

INVESTIGATION OF SILACYCLOPENTADIENE DERIVATIVES, I

By

G. PONGOR, J. RÉFFY and J. NAGY

Department of Inorganic Chemistry, Technical University, Budapest

(Received June 28, 1973)

Introduction

Investigations were carried out in connection with the bond structure of silacyclopentadiene derivatives, including the following compounds:

1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (I),
(m.p.: 225—6 °C)

1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (II)
(m.p.: 181—2 °C)

1,2,3,4,5-pentaphenyl-1-silacyclopentadiene (III)
(m.p.: 200 °C)

1,1,2,3,4,5-hexaphenyl-1-silacyclopentadiene (IV)
(m.p.: 190—2 °C)

decaphenyl-1,1'-bis-(1-silacyclopentadiene) (V)
(m.p.: 237—8 °C).

The compounds investigated were synthesized by RÜHLMANN and al. [1]. For preparation of compounds I and III BRAYE's method [2] was used, namely methylchlorosilane (compound I) and phenylchlorosilane (compound III) were reacted with 1,4-dilithium-1,2,3,4-tetraphenylbutadiene. Compound V was prepared by a reaction of sodium-1,2,3,4,5-pentaphenyl-1-silacyclopentadienate and 1-chloro-1,2,3,4,5-pentaphenyl-1-silacyclopentadiene [3]. Compounds II and IV were synthesized also with BRAYE's method.

Previously it was found [1] that compounds I and III showed an intensive reddish-violet colour reaction with sodium-bis-(trimethylsilyl)-amide, n-butyllithium or phenyllithium. A solid material of black violet colour, containing 0.7 g atom/mol of metal, could be separated from the solutions. Under similar conditions compounds II and IV did not react with sodium-bis-(trimethylsilyl)-amide. Nor could the analogous reaction of triphenylsilane be carried out.

From these facts the conclusion could be drawn that such an attack could only be effective on a suitably activated Si—H bond.

On the basis of his investigations M. D. CURTIS [4] came to the conclusion that in the course of reaction of compounds I and III with *n*-butyllithium, 1-*n*-butyl derivative and lithiumhydride was produced and the latter attached to the C=C double bond of the ring yielding an intensive colour C—Li derivative.

Reaction of compounds I—IV with potassium or sodium in a solution of tetrahydrofuran resulted without exception in a solution ranging in colour from blue to reddish-violet [5]. The blackish-violet solid material isolated from the solutions contained 1 or 2 g atom/mol of metal. These materials were extremely sensitive to oxygen and the ones containing 1 g atom/mol of metal gave a marked ESR peak.

Summarizing the reactions mentioned of silacyclopentadiene derivatives, it was found that "quasi-aromatic anions" could only be formed in the reaction of sodium-bis-(trimethylsilyl)-amide with compounds containing one methyl or phenyl group on the silicon atom. Reacting these compounds with alkali metals any of radical anions, di-anions and quasi-aromatic anions can occur in the solution. If derivatives with two methyl or two phenyl groups on the silicon atom are, however, treated by metals probably only a simple charge transfer reaction takes place, leading to radical anions and di-anions. The most complicated reaction is the one between pentaphenyl-1-silacyclopentadiene and *n*-butyllithium or phenyllithium. There is a great probability that in the case of *n*-butyllithium a derivative substituted with *n*-butyllithium on the silicon atom is formed, and the intensive violet colour of the solution is due to the lithiumhydride adduct. In the reaction with phenyllithium either a similar process occurs, or the larger steric hindrance leads to the formation of an anion more or less quasi-aromatic.

Our aim was to investigate the structure of compounds I to V and molecular structural causes of formation of radical anions, di-anions and quasi-aromatic anions which can be produced from the corresponding compounds with various reagents.

In the first part of our work we tried to verify the structure of the compounds, find the state of conformation and extent of conjugation by spectroscopy.

Infrared spectroscopy

The infrared spectra were recorded by a Zeiss UR-20 spectrophotometer using KBr tablet. The assignation of characteristic bands is seen in Table 1.

