Chromatography demonstrated that the reaction proceeded to completion (ferrocenecarbaldehyde was absent in the reaction mixture). The solution was filtered. $Et_2O$ (40 mL) and a 25% aqueous solution of $NH_4OH$ (25 mL) were added to the filtrate. When an aqueous ammonia solution was added, vigorous gas evolution was observed. Hexane (15 mL) was added to more completely remove the organic fraction. The organic layer was separated. The aqueous layer was extracted with $Et_2O$ (2×15 mL). The organic layers were combined and concentrated. The resulting yellow finely crystalline precipitate of methylferrocene was recrystallized from hexane. In the IR spectrum of the product, an absorption band at 1690 $cm^{-1}$, which corresponds to vibrations of the carbonyl group of ferrocenecarbaldehyde, is absent. The yield of methylferrocene was 0.27 g (95% with respect to the theoretical value), m.p. 36 °C (published data:[3] m.p. 35.5—36.5 °C). Found (%): C, 65.90; H, 6.52. $C_{11}H_{12}Fe$. Calculated (%): C, 66.04; H, 6.05.

***B* (with a solution of $Zn(BH_4)_2$ in THF).** Analogously, when a solution of ferrocenecarbaldehyde (0.135 g, 0.63 mmol) in THF (20 mL) reacted with a solution containing $Zn(BH_4)_2$ (0.059 g, 0.63 mmol) in THF (20 mL) for 10 min, methylferrocene formed as a yellow crystalline compound in a yield of 0.11 g (90%).

***C* (with the $2Zn(BH_4)_2 \cdot DB18C6$ complex in THF).** The $2Zn(BH_4)_2 \cdot DB18C6$ complex (0.275 g, 0.0005 mol) was added to a solution of ferrocenecarbaldehyde (0.21 g, 0.001 mol) in THF (30 mL). The suspension was stirred for 10 min. The color of the solution changed from red to yellow. Paper chromatography demonstrated that the reaction proceeded to completion. $Et_2O$ (40 mL) and a 25% aqueous solution of $NH_4OH$ (25 mL) were added to the reaction mixture. The solution was filtered off. The organic layer was separated. The inorganic layer was extracted with $Et_2O$ (2×30 mL). The organic layers were combined and concentrated to 2/3 of the initial volume. The white flocculent precipitate of crown ether that formed was filtered off. The solvent was distilled off from the filtrate. Methylferrocene was obtained as a yellow finely crystalline precipitate. The precipitate was recrystallized from hexane. The yield was 0.18 g (90% with respect to the theoretical value).

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# $^{13}C$ NMR study of 2,3,4,5-tetraphenylsilole dilithium salt

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The complete assignment of the signals in the $^{13}C$ NMR spectra of 2,3,4,5-tetraphenyl-1-$R^1$,$R^2$-1-silacyclopenta-2,4-dienes ($R^1 = R^2 =$ H, Me) and of the dianion of lithium salt $[(PhC)_4Si]^{2-} \cdot 2Li^+$ was carried out by 2D NMR spectroscopy.

**Key words:** silicon; 2,3,4,5-tetraphenylsiloles; silole dianion; $^{13}C$ NMR spectra.

Recently, we have reported a correct assignment of the signals of carbon atoms in the $^{13}C$ NMR spectra of 2,3,4,5-tetraphenylgermoles **1b** and corresponding dianion **2b** and showed that the values of their chemical shifts differ appreciably from those reported previously.[1—3] In this connection it was of interest to analyze the spectral data for the corresponding silole dianion **2a**.

The values of the chemical shifts and conclusions drawn on their basis and reported in the studies of the $^{13}C$ NMR spectra of siloles and their anions[4—8] are

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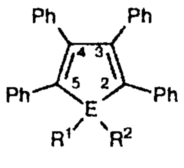
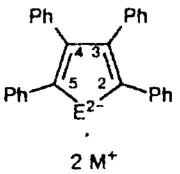


**1a,b**



**2a,b**

E = Si (**a**); Ge (**b**); M = Li, Na

contradictory, which is first of all explained by incorrect assignment of the signals of the ring carbon atoms in 2,3,4,5-tetraphenylheteroles. It is difficult to distinguish the signals of two carbon atoms of the heterocycle, α-C (C(2) and C(5)) and β-C (C(3) and C(4)), and those of the two *ipso*-C atoms of Ph groups (α-$C_{ipso}$ and β-$C_{ipso}$) in these compounds. Since these atoms are involved into π-delocalization of the negative charge and their chemical shifts should change appreciably on going from heteroles to their anions, it is of great importance to assign their signals correctly.

