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Synthesis and reactivity of 1,1-disodio-2,3,4,5-tetraphenyl-1-silacyclopentadiene

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Abstract

1,1-Disodio-2,3,4,5-tetraphenyl-1-silacyclopentadiene (II, 1,1-disodio-TPSCp) was obtained from the reaction of 1,1-dichloro-2,3,4,5-tetraphenyl-1-silacyclopentadiene (1,1-dichloro-TPSCp) with sodium. The reaction of II with MeI and $XSiMe_2Cl$ ($X = H$, Me, Cl) gave the corresponding 1,1-dimethyl-, and 1,1-bis($XSiMe_2$)-TPSCp's, respectively. In contrast, the reaction with Me_3ECl ($E = C$, Sn) gave bis(1-Me_3E-2,3,4,5-tetraphenyl-1-silacyclopentadienyl).

Introduction

A large number of reports about the synthesis and reactivity of 1,1-diorgano-2,3,4,5-tetraphenyl-1-silacyclopentadiene have appeared [1–7], but reports about the 1-halo substituted TPSCp * [8–11] and the corresponding 1-silacyclopentadienide anion are scarce, probably because they are difficult to synthesize. It was our goal to improve the synthetic procedure of 1-halo substituted TPSCp and to obtain the corresponding anion for further elucidation of the chemical behaviour.

Results and discussion

Leavitt et al. [1] reported that the synthesis of 1,1-dichloro-TPSCp was successful only when 1,4-dilithio-tetraphenylbutadiene in THF was carefully added to an organotrihalosilane or to tetrachlorosilane followed by reflux for three days, while 1,1-dimethyl-TPSCp was prepared by adding Me_2SiCl_2 to 1,4-dilithio-tetra-

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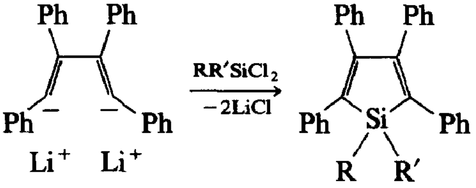
* 2,3,4,5-Tetraphenyl-1-silacyclopentadiene

phenybutadiene in THF. This seems to be very unusual because 1,4-dilithio-tetraphenylbutadiene is insoluble in diethyl ether but soluble in THF.

We prepared 1,1-dichloro-TPSCp (I) [12] in a short time simply by adding tetrachlorosilane to a suspension of 1,4-dilithio-tetraphenylbutadiene in diethyl ether. This reaction was also successful with $RR'SiCl_2$.



(1)

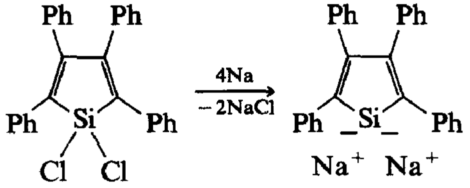
$R = R' = Cl$ (I), $R = Me/R' = Cl$, $R = Ph/R' = Cl$, $R = R' = Me$

It is generally accepted [13–15] that the silyl anion is obtained from the reaction of an organohalosilane or organodisilane with alkali metal.

$$R_3SiCl + 2M \longrightarrow R_3SiM + MCl \tag{2a}$$

$$R_3Si{-}SiR_3 + 2M \longrightarrow 2R_3SiM \tag{2b}$$

By analogy to reaction 2a, the solid 1,1-disodio-TPSCp (II) can be successfully isolated from the reaction of 1,1-dichloro-TPSCp (I) if more than four equivalents of sodium are used.



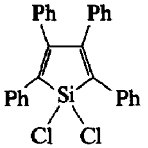
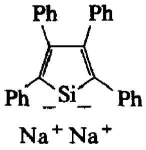
(I) (II)

(3)

The dianion II that results is reddish-brown, stable under nitrogen, but ignites spontaneously in air. The carbon-13 chemical shifts of II differ little from those the

Table 1

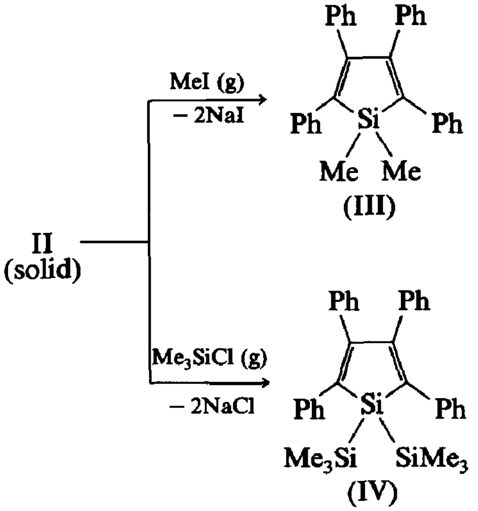
^{13}C NMR chemical shifts for 1,1-dichloro-TPSCp (I) and 1,1-disodio-TPSCp (II).

