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**THE PREPARATION, CHARACTERIZATION AND REACTIVITY OF THE
 CYCLOMETALLOSILANE, CYCLO-1,1-DI- h^5 -CYCLOPENTADIENYL-
 TITANA-2,2,3,3,4,4,5,5-OCTAPHENYLPENTASILANE,
 (h^5 -C₅H₅)₂TiSi(C₆H₅)₂[Si(C₆H₅)₂]₂Si(C₆H₅)₂ ***

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Summary

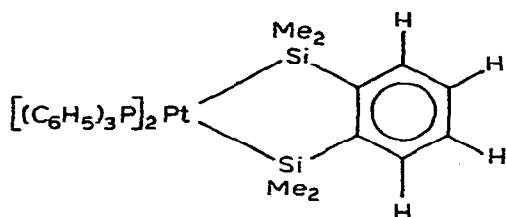
Titanium has been incorporated into a catenated silicon ring by means of the salt elimination reaction of dichlorodi- h^5 -cyclopentadienyltitanium(IV), (I), with 1,4-dilithiooctaphenyltetrasilane, Li₂Si₄(C₆H₅)₈, to yield the title compound (II). II was characterized as a cyclometallopolysilane by means of elemental analyses, base catalyzed hydrolyses, molecular weight determination, infrared and ¹H NMR spectroscopy. Electronic spectral data and electrochemical data are also discussed and support the formulation of II as a disubstituted (h^5 -C₅H₅)₂Ti^{IV} derivative. The reactivity of II, with CHCl₃, is described in terms of a radical decomposition pathway.

Introduction

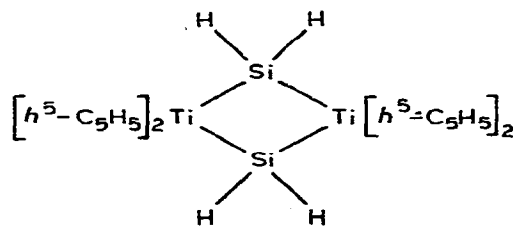
Molecular compounds containing a transition metal–silicon bond have been known since 1956 [2] and have been the subject of a number of reviews [3–6]. Subsequently several metallo-cyclic systems have been reported with the ring atoms including silicon directly bonded to the transition metal: e.g. (CO)₄-M̄SiMe₂(CH₂)₂SiMe₂, where M = Fe, Ru, Os, Cp and Me = CH₃ [7]. In a related fashion species of the type M̄SiMe₂OSiMe₂ and M̄SiMe₂CH₂SiMe₂, where M = Pd, Ir, Pt and Rh, have been prepared [8], as well as a metallocycle containing an aromatic moiety (structure A) [9].

* Presented at the 11th Central Regional Meeting of the American Chemical Society, May 7–9, 1979, Columbus, Ohio [1a].

** Completed in partial fulfillment of the Ph. D. degree [1b].



(A)



(B)

Several examples of compounds containing a transition metal to catenated silicon bond are known: $[(CO)_9Co_3Si]_2$ [10], $[h^5-C_5H_5](CO)_2Fe-SiMe_2SiMe_3$ [11], $(Me_3Si)_3SiMn(CO)_5$ [12], and the corresponding Re [13] and Fe [14] derivatives. The first example of incorporation of a transition metal into a polysilane ring was recently reported $[(C_6H_5)_3P]_2PtSi(C_6H_5)_2[Si(C_6H_5)_2]_2Si(C_6H_5)_2$ [15].

Few well documented examples of early first row transition metals bonded to silicon are known with the notable exceptions: $Ti[Si(C_6H_5)_3]_4$ [16], $[h^5-(C_5H_5)_2Ti[Si(C_6H_5)_2]_2$ [16] and the cyclic species B [17].

An extremely interesting property of cyclopolysilanes is their ability to form delocalized radical anions, e.g. $Si_5(CH_3)_{10}$ [18], $Si_4(t-Bu)_4(CH_3)_4$ [19] and $Si_4-(C_6H_5)_8$ and $Si_5(C_6H_5)_{10}$ [20]. One of the objects of this current study was the incorporation of titanium(IV) into a polysilane ring and subsequent study of its chemical reactivity including electrochemical and chemical reductions.