The spectra correspond to the assumed structures. In the case of compound V the expectation was verified that because of the symmetrical nonpolar character of its bonds the bands appear with relatively less intensity than the

analogous bands of the other compounds. On the basis of assignation related to the carbon — carbon double bond of the silacyclopentadiene ring (1578—1600 cm^{-1}) a d-orbital effect could be concluded. Thus the d-orbital of the silicon atom participates in the conjugated π system formed in the ring.

Table 1

Assignation of characteristic IR-bands of phenyl substituted silacyclopentadiene derivatives (frequency in cm^{-1})

Compound	I	II	III	IV	V
$\nu_{\text{C}_{\text{Ar}}\text{H}}$	3104 vw	3105 w	3078 m	3078 m	3080 vw
	3080 w	3082 m	3065 m	3065 m	3059 m
	3060 w	3062 m	3030 m	3035 m	3028 m
	3030 w	3026 m	3005 w	3010 vw	3000 vw
ν_{CH_3}	3018 w	2996 w	—	—	—
	2980 vw	2960 m			
	2890 vw	2896 w			
ν_{SiH}	2124 s	—	2122 m	—	—
$\nu_{\text{C}_{\text{Ar}}\text{C}_{\text{Ar}}}$	1600 m	1600 m	1610 w	1624 m	1602 m
	1493 m	1491 m	1499 m	1509 m	1488 m
$\delta_{\text{C}=\text{C}}$ (hetero ring)	1578 w	1579 w	1590 w	1600 w	1579 w
$\text{C}_{\text{Ar}}\text{C}_{\text{Ar}}(\text{Si})$	—	—	1440 m	1449 m	1431 m
$\delta_{\text{s}}(\text{Si})\text{CH}_3$	1253 w	1254 m	—	—	—
		1247 m			
$\nu_{\text{Si}-\text{Ar}}$	—	—	1120 m	1120 m	?
$\nu_{\text{SiC}}(\text{H}_3)$	849 w	837 m	—	—	—
$\gamma_{\text{C}_{\text{Ar}}\text{H}}$	730 m	756 m	748 m	773 m	763 m
			742 m	750 m	739 m
$\gamma_{\text{C}_{\text{Ar}}\text{C}_{\text{Ar}}}$	713 m	710 m	709 s	722 s	710 m
	700 ss	697 vs	699 s	705 vs	698 vs

vw = very weak, w = weak, m = medium, s = strong, vs = very strong.

Ultraviolet spectroscopy

The ultraviolet spectra were taken in a Spektromom 201 spectrophotometer in the 210 to 460 nm range using tetrahydrofuran as solvent. The spectra of compounds I to V are shown in Figs 1 and 2, the positions and intensities of the ultraviolet maxima with the assignation are included in Table 2.

The existence of conjugation between the phenyl groups and the silacyclopentadiene ring is proven by the appearance of an electron transfer band, the relatively small intensity is characteristic of the extent of conjugation (it is evident that no coplanar position can be realized). It is worth to mention

Table 2
Data of ultraviolet spectra of phenyl substituted silacyclopentadiene derivatives

Compound	λ_{\max} (phenyl chromophore) (nm)	ϵ_{\max}	λ_{\max} (nm) (electron transfer)	ϵ_{\max}	λ_{\max} (phenylsilane) (nm)	ϵ_{\max}
I	248	22540	364	9099	—	—
II	245	23820	359	8570	—	—
III	247	21680	370	8770	230*	24000
IV	248	23170	365	8035	230*	24000
V	226—242	56230	359	10620	230*	57500

* In the ultraviolet spectrum of the compound a local minimum around the indicated wavelength is missing — as against compounds I and II.