On the basis of the slight increase in the shielding for the α-C and β-C atoms of the heterocycle ($\Delta\delta^{13}C$ = −5.83 and −1.06 ppm, respectively) observed in the $^{13}C$ NMR spectra of the silole dianion $[(PhC)_4Si]^{2-}\cdot 2Na^+$ as compared to dichlorosilole **1a** ($R^1 = R^2 = Cl$) it was suggested that the negative charge is localized mainly on the silicon atom.[4] However, in the case of the lithium salt $[(PhC)_4Si]^{2-}\cdot 2Li^+$ similar high-field shifts of the signals of the ring α-C and β-C atoms ($\Delta\delta^{13}C$ = −2.57 and −3.52 ppm, respectively) as well as the increase in the $\delta^{29}Si$ chemical shift by 61.7 ppm relative to neutral dichlorosilole **1a** ($R^1 = R^2 = Cl$) were interpreted[5] as evidence of negative charge delocalization over the silole ring $C_4Si$.

The authors of Ref. 6 believe that the increase in the shielding of the ring α-C and β-C atoms ($\Delta\delta^{13}C$ = −5.26 and −2.28 ppm, respectively) as well as the decrease in the $\Delta\delta^{29}Si$ shielding by 21.48 ppm in the NMR spectra of the $[(PhC)_4SiBu^t]^-\cdot Li^+$ monoanion relative to the neutral compound $[(PhC)_4SiBu^t]_2$ is due to the negative charge delocalization, *i.e.*, to the increase in the π-electron density on the heterocycle. However, it was shown later[7] that this anion has a pyramidal structure and the barrier to inversion is 8.4 kcal $mol^{-1}$.

Similar reasoning was also used for a simpler (from the viewpoint of identification of the signals of carbon atoms) tetramethylsilole salt $[(MeC)_4Si]^{2-}\cdot 2Li^+$. On the basis of the high-field shifts of the signals of the ring α-C and β-C atoms ($\Delta\delta^{13}C$ = −4.13 and −13.23 ppm, respectively) and the low-field shift of the signal of the Si atom ($\Delta\delta^{29}Si$ = 21.63 ppm) on going from dichlorotetramethylsilole to the corresponding dilithium salt, it was also concluded that the tetramethylsilole dianion is characterized by some aromaticity.[8]

According to the recently reported data,[9] interchange of the assignment of the signals of the α-C and β-C atoms leads to a better correlation between the calculated chemical shifts of carbon atoms in the $[(PhC)_4Si]^{2-}\cdot 2M^+$ dianions (M = Li, Na) and the experimental values.[4,5] The calculations have shown that the decrease in the shielding of the Si atom observed in the salts is due to the paramagnetic contribution of the α-C—Si bond and the out-of-plane deviation of the lone electron pair. Despite these contradictions, a high degree of aromaticity of the simplest siloles $[(HC)_4Si]^{2-}\cdot 2M^+$ (M = Li, Na) has also been confirmed theoretically.[9] In a number of NMR studies of siloles[10] and their dianions[11] the experimental values of the $\delta^{13}C$ chemical shifts were reported without assigning them to specific carbon atoms.

To resolve the above contradictions, we made a correct assignment of the signals in the $^{13}C$ NMR spectra of silole **1a** and dianion **2a**.

The main problem in assigning the signals in the $^{13}C$ NMR spectra of tetraphenylsiloles and tetraphenylgermoles[2] is associated with diffuculties in identifying the signals of the α-C, β-C, α-$C_{ipso}$, and β-$C_{ipso}$ atoms. By employing 2D NMR spectroscopy methods successfully used previously[2] for correct assignment of the signals in the $^1H$ and $^{13}C$ NMR spectra of 2,3,4,5-tetraphenylgermoles we obtained exact values of the chemical shifts of carbon and hydrogen atoms for two groups of the signals corresponding to nonequivalent α-C—Ph or β-C—Ph fragments. Each fragment is characterized by the internal spin-spin coupling constants $J_{H-C}$ and $J_{H-H}$. The signal of *ortho*-protons of the Ph group in the α-position of the heterocycle served as a starting point for the determination of the partners involved in the spin-spin interaction in siloles. Their signal in the $^1H$ NMR spectrum was detected using the nuclear Overhauser effect (NOE).