Results and discussion

Synthesis and characterization of cyclo-1,1-di- h^5 -cyclopentadienyltitana-2,2,3,3,4,4,5,5-octaphenylpentasilane, $(h^5-C_5H_5)_2TiSi(C_6H_5)_2[Si(C_6H_5)_2]_2Si(C_6H_5)_2$, II. Addition of a solution of 1,4-dilithiooctaphenyltetrasilane to a solution of I yields II, LiCl and a small amount of the cyclic pentamer III. The formation of III is most likely the result of oligimerization of unreacted α,ω -dilithiopentasilane which cyclizes to produce III in a manner similar to that postulated for the formation of $Si_5(C_6H_5)_{10}$ from $Si_4(C_6H_4)_8$ on treatment of the latter with lithium [21].

The base catalyzed oxidative hydrolysis of polysilanes results in the formation of 1 mol H_2 /mol of Si—Si bonds [22–24]. This same reaction has also been utilized for the characterization of species containing Si—Ti bonds [16]. The oxidative hydrolysis of II is summarized by eq. 1. The qualitative rate of $(C_6H_5)_2TiSi_4(C_6H_5)_8 + 10 H_2O \rightarrow 5 H_2 + (C_5H_5)_2Ti(OH)_2 + 4 (C_6H_5)_2Si(OH)_2$ (1) dihydrogen evolution, 3 H_2 /mol II during the first 45 min, followed by 2 H_2 /mol II during an additional 2 h reaction time, is consistent with initial oxidation of 3 Si—Si bonds followed by cleavage of 2 Ti—Si bonds. This apparent 2 stage hydrolysis is consistent with the relative rates of oxidative hydrolysis of polysilanes [22–24] as compared with Ti—Si systems [16]. Elemental analyses of the hydrolysis residues for Ti and Si were satisfactory and molecular weight

determinations support the formulation (II) as a monomeric cyclic species containing a TiSiSiSiSiSi backbone.

Infrared spectroscopy. The infrared spectrum of II contains absorptions at 3140 ($\nu(\text{CH})$), 1435 ($\nu(\text{C}-\text{C})$), 1028 ($\delta(\text{CH})$) and 825 cm^{-1} ($\gamma(\text{CH})$) assigned to the h^5 -cyclopentadienyl ligands of Ti. The presence of these four absorptions are characteristic of π -bonded cyclopentadienyl groups attached to Ti [25]. The remaining absorptions are characteristic of phenyl polysilanes [26–28]. A cyclic structure for II is inferred by comparison of the strong, intense $\gamma(\text{CH})$ absorptions observed for linear and cyclic phenyl silanes (Table 1). Linear silanes have a minimum of four such absorptions while the cyclosilanes exhibit only two absorptions. The metallopolysilane, II, is similar to the other cyclic compounds with only two such absorptions, 740 and 705 cm^{-1} , consistent with a cyclic structure. Furthermore, a metallocycle structurally similar to II, $(h^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{C}_6\text{H}_5)_2[\text{C}(\text{C}_6\text{H}_5)_2]_2\text{C}(\text{C}_6\text{H}_5)_2$ (IV) has been reported [29] and exhibits infrared absorptions remarkably similar to II. The structure of IV, confirmed by X-ray analysis [30], involves a cyclic geometry.

^1H NMR spectroscopy. The ^1H NMR spectrum of II, in CS_2 , consists of a multiplet whose most intense signal occurs at δ 7.06 ppm and a sharp singlet at δ 6.40 ppm in the ratio of 4.1/1, respectively. The multiplet is assigned to the phenyl protons of II while the singlet is assigned to cyclopentadienyl protons. The observed area ratio is in accord with the proposed cyclic geometry of II.