Carbon atom				
C2,5	136.75		130.92	
C3,4	154.80		153.74	
	C2-Ph	C3-Ph	C2-Ph	C3-Ph
C1	132.39	135.93	146.71	151.29
C2,6	129.29	129.53	128.48	133.16
C3,5	127.83	128.23	126.55	126.72
C4	127.13	127.37	118.25	121.42

starting compound 1,1-dichloro-TPSCp (I). We suggest therefore, that the butadiene moiety of II remains and its negative charges are located mainly on the silicon atom (Table 1).

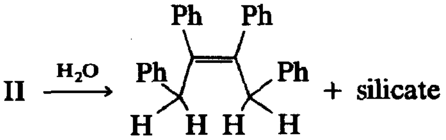
The carbons C2,5, C3,4, C2–Ph–Cl, and C3–Ph–C1 can be distinguished from C2–Ph–C2,3,4 and C3–Ph–C2,3,4 by $^{13}C-^{1}H$ correlation and from their DEPT NMR spectra. The carbons of C2–Ph–C4 and C3–Ph–C4 can be distinguished from C2–Ph–C2,3 and C3–Ph–C2,3 carbons by their relative intensities.

Further chemical evidence for II is obtained from its reaction with methyl iodide and with trimethylchlorosilane, which gives the expected products 1,1-dimethyl-TPSCp (III) and 1,1-bis(trimethylsilyl)-TPSCP (IV).



(4)

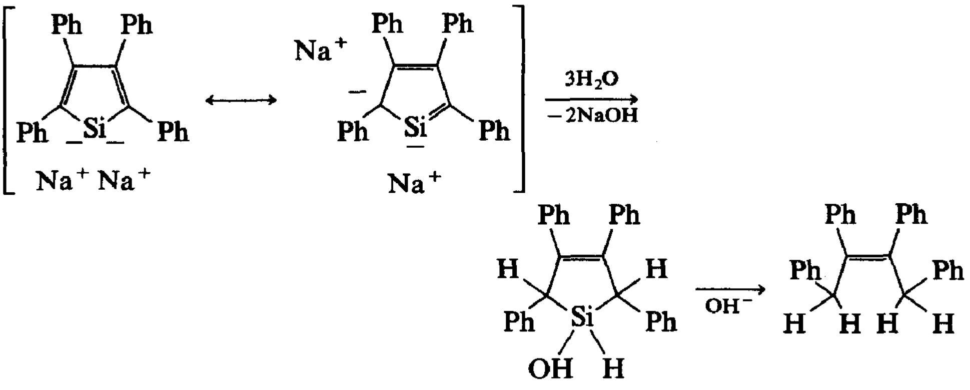
Quenching the dianion (II) with H_2O gives 1,2,3,4-tetraphenyl-2-butene (V) and silicate, whereas Curtis [9] reported that quenching of 1-methyl-1-chloro-TPSCp with H_2O in a strong alkaline medium gave 1,2,3,4-tetraphenylbutadiene.



(V)

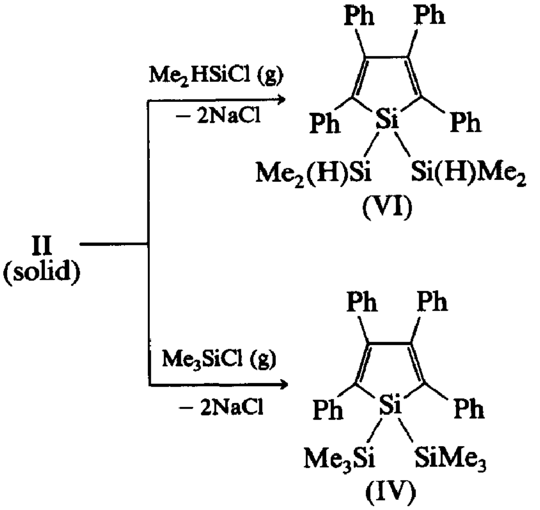
(5)

We propose the probable reaction pathway for the formation of V as shown in eq. 6.