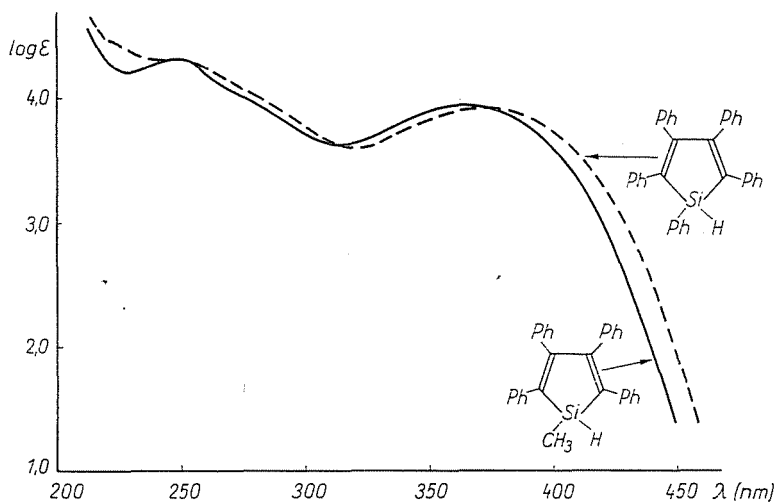


Fig. 1. Ultraviolet spectra of compounds I and III

that in the ultraviolet spectrum of the 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene [6] the electron transfer band is of considerably higher intensity ($\epsilon_{\max} = 20650$) than one in the spectra of compounds I and II containing four phenyl groups, since in the case of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene there is a greater possibility for the coplanar position of the phenyl groups because of the lesser steric hindrance. Intensity ratios show that the

size of the substituents on the silicon atom has an effect on the out of plane position of the phenyl groups attaching to carbon atoms and therefore on the extent of conjugation. The decrease of the conjugation is indicated by the small hypsochromic shift appearing in the absorption spectrum in the case of the band of lower intensity.

For the compounds III to V an absorption characteristic of phenylsilanes appears with bathochromic shift. (In the case of phenylsilane there is a maximum of great intensity between 210 and 220 nm.) Absorption ultraviolet

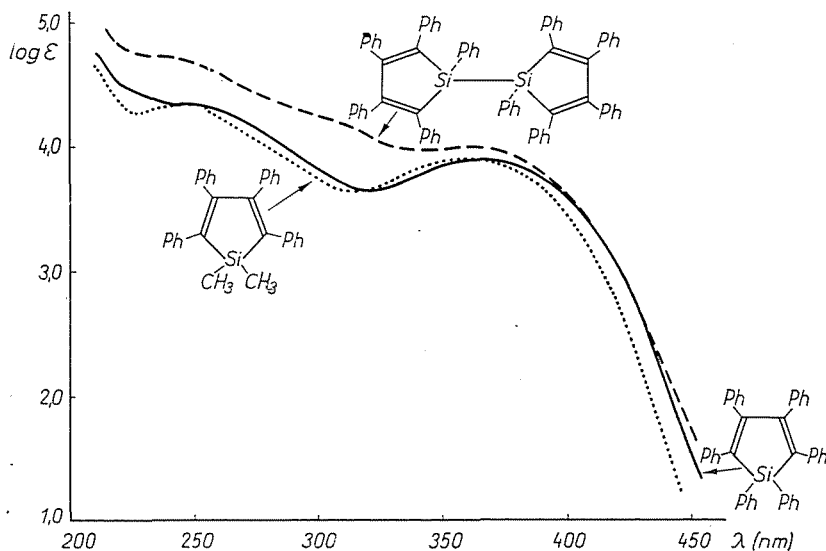


Fig. 2. Ultraviolet spectra of compounds II, IV and V

spectra of compounds I and II display a marked minimum at 230 nm. For compounds III to V the extinction coefficient value of absorption band characteristic of phenylsilanes is added to the value of extinction coefficient belonging to this minimum. The intensity of the band, originated from phenylsilane chromophore, of 1,1-diphenyl-1-silacyclopentadiene at 230 nm is about 10 000 [7]. If there is a single phenyl group on the silicon, the intensity is expected to be twice less. In the spectrum of compound I the extinction coefficient at 230 nm equals 17300. The extinction coefficient of compound III (which differs from compound I by a single phenyl group attached to the silicon atom) at 230 nm is expected to be $17300 + 5000 = 22300$. This value is close to the measured value of 24000. The appearance of phenylsilane band proves not to be any remarkable conjugation between the phenyl groups on the silicon atom and the π -system of the silacyclopentadiene ring. The deviations in the ultraviolet spectrum of compound V are due to sterical and structural differences.