Electronic spectroscopy. The electronic spectra of I and II are reproduced in Fig. 1. I has two absorptions at 390 nm ($\log \epsilon = 3.30$) and at 520 nm ($\log \epsilon = 2.30$). II has a remarkably similar spectrum, at lower energies, with absorptions at 600 nm ($\log \epsilon = 3.30$) and 830 nm ($\log \epsilon = 2.00$). Comparison of the two spectra indicates a structural similarity about Ti for these two compounds. The spectra of $(h^5\text{-C}_5\text{H}_5)_2\text{Ti}^{\text{IV}}$ derivatives has been considered from a molecular orbital viewpoint by extended Hückel MO calculations on a series of $(h^5\text{-C}_5\text{H}_5)_2\text{TiXY}$ compounds, where $\text{X} = \text{Y} = \text{Cl, Br, I}$; $\text{X} = \text{Xl, Y} = \text{OCH}_3, \text{OC}_2\text{H}_5$, assuming local C_{2v} symmetry [31]. For symmetrically substituted compounds two absorptions are predicted and observed. The absorption at lowest energy is assigned to the $^1\text{A}_1 \leftarrow ^1\text{B}_1$ transition while the other transition is associated with $^1\text{A}_1 \leftarrow ^1\text{B}_2$. A third transition, $^1\text{A}_1 \leftarrow ^1\text{A}_2$, of intermediate energy, is observed only for cases of asymmetric substitution. Furthermore, the calcula-

TABLE 1

INFRARED FREQUENCIES FOR CH DEFORMATION IN LINEAR AND CYCLIC PERPHENYLPOLYSILANES

Compound	Frequency (cm^{-1})
$1,4\text{-Cl}_2\text{Si}_4\text{Ph}_8$ ^a	750, 740, 738, 708, 699
$1,4\text{-H}_2\text{Si}_4\text{Ph}_8$	735, 730, 720, 694
$1,5\text{-H}_2\text{Si}_4\text{Ph}_8$	740, 732, 725, 698
Si_4Ph_8	735, 700
$\text{Si}_5\text{Ph}_{10}$	735, 699
$\text{Cp}_2\text{TiSi}_4\text{Ph}_8$	740, 705

^a Ph = C_6H_5 .

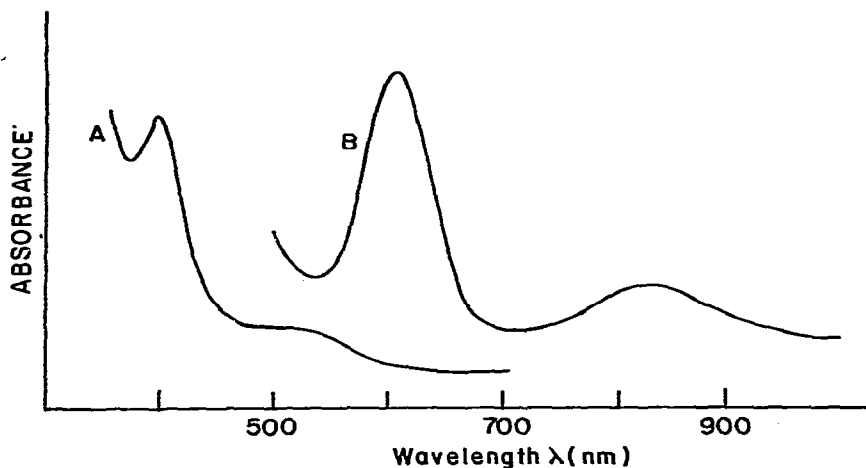


Fig. 1. Electronic spectra of $(h^5-C_5H_5)_2TiCl_2$, (A), and $(h^5-C_5H_5)_2TiSi_4(C_6H_5)_8$ (B).

tions indicate that the lowest energy transition should have an extinction coefficient one power of 10 less than the transition occurring at higher energy. This trend is observed in the spectra of $(h^5-C_5H_5)_2TiX_2$, $X = Cl, Br, I$ [31].