(6)

The reaction of the dianion II has been investigated with dimethylchlorosilane ($H-SiMe_2Cl$), trimethylchlorosilane ($Me-SiMe_2Cl$) and dimethyldichlorosilane ($Cl-SiMe_2Cl$) whose steric bulk becomes larger proceeding from H through Me to Cl. In these reactions, the solid dianion II is treated under reduced pressure with the vapor of dimethylchlorosilane and trimethylchlorosilane at room temperature. As the reaction proceeds, the color of the solid changes from reddish-brown to yellow. The expected coupling products of 1,1-bis(dimethylsilyl)-TPSCp (VI) and 1,1-bis(trimethylsilyl)TPSCp (IV) are obtained, respectively.

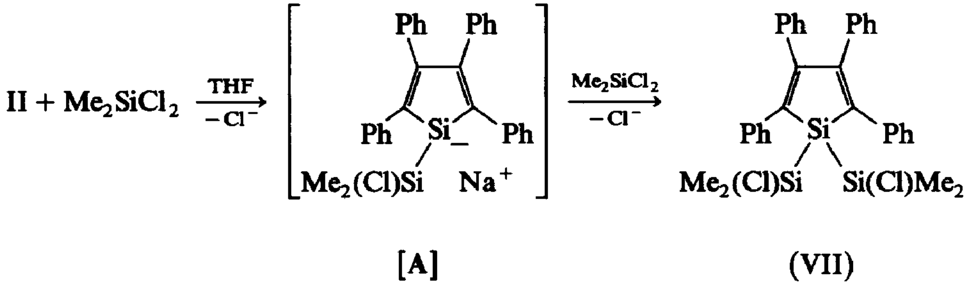


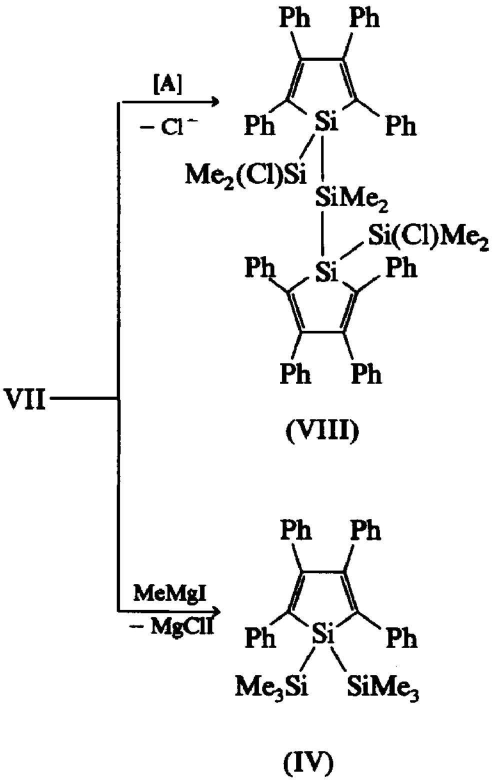
(7)

Surprisingly, the reaction of dianion II with dimethyldichlorosilane has a somewhat different outcome. Two reaction products were isolated: a very unstable 1,1-bis(dimethylchlorosilyl)TPSCp (VII) and a stable bis(1-dimethylchlorosilyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)dimethylsilane (VIII). VII decomposes in air immediately. The reaction of VII with the methyl-Grignard gives the expected 1,1-bis(trimethylsilyl)TPSCp (IV). VIII probably is results from the reaction of VII with [A], which is formed from the coupling reaction of II with one equivalent of dimethyldichlorosilane. The reaction pathways are shown schematically in eq. 8.

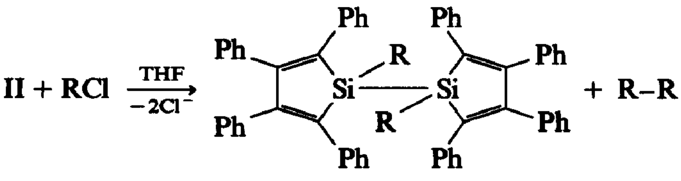
The reactions of dianion II with Me_3ECl, where E is C, Si and Sn have also been investigated. The reaction of dianion II with trimethylchlorosilane gives 1,1-bis(trimethylsilyl)TPSCp (IV), as shown in eq. 4. The solid dianion II does not react with the vapor of tert-butyl chloride. There is no solid-gas reaction of the dianion II with trimethylstannyl chloride because they are both solid. However, when the dianion II was treated with tert-butyl chloride and trimethylstannyl chloride in THF solution, bis(1-tert-butyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl) (IX) and bis(1-trimethylstannyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl (X) are obtained, respectively.