The assignment of the signals in the $^{13}C$ NMR spectrum of dianion **2a** was based on identification of the signals of the carbon atoms in the *para*-positions of Ph substituents, which can be easily done since the intensities of the above signals differ from those of all other signals. The observed chemical shifts (δ 119.35 and 121.59) are close to the corresponding values for germole dianion (δ 119.20 and 121.82). Taking into account that the α-$C_p$ atoms are separated from Si (Ge) atoms by five covalent bonds, we assumed that the positions of these signals on the δ scale are very close for both dianions and, hence, the signal at δ 119.35 corresponds to α-$C_p$ atoms and that at δ 121.59 corresponds to β-$C_p$ atoms.

Our assignment of the signals in the $^{13}C$ NMR spectra of dianion **2a** is given in Table 1. This assignment differs from the results reported previously[4,5] and, thus, can affect the correctness of the inferences about the electron density distribution drawn on their basis.

Previously,[2] reasonably good correlations between the chemical shifts of the $C_{ipso}$ and $C_p$ atoms in the

**Table 1.** Chemical shifts in the $^{13}C$ NMR spectra of siloles **1** (in $CDCl_3$) and dianion **2** (in THF) and the assignments of the siganls taken from Ref. 10 made using correlation equations (1)—(4)

| $R^1$, $R^2$ | $\delta^{13}C$ | | | | | | | | | | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | α-C | β-C | $C_{ipso}$ | | $C_o$ | | $C_m$ | | $C_p$ | | |
| | | | α | β | α | β | α | β | α | β | |
| Me, Me | 141.73 | 153.86 | 139.76 | 138.69 | 129.78 | 129.94 | 127.91 | 127.36 | 126.14 | 125.48 | |
| | 141.89 | 154.01 | 138.87 | 139.91 | | | | | 125.52 | 126.18 | 4 |
| | 141.7 | 153.7 | 139.7 | 138.6 | 129.8 | 129.4 | 129.8 | 129.1 | 126.0 | 125.4 | 12 |
| H, H | 135.15 | 157.44 | 138.62 | 138.68 | 129.32 | 129.57 | 128.06 | 127.69 | 126.20 | 126.60 | |
| | 135.16 | 157.47 | 138.65 | 138.70 | 129.35 | 129.61 | 128.08 | 127.71 | 126.20 | 126.63 | 10 |
| Li, Li | 151.10 | 129.52 | 151.51 | 145.62 | 129.80 | 133.22 | 126.21 | 126.21 | 119.35 | 121.59 | |
| | 129.71 | 151.22 | 145.83 | 151.67 | 133.43 | 129.97 | 126.38 | 126.38 | 119.48 | 121.83 | 5 |
| Na, Na | 168.28 | 130.96 | 151.44 | 147.04 | 130.96 | 133.11 | 126.59 | 126.45 | 118.04 | 121.38 | |
| | 130.92 | 153.74 | 146.71 | 151.29 | 128.48 | 133.16 | 126.55 | 126.72 | 118.25 | 121.42 | 4 |
| Cl, Cl | 132.39 | 154.80 | 135.93 | 136.75 | 129.29 | 129.53 | 128.23 | 127.83 | 127.37 | 127.13 | 4 |
| | 132.28 | 154.74 | 135.37 | 136.67 | 129.27 | 129.48 | 128.24 | 127.84 | 127.37 | 127.13 | 5 |
| Cl, H | 134.08 | 156.54 | 136.83 | 137.57 | 129.51 | 129.40 | 127.79 | 128.46 | 127.08 | 126.73 | 10 |
| Ph, H | 138.65 | 156.93 | 138.74 | 137.41 | | | | | 125.91 | 126.54 | 10 |
| Me, H | 138.76 | 155.66 | 140.31 | 139.41 | 129.16 | 129.81 | 128.00 | 127.53 | 125.51 | 125.99 | 10 |
| $Bu^t$, H | 141.07 | 152.51 | 140.72 | 138.70 | 129.45 | 129.85 | 127.74 | 127.21 | 125.44 | 125.97 | 10 |
| $SiMe_3$, $SiMe_3$ | 145.36 | 154.67 | 139.77 | 141.43 | | | | | 125.16 | 125.82 | 4 |