The spectrum of II fits this trend and the absorptions at 600 and 830 nm are assigned in accordance with the Hückel model. These transitions are orbitally allowed excitations within the d orbital system of Ti.

Electrochemical studies. Electrochemical data were obtained for II in order to evaluate the reversibility of electron transfer to the metallocycle. The formation of a stable radical anion of II would be an example of a species isorbital and isoelectronic with $Si_5(CH_3)_{10}^-$ [18] and $Si_5(C_6H_5)_{10}^-$ [20]. The cyclic voltammograms (25°C) for I, II and $Si_5(C_6H_5)_{10}$ III appear in Fig. 2 with the data summarized in Table 2. The data obtained for I is in agreement with that previously reported [32] with the first reduction at -1.07 V interpreted as a

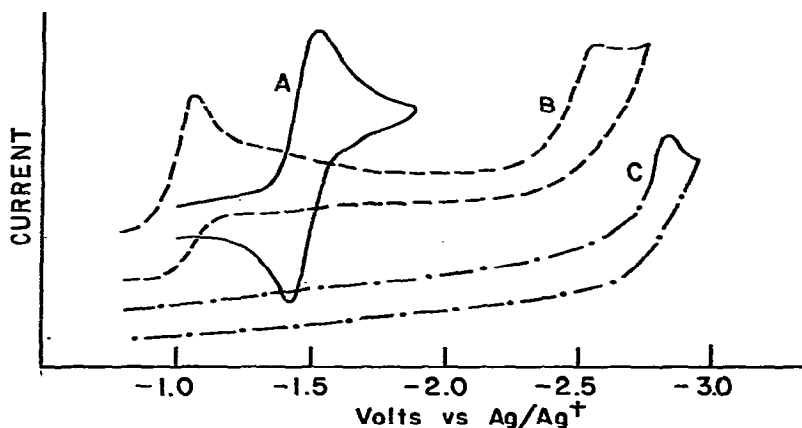


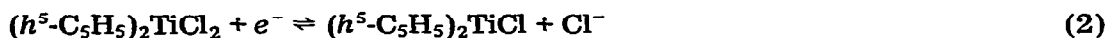
Fig. 2. Cyclic voltammetry data for $(h^5-C_5H_5)_2TiSi_4(C_6H_5)_8$ (A); $(h^5-C_5H_5)_2TiCl_2$ (B); and $Si_5(C_6H_5)_{10}$ (C).

TABLE 2

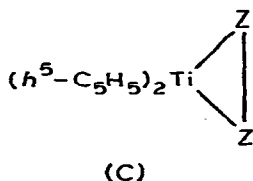
ELECTROCHEMICAL DATA FOR REDUCTION OF $\text{Si}_5(\text{C}_6\text{H}_5)_1\text{O}$, $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ AND $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{-TiSi}_4(\text{C}_6\text{H}_5)_8$

Compound	Reduction potential (volts vs. Ag/Ag^+)
$(\text{h}^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ (I)	-1.07, -2.57
$(\text{h}^5\text{-C}_5\text{H}_5)_2\text{TiSi}_4(\text{C}_6\text{H}_5)_8$ (II)	-1.54
$\text{Si}_5(\text{C}_6\text{H}_5)_{10}$ (V)	-2.85

quasi-reversible process, eq. 2, with the second irreversible reduction at



-2.57 V involving scission of the remaining TiCl bond. The result of the current electrochemical investigation of III indicates a single irreversible reduction at -2.85 V and probably corresponds to the breaking of a Si-Si bond at 25°C as the radical anion of III has been shown to be stable only below -63°C [20]. The metallocycle II undergoes quasi-reversible reduction at -1.54 V at 25°C. This reduction most probably involves the $\text{Ti}^{\text{IV}}/\text{Ti}^{\text{III}}$ couple followed by Ti-Si bond rupture and subsequent reaction of titanium (III) with solvent analogous to that of species such as C,



where $\text{Z}-\bar{\text{Z}}$ is a deprotonated diphenol or dithiol [33].