Surprisingly, it takes more than 12 h before the reaction mixture becomes yellow. It is probable that a substitution reaction takes place instead of the usual coupling reaction. We suggest, therefore, that when 1,1-bis(tert-butyl)- or 1,1-bis(trimethylstannyl)-TPSCp is formed in part, an immediate substitution reaction with 1-sodio-1-tert-butyl- or 1-sodio-1-trimethylstannyl-TPSCp takes place to give IX or X, respectively, as depicted in Scheme 1.





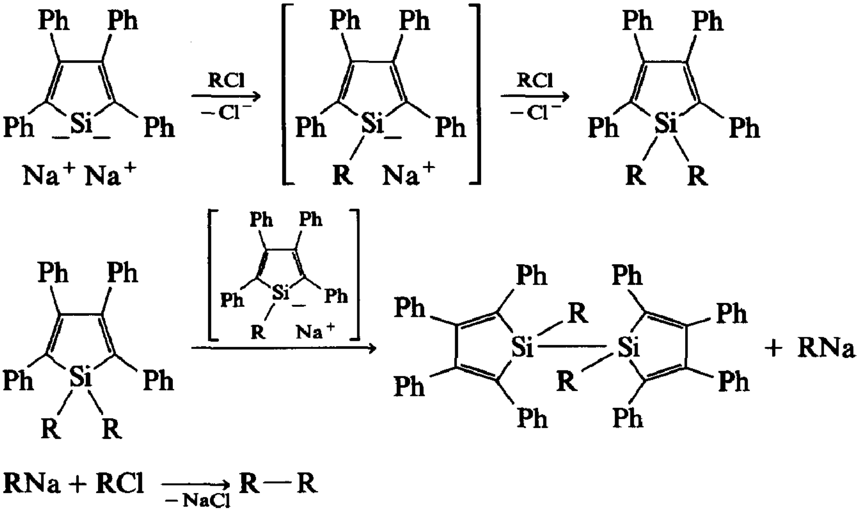
(8)



(9)

R = t-Bu (IX)

R = Me_3Sn (X)



Scheme 1

Experimental

The NMR spectra were recorded with a Bruker WP 80 SY, 80 MHz FT-NMR, Bruker AM 200, 200MHz superconductor NMR, mass-spectra with a JEOL gas chromatograph and a DMX 300 mass spectrometer, IR as KBr pellets with a Shimadzu IR-440, and melting points on Wagner & Münz Co., capillary type instruments. Elemental analyses were performed by Yanaco elemental analyzer at the Analytic Center of the College of Engineering, Seoul National University.

1,1-Dichloro-TPSCp (I)

Tetrachlorosilane (12 ml, 105 mmol) at 77 K was added to a suspension of 1,4-dilithio-tetraphenylbutadiene in 120 ml of diethyl ether, which had been obtained from 10.7 g (60 mmol) of diphenylacetylene and 0.5 g (71 mg atom) of lithium. The reaction mixture was allowed to warm to room temperature under vigorous stirring for 3 h. The greenish-yellow solution was separated from the precipitate by decantation. The residue was extracted twice with 100 ml of diethyl ether. The solution thus obtained was concentrated to a half of its volume, and was then kept at −20 °C for 24 h. Greenish-yellow crystals of 1,1-dichloro-TPSCp (I) were obtained. Yield: 10.7 g (70%). m.p. 196 °C (lit. [11] 197 °C). Anal. Found: C 73.07, H 4.44. $C_{28}H_{20}Cl_2Si$ calcd.: C 73.84, H 4.42%. MS: *m/e* 456 (M^+). ^{13}C NMR ($CDCl_3$, ppm): 154.80(C3,4), 136.75(C2,5), 135.93(C3–Ph–C1), 132.39(C2–Ph–C1), 129.53, 128.23(C3–Ph–C2,3,5,6), 129.29, 127.83 (C2–Ph–C2,3,5,6), 127.37(C3–Ph–C4), 127.13 (C2–Ph–C4). IR (cm^{-1}): ν(Si–Cl) 535, 570.