NMR spectroscopy

The NMR spectra were recorded by a Perkin-Elmer R-12 instrument (Figs 3 to 7). The τ proton signs of the compounds investigated are compiled in Table 3. The τ value of the hydrogen belonging to the silicon atom indicates the existence of $d\pi-p\pi$ interaction between the vacant d-orbitals of the silicon and the π electrons of the ring. In the compounds containing silicon,

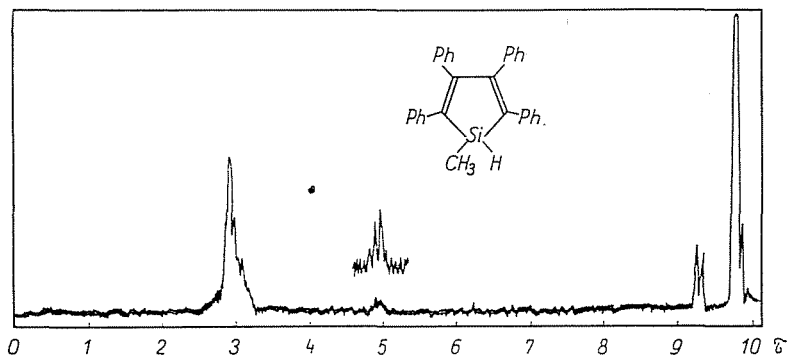


Fig. 3. NMR spectrum of compound I

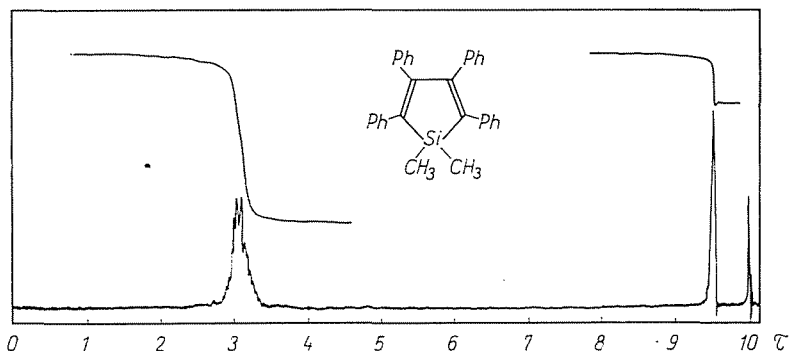


Fig. 4. NMR spectrum of compound II

where there is no possibility for a $d\pi-p\pi$ interaction, the chemical shift of the hydrogens on silicon atom can be found in the 6.1 to 6.7 range of τ [8] [e.g. $(\text{CH}_3)_3\text{SiH}$:6.149, $(\text{C}_2\text{H}_5)_3\text{SiH}$:6.388, $(\text{CH}_3\text{CHCH}_3)_3\text{SiH}$:6.701]. In trimethylvinylsilane (τ :5.672) and trimethylphenylsilane (τ :4.579), however, where the existence of a $p\pi-d\pi$ interaction can be taken to be proved, the Si-H τ sign is lower in value. In the NMR spectrum of compound III the aromatic multiplet is found at about $\tau = 3.08$. The chemical shifts of the hydrogen atoms in the phenyl groups attached to the silicon atom appear at