Chemical reactivity of $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{TiSi}_4(\text{C}_6\text{H}_5)_8$ with CHCl_3 . Solutions of II are unstable in CHCl_3 , in vacuo, as evidenced by a gradual color change from green to yellow. Subsequent examination of the reaction mixture results in the isolation of I, $\text{Si}_5(\text{C}_6\text{H}_5)_{10}$, C_2Cl_4 and an unknown silicon hydride.

The formation of the observed products most likely involves a radical pathway where Cl^\cdot can react with II to eventually produce I. It has been shown [34] that I forms during photolysis of $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{Ti}[\text{Ge}(\text{C}_6\text{H}_5)_2]_2$, in CHCl_3 , by what was presumed to be a radical path. In addition $\text{HMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ will afford $\text{ClMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ with CHCl_3 , in the dark, and Cl^\cdot abstraction was postulated via a thermal pathway [35]. Thus the formation of M-Cl species, upon CHCl_3 exposure, is not unusual and either photolytic or thermal pathways are available.

In this study, upon formation of I with CHCl_3 , the polysilane fraction could oligomerize and cyclize to form the observed $\text{Si}_5(\text{C}_6\text{H}_5)_{10}$ in a fashion similar to that proposed to explain the formation of $\text{Si}_5(\text{C}_6\text{H}_5)_{10}$ from silyl lithium species via a radical path [21]. If a radical path is available, then the polysilane fraction could also abstract H^\cdot from CHCl_2^\cdot (formed after abstraction of Cl^\cdot) to produce the spectroscopically observed Si-H species. This would generate CCl_2 which could dimerize to account for the formation of the observed C_2Cl_4 .

Experimental

Equipment

Small scale syntheses of air sensitive compounds were performed on a standard vacuum line whereas large scale syntheses were carried out using standard inert atmosphere techniques. All manipulations of non-volatile air sensitive compounds were performed in a dry box manufactured by Kewanee Scientific. Prepurified nitrogen was circulated through Linde 13X Molecular Sieves and Fisher Radox. Molecular weights were obtained using a Mechrolab Model 301A Vapor Pressure Osmometer. Samples were run on $\sim 0.05 M$ solutions with molecular weights calculated from a calibration curve of standard azobenzene solutions. Melting points reported are uncorrected and were obtained on a Mel-Temp apparatus manufactured by Laboratory Devices, Cambridge, Mass. Infra-red spectra were obtained on a Perkin-Elmer Model 457 spectrophotometer. Samples were run as mulls in fluorolube or Nujol using CsBr plates and calibrated against polystyrene. 1H NMR spectra were obtained at 60 MHz on a Varian EM360 spectrometer in deuterated solvents with TMS as an internal standard. Electronic spectra were obtained using a Cary 17 Recording Spectrophotometer. Cyclic voltammograms were run on solutions in dry DMF vs. Ag/Ag⁺ electrode with 0.1 M tetra-*t*-butylammoniumtetrafluoroborate as the supporting electrolyte.

Elemental analyses

Silicon and titanium were determined according to a method described in the literature [36]. Pretreatment involved hydrolysis of a weighed sample with moist piperidine to cleave all Si-Si and Ti-Si bonds. Analyses of standard Si₅(C₆H₅)₁₀, I and a mixture of the two gave satisfactory results: found: Si, 14.83, Si₅(C₆H₅)₁₀ calcd.: Si, 15.38%. I: found: Ti, 19.13; calcd.: 19.34%. A mixture of 119 mg Si₅(C₆H₅)₁₀ and 111 mg I: found: Si, 8.31; Ti, 8.70; calcd.: Si, 7.97; Ti, 9.32%.

Reagents

Dichlorobis(*h*⁵-cyclopentadienyl)titanium(IV) was obtained from Strem Chemicals, Danvers, MA and used as received. Diphenyldichlorosilane, PCR Inc. Gainesville FL, was used as received. Titanium tetrachloride, ROC/RIC was purified prior to use by repeated fractionation into a $-22^\circ C$ trap until the liquid was colorless.