1,1-Disodio-TPSCp (II)

After 0.6 g (26 mg atom) of sodium had been added under nitrogen to a dioxane solution (30 ml) of 2.28 g (5 mmol) of 1,1-dichloro-TPSCp (I), the reaction mixture was refluxed with stirring during 2 h. The greenish-yellow color of the solution began to change to deep violet and at the same time a solid precipitated. Reflux was continued with stirring for an additional 5 h.

After filtration the residue was extracted with THF. The extract was condensed to a half of its volume and then allowed to stand several days at room temperature. The solid thus obtained was separated by decantation and dried in high vacuum. A reddish-brown solid was isolated. This product was stable under nitrogen but ignites spontaneously in air. Yield: 1.63 g (80%). ^{1}H NMR (THF-d$_8$, reference; dioxane 3.70 ppm), 6.40–7.0 (brd.m,Ph). ^{13}C NMR (THF-d_8, reference; solvent 67.40 ppm), 153.74 (C3,4), 130.92 (C2,5), 151.29 (C3–Ph–C1), 146.71 (C2–Ph–C1), 133.16, 126.72 (C3–Ph–C2,3,5,6), 128.48, 126.55 (C2–Ph–C2,3,5,6), 121.42 (C3–Ph–C4), 118.25 (C2–Ph–C4).

1,1-Dimethyl-TPSCp (III)

Solid II (1.81 g, 4.2 mmol) and the methyl iodide (0.6 ml), both under nitrogen, were placed in separate flasks connected to a vacuum line. Methyl iodide was frozen with liquid nitrogen. After evacuation of this reaction system in high vacuum, the reaction temperature was raised up to room temperature. Then solid II was exposed to methyl iodide vapor for 2 h. The reddish brown color changed to yellow. After addition of 50 ml of pentane to this reaction mixture, the insoluble NaI was removed by decantation. The pentane solution was kept at −20 °C for one day to give the greenish yellow crystals of 1,1-dimethyl-TPSCp (III). Yield: 1.63 g (93%, based on II). m.p. 181 °C (lit. [17] 181–183 °C). MS: m/e 414 (M^+), 399 ($M^+ -$ Me). ^{1}H NMR (CDCl$_3$, ppm): 0.47 (s,6H, Me$_2$Si), 6.7–7.3 (brd.m,20H,Ph). ^{13}C NMR (CDCl$_3$, ppm): −3.92 (Me$_2$Si), 154.01 (C3,4), 141.89 (C2,5), 139.91 (C3–Ph–C1), 138.87 (C2–Ph–C1), 130.01, 127.92 (C3–Ph–C2,3,5,6), 128.83, 127.83 (C2–Ph–C2,3,5,6), 126.18 (C3–Ph–C4), 125.52 (C2–Ph–C4). IR (cm^{-1}): δ(Si–Me) 1240.

1,1-Bis(trimethylsilyl)-TPSCp (IV)

The reaction of the solid II (2.06 g, 4.8 mmol) with trimethylchlorosilane (1.5 ml) was carried out as described for III, the color change and further work-up were also as described for III. Greenish-yellow crystals of 1,1-bis(trimethylsilyl)-TPSCp (IV) were obtained quantitatively. Yield: 2.41 g (95%, based on II). m.p. 99–100 °C. Anal. Found: C 76.89, H 7.23. $C_{34}H_{38}Si_3$, calcd.: C 76.92 H 7.21%. MS: m/e 530 (M^+). ^{1}H NMR(CDCl$_3$.ppm): 0.1 (s,18H,Me$_2$Si), 6.7–7.2 (brd.m,20H,Ph). ^{13}C NMR (CDCl$_3$, ppm): −0.36(Me$_2$Si), 154.67 (C3,4), 145.36 (C2,5), 141.43 (C3–Ph–C1), 139.77 (C2–Ph–C1), 130.52, 127.68 (C3–Ph–C2,3,5,6), 129.60, 127.23 (C2–Ph–C2,3,5,6), 125.82 (C3–Ph–C4), 125.16 (C2–Ph–C4). IR (cm^{-1}): δ(Si–Me) 1245(vs).

