-chain crystallization also changes with the melting of the *n*-hexyl groups. This strongly suggests that the shift in the UV absorption from 374 to 317 nm upon heating simply reflects the disorder introduced into the backbone induced by the melting of the side groups. It seems likely that this disorder is associated with changes in the dihedral angles of the silicon backbone. The reversibility of this phase transition is shown in Figure 2 although the crystallization of the sample upon cooling often takes some time. With this particular sample, which was a mixture of higher (2M) and lower (40K) molecular weight components, recrystallization (as monitored by changes in the infrared spectrum) was complete after 75 min. The DSC measurements as described earlier indicated that **2c** supercooled by as much as 25 °C, thus explaining the slow rate of recrystallization at 30 °C.

In summary it appears then that **2c** provides a unique example of a conformationally controlled electronic transition in a high polymer. Although changes in backbone conformations due to the melting of side chains have been previously observed in isotactic polyolefins,⁷ this is the first example where disordering the polymer backbone has been observed to cause such a remarkable change in the electronic absorption spectrum. It appears now that the limiting absorption maxima previously reported for amorphous alkyl polysilanes may be a result of disorder caused by conformational equilibration of the silicon chain.

Further studies of the chemistry and spectroscopy of organosilane high polymers is proceeding.

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Registry No. PDHS (SRU), 94904-85-5; (*n*-hexyl)₂SiCl₂, 18204-93-8.

The Isolation and X-ray Structures of Lithium Crown Ether Salts of the Free Carbanions [CHPh₂]⁻ and [CPh₃]⁻

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Numerous publications have shown that salts of delocalized carbanions can exist in solution as ion pairs^{1,2} and their structures, either in solution or solid phase, have generated considerable interest.³ In addition, several groups have shown that crown ethers and glymes may react in solution with the carbanion-alkali-metal complex to form an ion pair having the metal ion coordinated with a polydentate ether.^{4,5} In the crystal phase, the pioneering work of Stucky has resulted in the publication of the structures of several ligand-complexed metal salts of delocalized carbanions.⁶ None of these studies, however, have afforded detailed structures of well-separated noninteracting hydrocarbyl carbanions. Work in this laboratory has shown that crown ethers can be used to obtain crystals of separate anions in other groups of the periodic table, for example, the [Li(12-crown-4)]⁺ salts of [PPh₂]⁻ or [CuPh₂]⁻.⁸ We now describe the extension of this technique to the more important carbanions⁹ and give details of the X-ray crystal structures¹⁰ of [Li(12-crown-4)₂][CHPh₂]⁻ (**1**) and [Li(12-crown-4)₂][CPh₃]⁻·THF (**2**).

The isolation of **1** and **2** was as follows. Ten millimoles of CH₂Ph₂ or CHPh₃ were dissolved in THF (100 mL). The addition of *n*-BuLi (6.25 mL of a 1.6 M solution in *n*-hexane) gave an orange color for CH₂Ph₂ and red in the case of CHPh₃. Then 12-crown-4 (3.5 g, 20 mmol) in THF (5 mL) was added dropwise, giving a yellow-orange precipitate of **1** and a slightly cloudy red solution for **2**. Warming completely dissolved the solids and slow cooling to -20 °C afforded the crystalline products **1** and **2**. **1** was isolated as orange needles that turn slowly red on heating, soften at 85 °C, and decompose at 160 °C; **2** was isolated as red needles that decompose at 120 °C. Both **1** and **2** are quite stable

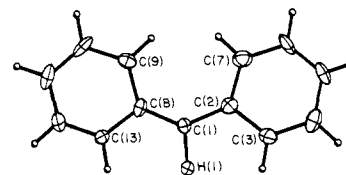


Figure 1. Bond distances (Å) and angles (deg) for **1**: C(1)-C(2) = 1.435 (6); C(1)-C(8) = 1.404 (6); C(2)-C(3) = 1.433 (7); C(3)-C(4) = 1.399 (7); C(4)-C(5) = 1.429 (8); C(5)-C(6) = 1.367 (7); C(6)-C(7) = 1.376 (7); C(7)-C(2) = 1.439 (6); C(2)C(1)C(8) = 132.1 (4); C(1)C(2)C(3) = 117.6 (4); C(1)C(2)C(7) = 119.4 (4); C(2)C(3)C(4) = 123.0 (4); C(3)C(4)C(5) = 120.9 (5); C(4)C(5)C(6) = 116.7 (5); C(5)C(6)C(7) = 123.0 (5); C(2)C(7)C(6) = 123.5 (4). Distances and angles in the C(8) phenyl ring are similar.

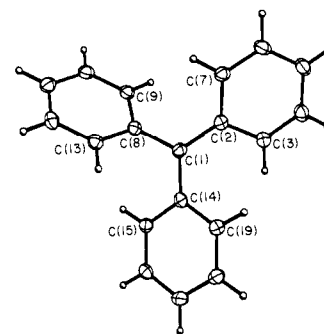


Figure 2. Bond distances (Å) and angles (deg) for **2**: C(1)-C(2) = 1.451 (5); C(1)-C(8) = 1.459 (5); C(1)-C(14) = 1.450 (4); C(2)C(1)C(8) = 119.4 (3); C(8)C(1)C(14) = 118.4 (3); C(2)C(1)C(14) = 122.3 (3). Distances and angles in phenyl rings are similar to those in **3**.

compounds in the absence of air or moisture and THF solutions show little decomposition after several days in the freezer (-20 °C). The solids appear to be indefinitely stable at 0 °C.

The structures of the anions of **1** and **2** are illustrated in Figures 1 and 2.¹¹ The main feature is the planar geometry at each central carbon atom. The coplanarity of the two phenyl rings in **1** and its wide C(2)C(1)C(8) angle of 132.1 (4)° are also noteworthy. The planar cores of **1** and **2** and the total planarity in **1** are manifestations of extensive delocalization. Steric constraints prevent the rings in the anion of **2** from being coplanar and the familiar propeller arrangement is the result. The rings are at angles of 21.3°, 30.3°, and 42.0° (average 31.2°) to the central C(1)C(2)C(8)C(14) plane. There are no really close intramolecular contacts between the central carbon and other atoms in either molecule. For example the closest nonbonded contacts in **2** involve the six ortho hydrogens, which are all approximately 2.7 Å distant.

Structural comparisons are possible between **2** and the previously reported complexes TMEDALi-CPh₃ (**3**)⁶ or its sodium analogue.¹² These complexes are contact ion pairs between [TMEDALi(Na)]⁺ and [Ph₃C]⁻. The main difference is that C(1) in **3** is 0.12 Å out of the plane of C(2), C(8), and C(14), whereas in **2** C(1) has a planar environment. In the more ionic sodium derivative C(1) is also planar. Other bond distances and angles in the molecules are similar.

When **1** and **2** are compared, the C(1)-C(2) and C(1)-C(8) lengths in **1** average slightly shorter than the corresponding C(1)-C(phenyl) distances in **2**. This could be due to better delocalization in coplanar **1** but it also might be a result of greater crowding in **2**. Support for the latter view comes from the C-C distances in the phenyl rings, which average to almost identical lengths in both anions.

An analogous preparation of the unassociated benzyl anion gave a yellow solid, presumably [Li(12-crown-4)]⁺[CH₂Ph]⁻, from ether. Unfortunately, we were unable to isolate crystals due to its rapid decomposition upon addition of THF. Work involving the isolation

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