Alumina, used for chromatographic separations, was obtained from Fisher Scientific, 80-200 mesh, and dried at $300^\circ C$ under dynamic vacuum prior to use. All deuterated solvents were used as received from Merck and Co. All other solvents were obtained commercially, of reagent grade, dried by standard methods and distilled, in vacuo, immediately prior to use. All other reagents used were obtained commercially, of reagent grade and used as received. Decaphenylcyclopentasilane, Si₅(C₆H₅)₁₀, and 1,4-dilithiooctaphenyltetrasilane, Li₂Si₄(C₆H₅)₈, were prepared according to literature methods [37].

Synthesis of (*h*⁵-C₅H₅)₂TiSi(C₆H₅)₂[Si(C₆H₅)₂]₂Si(C₆H₅)₂, (II). A dry THF solution of Li₂Si₄(C₆H₅)₈, generated from 2.96 g (4.07 mmol) of Si₄(C₆H₅)₈ and 0.5 g (70 mmol) Li slivers, was placed in a small addition funnel in a dry box

and added dropwise to a stirred, dry THF solution of 1.00 g (4.07 mmol) of I. During the addition a color change from red to green occurred along with the appearance of a white precipitate. After stirring for 2 h the solution was filtered in the dry box, the dark green filtrate transferred to an O-ring equipped bulb with stopcock, and attached to the vacuum line. The white solid on the frit was removed from the dry box, dissolved in deionized water, and gave a white ammonia soluble precipitate when treated with $\text{Ag}^+(\text{aq})$, confirming the presence of Cl^- (LiCl). The green filtrate was evaporated to dryness, in vacuo, and 100 ml dry cyclopentane was distilled onto the residue which was taken into the dry box and loaded onto an alumina column. The green residue was eluted with 300 ml dry cyclopentane, from which a white solid was recovered and identified as $\text{Si}_5(\text{C}_6\text{H}_5)_{10}$ by comparison of its infrared spectrum to that of an authentic sample [15]. Approximately 300 mg, 12%, $\text{Si}_5(\text{C}_6\text{H}_5)_{10}$ was recovered. The green band remaining on the column was next eluted with dry THF (~300 ml) and a dark purple band, trailed by a green band separated. The purple band was collected and set aside. The green band was removed from the column by elution with dry acetone (ca. 700 ml) and stored. A red brown material remained near the top of the column which could not be eluted. Attempts to chromatograph dilute solutions of I under identical conditions also yielded a red-brown band at the top of the column that could not be eluted. A residual yellow color was noted over the length of the column.

The dark purple solution was removed from the dry box, placed on the vacuum line, and the solvent was removed to yield an intractable dark purple oil whose infrared spectrum showed the presence of cyclopentadienyl (820 cm^{-1}), phenyl on silicon ($1420, 700\text{ cm}^{-1}$) and a band near 2100 cm^{-1} possibly due to Si—H. A ^1H NMR spectrum in THF consisted of a broad resonance near $\delta 7.0$ ppm with a small absorption near $\delta 5.2$ ppm consistent with the presence of $(\text{C}_6\text{H}_5)_2\text{Si}$ and Si—H moieties. This material, 50 mg, was not investigated further.

The green solution was evaporated, in vacuo, to yield a dark green oil. Sufficient dry acetone was added to dissolve the oil and dry petroleum ether was added until the solution became cloudy. Refrigeration overnight yields small, green crystals of II. Upon subjecting these crystals to vacuum they turned to powder. Total yield of II was 700 mg (19%).

Physical and chemical properties of II

II is a green air stable solid that decomposes above 140°C , in vacuo, to a red-brown tar. It is very soluble in aromatic solvents, ethers and hydrocarbons. Chloroform solutions are unstable as evidenced by a color change from green to yellow. II forms bis-solvates with THF, acetone, benzene and toluene.