1,2,3,4-Tetraphenyl-2-butene (V)

The reaction of solid II (1.28 g, 3.0 mmol) with water vapor was carried out for 30 min as described for III. The reddish-brown color changed to pale yellow immediately. After 30 ml of diethyl ether had been added, the solution was filtered and the filtrate was kept at −20 °C for 24 h. Colorless crystals of 1,2,3,4-tetraphenyl-2-butene (V) were obtained. Yield: 0.76 g (71%, based on II). m.p. 136–138 °C. Anal. Found: C 93.26, H 6.42. $C_{28}H_{24}$ calcd: C 93.29, H 6.66%. MS: m/e 360 (M^+). ^{1}H NMR (CDCl$_3$, ppm): 4.02 (s,4H,–CH$_2$), 6.95–7.19 (brd.s,20H,Ph). ^{13}C NMR (CDCl$_3$, ppm): 40.71 (CH$_2$), 142.87 (C=C), 139.51, 138.12 129.89, 128.56, 128.34, 127.47, 125.98, 125.89 (Ph). The residue was colorless, insoluble in polar solvents such as water and in nonpolar solvents such as ether and THF, and did not melt above 360 °C.

1,1-Bis(dimethylsilyl)-TPSCp (VI)

The reaction of solid II (0.53 g, 1.1 mmol) with dimethylchlorosilane (0.5 ml) was carried out as described for III. The reddish-brown color of II changed to yellow. After the excess vapor of the dimethylchlorosilane was removed in vacuum, 30 ml of n-hexane was added to the reaction mixture. Then the procedure for product III was resumed. Greenish yellow crystals of 1,1-bis(dimethylsilyl)-TPSCp (VI) were obtained. Yield: 0.43 g (95%, based on II). m.p. 132–134 °C. Anal. Found: C 76.02, H 6.68. $C_{32}H_{34}Si_3$ calcd.: C 76.43, H 6.81%. MS: *m/e* 502 (M^+). ^{1}H NMR ($CDCl_3$, ppm): 0.1 (d, J 4.4 Hz,12H,Me_2Si), 4.2(sept,J 4.4 Hz,2H, H–Si), 6.7–7.2 (brd.m,20H,Ph). ^{13}C NMR($CDCl_3$. ppm), −5.73(Me_2Si), 154.89 (C3,4), 143.92 (C2,5), 140.58 (C3–Ph–C1), 139.53 (C2–Ph–C1), 130.36, 127.83 (C3–Ph–C2,3,5,6), 129.44, 127.39 (C2–Ph–C2,3,5,6), 126.05 (C3–Ph–C4), 125.44 (C2–Ph–C4). IR(cm^{-1}): ν(Si–H) 2110, δ(Si–Me) 1240.

1,1-Bis(dimethylchlorosilyl)-TPSCp (VII) and bis(1-dimethylchlorosilyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)dimethylsilane (VIII)

When the reaction mixture of solid II (1.76 g, 4.1 mmol) and excess of dimethyldichlorosilane in THF was stirred for 12 h, the reddish-brown color of the solution changed slowly over red to yellow. After the unchanged dimethyldichlorosilane and the solvent (THF) had been removed under reduced pressure, 30 ml of diethyl ether was added and the insoluble NaCl was removed by decantation. The solution yielded two reaction products; one soluble in pentane and the other insoluble in pentane but soluble in diethyl ether. The pale yellow crystals of 1,1-bis(dimethylchlorosilyl)-TPSCp (VII) and the pale yellow crystals of bis(1-dimethylchlorosilyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)dimethylsilane (VIII) were crystallized from pentane and diethyl ether, respectively, at −20 °C. The product (VII) decompose immediately in air, whereas the product (VIII) was stable.

When VII was treated with methyl-Grignard in diethyl ether, the expected 1,1-bis(trimethylsilyl)-TPSCp (IV) was obtained.

1,1-Bis(dimethylchlorosilyl)-TPSCp(VII). Yield: 1.40 g (60%, based on II). Anal. Found: C 66.24, H 5.93. $C_{32}H_{32}Cl_2Si_3$ calcd.: C 67.22, H 5.64%. ^{1}H NMR ($CDCl_3$, ppm): 0.42 (s,12H,Me_2Si), 6.7–7.2(brd.m,20H,Ph).