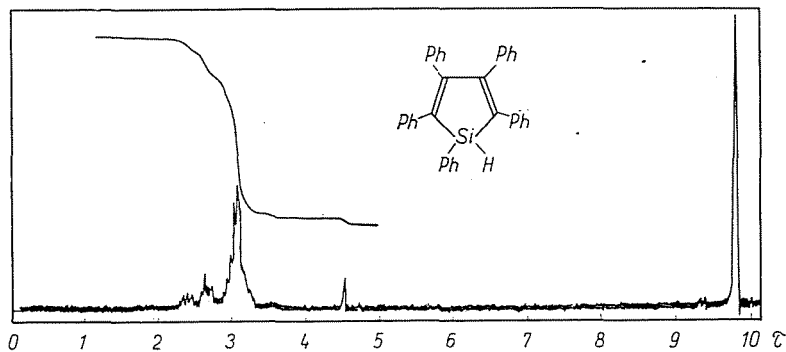


Fig. 5. NMR spectrum of compound III

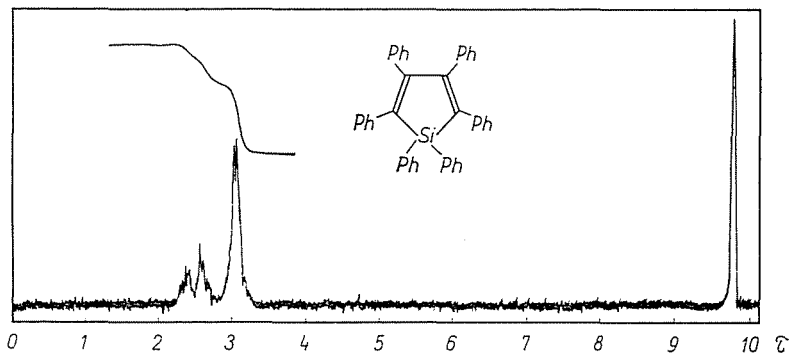


Fig. 6. NMR spectrum of compound IV

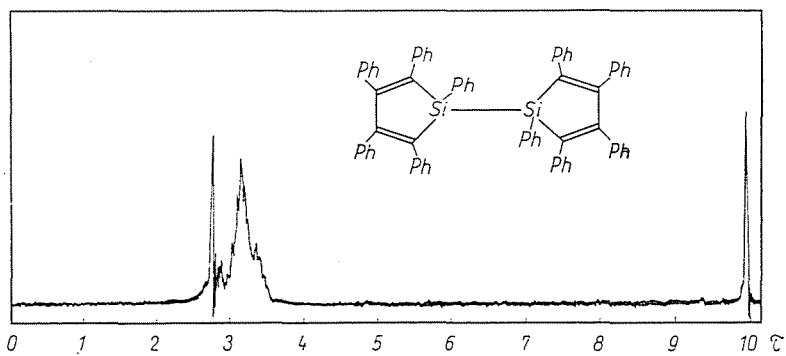


Fig. 7. NMR spectrum of compound V

Table 3
Chemical shifts in the NMR spectra of phenyl
substituted silacyclopentadiene derivatives

Compound	τ (Si—H)	τ (Si—CH ₃)	τ (C ₆ H ₅)	τ (Si—C ₆ H ₅)
I	4.98	9.43	2.92	—
II	—	9.52	3.04	—
III	4.56	—	3.08	2.62 2.40
IV	—	—	3.08	2.62 2.40
V	—	9.52	3.11	2.73

lower τ values. As to these phenyl groups the NMR sign of the hydrogens in ortho and para positions ($\tau = 2.62$) differs from that of hydrogens in meta position ($\tau = 2.40$). The same is true for compound IV. In the spectrum of compound V the chemical shifts of the hydrogens in ortho and para positions cannot be distinguished from those of the hydrogens in meta position.

Acknowledgement

The authors wish to thank K. RÜHLMANN and V. HAGEN (Humboldt University, Berlin) for the preparation of the compounds investigated.

Summary

Infrared, ultraviolet and NMR spectroscopy investigations were carried out in connection with phenyl substituted silacyclopentadiene derivatives. On the basis of spectrum data the silicon atom in the ring was found to participate in the π system of the ring by means of its vacant d-orbitals, the phenyl groups on the silicon atom, however, did not form a considerable conjugative relation with the silacyclopentadiene ring.

References

1. RÜHLMANN, K.: *Z. Chem.* **5**, 354 (1965).
2. BRAYE, I. E. H.—BUEBEL, W.—CHAPLIER, I.: *J. Am. Chem. Soc.* **83**, 4406 (1961).
3. HAGEN, V.—RÜHLMANN, K.: *Z. Chem.* **3**, 114 (1968).
4. CURTIS, M. D.: *J. Am. Chem. Soc.* **89**, 4241 (1967).
5. RÜHLMANN, K.—HAGEN, V.—SCHILLER, K.: *Z. Chem.* **7**, 353 (1967).
6. GILMAN, H.—COTTIS, S. G.—ATWELL, W. H.: *J. Am. Chem. Soc.* **86**, 1596 (1964).
7. BENKESER, R. A.—GROSSMANN, R. F.—STANTON, G. M.: *J. Am. Chem. Soc.* **84**, 4727 (1962).
8. WEBSTER, D. E.: *J. Chem. Soc.* 5132 (1960).

Ass. Prof. Dr. József NAGY Gábor PONGOR Dr. József RÉFFY	}	H—1521 Budapest
--	---	-----------------