Excess acetone was added to 51.0 mg (0.057 mmol) of dry II and stirred to yield a dark green solution. After removal of acetone at 25°C , in vacuo. A weight gain of 5 mg was noted corresponding to a 1.9 mmol acetone/mmol II. This sample was next dissolved in dry benzene, stirred and evaporated to dryness, in vacuo, at 25°C and a weight gain of 8.9 mg over the original weight (51.0 mg) was recorded, 2.1 mmol/ benzene/mmol II. Upon warming to 80°C , in vacuo, a condensable material was collected and identified as benzene by its infrared spectrum. No acetone was detected in the condensate and a weight loss

of 8.8 mg to 51.1 mg was recorded. A 54.2 mg sample of II was treated as above with dry THF and after removal of THF, in vacuo, at 25°C, a weight gain of 8.6 mg (to 62.8 mg) was recorded, 2 mmol THF/mmol II. Treatment of this latter sample with toluene as previously described resulted in a weight gain of 11.0 mg over the initial weight of II, 65.2 mg, corresponding to 2 mmol toluene/mmol II. Pyrolysis of this solvate at 180°C afforded only toluene and a red brown tar.

The average molecular weight of II, in benzene, was 880 (875, 884), calc.: 907.

The infrared spectrum of II contained absorptions at 3140w, 3070m, 3055m, 1970w, 1900w, 1830w, 1590w, 1570w, 1490m(sh), 1435vs, 1315m, 1260m, 1160w, 1090s, 1030m, 1028m, 1002m, 975w, 920w, 845w, 875m, 825s, 749vs, 705vs, 680w, 629w, 495m(sh), 490s, 400m, 345m(sh), 330m, 310w, 297vs, 285vs, 275vs and 260vs cm^{-1} .

Reactions of II

Basic hydrolysis. II, 196.6 mg (0.22 mmol) was treated with moist piperidine (19 ml piperidine: 1 ml H_2O). The resulting green solution was stirred and an initial rapid evolution of a gas was noted over a 45 minute period (~60% total) followed by a slower evolution of gas over a 2 h period (~40% total). The gas (1.09 mmol) was identified as H_2 by its quantitative combustion to H_2O at 300°C over CuO. The observed ration of H_2/II was 4.95 mmol $\text{H}_2/1$ mol II (theor 5/1). Hydrolysis of I under identical conditions yielded no H_2 .

With CHCl_3 . A dry chloroform solution of II, 81.3 mg (0.09 mmol), was stirred, in vacuo, for 80 h until the color change from green to yellow was complete. The solvent was removed, in vacuo, and the residue, a reddish colored oil was dissolved in acetone. The ^1H NMR spectrum of this solution consisted of a large singlet at δ 7.20 ppm (residual CHCl_3) a multiplet centered at δ 7.10 ppm ($\text{C}_6\text{H}_5\text{—Si}$), a singlet at δ 6.60 ppm I, and a barely discernible singlet at δ 5.00 ppm (Si—H). Addition of hexane to the acetone solution caused precipitation of an oily red solid whose infrared spectrum resembled a mixture of I and a perphenylated polysilane. The material contained infrared absorptions at: 3080m(sh), 3040m(sh), 3100m, 1960w, 1890w, 1830w, 1710w, 1590w, 1570w, 1435s, 1310m, 1260m, 1190w, 1160w, 1100s(br), 1070w, 1020m(br), 1000m, 950w(br), 900m(br), 820m, 790w, 760m, 740vs, 725vs, 700vs, 620vw, 525m, 485s, 439m and 390w cm^{-1} .

A second sample of II, 80 mg (0.09 mmol) was treated with CHCl_3 as before. The volatile species from the reaction mixture were fractionated at -35 and -196°C and identified (by infrared spectroscopy) as C_2Cl_4 at -35°C . The residue from the reaction, a reddish colored oil, was crystallized from hot benzene/hexane to yield a white solid whose infrared spectrum matched that of $\text{Si}_5\text{—}(\text{C}_6\text{H}_5)_{10}$. The yield of $\text{Si}_5(\text{C}_6\text{H}_5)_{10}$ was 50 mg (77%).

Acknowledgement

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