Bis(1-dimethylchlorosilyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)dimethylsilane (VIII). Yield: 0.75 g (30%, based on II). m.p. 244–250 °C. Anal. Found: C 72.90, H 6.15. $C_{62}H_{58}Cl_2Si_5$ calcd.: C 73.41, H 5.76%. MS: *m/e* 1014 (M^+), 921 ($M^+ - Me_2SiCl$). ^{1}H NMR($CDCl_3$.ppm): 0.24 (s,18H,Me_2Si), 6.8–7.2 (brd.m,40H,Ph). ^{1}H NMR (C_6D_6, ppm): 0.34 (s,12H,Me_2SiCl), 0.54 (s,6H,Si–Me_2Si–Si), 6.8–7.4 (brd.m,40H,Ph). ^{13}C NMR($CDCl_3$, ppm): −1.57 (Si-SiMe_2-Si), 3.21 (Me_2SiCl), 156.03 (C3,4), 142.34 (C2,5), 139.68 (C3–Ph–C1), 139.25 (C2–Ph–C1), 130.40, 128.00 (C3–Ph–C2,3,5,6,), 130.25, 127.47 (C2–Ph–C2,3,5,6), 126.36 (C3–Ph–C4), 125.87 (C2–Ph–C4). IR (cm^{-1}): δ(Si–Me) 1250, 1260.

Bis(1-tert-butyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl) (IX)

A mixture of solid II (2.15 g, 5.0 mmol) and tert-butyl chloride (1.36 ml, 12.5 mmol) in 70ml of THF was stirred at room temperature for one day. The reddish-brown color of the solution changed very slowly to a brownish-yellow. The unchanged tert-butyl chloride and the solvent (THF) were removed under reduced pressure, and 50 ml of diethyl ether was added to the reaction products. Then the procedure described for product III was followed. Greenish yellow crystals of bis(1-tert-butyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)(IX) were obtained. Yield: 1.88 g (85%, based on II). m.p. 296–307 °C. Anal. Found: C, 87.52, H 6.84. $C_{64}H_{58}Si_2$ calcd.: C 87.02, H 6.62%. MS: m/e 882 (M^+), ^{1}H NMR ($CDCl_3$, ppm): 0.84 (s,18H,Me_3), 6.7–7.1 (brd.m,40H,Ph). ^{13}C NMR ($CDCl_3$, ppm): 21.96 (t-C), 29.58 (Me_3), 156.96 (C3,4), 143.93 (C2,5), 141.38 (C3–Ph–Cl), 139.41 (C2–Ph–C1), 130.59, 127.53 (C3–Ph–C2,3,5,6), 130.43, 127.19 (C2–Ph–C2,3,5,6), 126.01 (C3–Ph–C4), 125.43 (C2–Ph–C4). The 2,2,3,3-tetramethylbutane was identified from its ^{1}H NMR signal at 0.88 ppm in $CDCl_3$.

Bis(1-trimethylstannyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl) (X)

A mixture of solid II (2.15 g, 5.0 mmol) and trimethylstannyl chloride (1.49 g, 12.5 mmol) in 70 ml of THF was stirred at room temperature for 12 h. The reddish-brown color of the solution changed to yellow. The solvent (THF) was evaporated off under reduced pressure and the residue was washed with pentane (15 ml) followed by diethyl ether (50 ml). Then the procedure as described for product III was followed. Greenish yellow needle-like crystals of bis(1-trimethylstannyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl) (X) were obtained. Yield: 2.33 g, (85%, based on II). m.p. 268–273° C. Anal. Found: C 67.99, H 5.92, $C_{62}H_{58}Si_2Sn_2$ calcd.: C 67.90, H 5.33%. MS: m/e 933 ($M^+ - SnMe_3$, Scanning was available upto $m/e = 1,000$). ^{1}H NMR ($CDCl_3$, ppm): -0.20 (s,18H,Me_3Sn), 6.7–7.1 (brd.m,40H,Ph). ^{13}C NMR ($CDCl_3$, ppm): -10.06 (Me_3Sn), 153.95 (C3,4), 145.77 (C2,5), 139.80 (C3–Ph–C1), 139.60 (C2–Ph–C1), 130.43, 127.95 (C3–Ph–C2,3,5,6), 129.78, 127.49 (C2–Ph–C2,3,5,6), 126,14 (C3–Ph–C4), 125.69 (C2–Ph–C4). IR (cm^{-1}): δ(Sn–Me) 765. Hexamethyldistannane was identified from its ^{1}H NMR signal at 0.21 ppm($CDCl_3$).

Acknowledgment

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