α- and β-positions of Ph groups and the Taft constants of the substituents at the Ge atom were reported for germoles **1b** and dianion **2b**. We also obtained similar dependences with high correlation coefficients for the two studied siloles **1a** and dianion **2a** (the $\sigma^*$ value for lithium (−6.15) was taken from Ref. 2):

$$\delta(\alpha\text{-}C_{ipso}) = 139.66 - 0.964\cdot\Sigma\sigma^*,\ r = 0.999; \tag{1}$$

$$\delta(\beta\text{-}C_{ipso}) = 138.96 - 0.540\cdot\Sigma\sigma^*,\ r = 0.998; \tag{2}$$

$$\delta(\alpha\text{-}C_p) = 125.88 + 0.529\cdot\Sigma\sigma^*,\ r = 0.998; \tag{3}$$

$$\delta(\beta\text{-}C_p) = 125.88 + 0.351\cdot\Sigma\sigma^*,\ r = 0.989. \tag{4}$$

Using these relationships, we also compared the assignment of the signals of six siloles reported in Refs. 4, 5, and 10 (see Table 1). The inclusion of additional points into the correlation equations (1)—(4) only insignificantly impairs quality of correlations (5)—(8) ($n = 9$):

$$\delta(\alpha\text{-}C_{ipso}) = 140.32 - 1.015\cdot\Sigma\sigma^*,\ r = 0.997; \tag{5}$$

$$\delta(\beta\text{-}C_{ipso}) = 139.21 - 0.570\cdot\Sigma\sigma^*,\ r = 0.983; \tag{6}$$

$$\delta(\alpha\text{-}C_p) = 125.59 + 0.496\cdot\Sigma\sigma^*,\ r = 0.967; \tag{7}$$

$$\delta(\beta\text{-}C_p) = 125.65 + 0.330\cdot\Sigma\sigma^*,\ r = 0.982. \tag{8}$$

For siloles, the chemical shift of the resonance of β-C atoms varies irregularly in the narrow range 156.2±2.3 ppm on going from electron-acceptor (Cl, Cl) to electron-donor ($SiMe_3$, $SiMe_3$) substituents. For germoles, this range is 151.9±2.0 ppm.[2] The signals of other quaternary (α-C, α-$C_{ipso}$, and β-$C_{ipso}$) carbon atoms of siloles are shifted to lower field as the electron-donor properties of substituents are strengthened. It should be noted that the range of variations of the chemical shift of the β-$C_{ipso}$ atom (from 136.67 to 139.77 ppm) lies within the range characteristic of the α-$C_{ipso}$ atom (from 135.37 to 141.43 ppm) and that the latter, in turn, lies within the range in which the chemical shift of the α-C atom varies (from 132.28 to 145.36 ppm). It is this circumstance that makes the assignment of the signals of quaternary carbon atoms in the $^{13}C$ NMR spectra of siloles difficult. The interval of 13.08 ppm corresponding to the change in the shielding of the α-C atoms far exceeds those of changes in the chemical shifts of α-$C_{ipso}$ and β-$C_{ipso}$ atoms (6.06 and 3.10 ppm, respectively), which reflects a gradual increase in their distance from the Si heteroatom, *viz.*, α-C—Si → α-$C_{ipso}$—C—Si → β-$C_{ipso}$—C—C—Si.

## Experimental

$^1H$ and $^{13}C$ NMR spectra were recorded on Bruker DRX-500 and Bruker AM-300 spectrometers operating at 125.759 and 70.45 MHz, respectively, using standard 2D NMR spectroscopy procedures (COLOC, COSY, and XHCORRD). Chemical shifts were calculated relative to $CHCl_3$ signal at δ 77.0 or THF signal at δ 25.2. Siloles **1a** ($R^1 = R^2 = Me$,[13] $R^1 = R^2 = H$ [14]) and dianion **2a** [5] were synthesized following the known procedures.

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