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Preparation of 1,8-Dichlorohexadecaphenyloctasilane *via* Reductive Coupling of 1,4-Dichlorooctaphenyltetrasilane in the Presence of Dihydridotetrakis(triphenylphosphine)ruthenium(II)

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As part of our continuing interest in cyclometallopolysilane chemistry [1, 2], we have investigated the system $(PPh_3)_4RuH_2$–$Cl_2Si_4Ph_8$–NEt_3 and have characterized the initial ruthenium product as $[(PPh_3)_3RuHCl]_2$ [3]. Herein we report the isolation and characterization of the silane product, 1,8-dichlorohexadecaphenyloctasilane, $Cl_2Si_8Ph_{16}$.

Results and Discussion

Treatment of dihydridotetrakis(triphenylphosphine)ruthenium(II), I, with 1,4-dichlorooctaphenyltetrasilane, II, in the presence of NEt_3 affords H_2, $[(PPh_3)_3RuHCl]_2$, PPh_3 and $Cl_2Si_8Ph_{16}$, III. Extraction of the reaction mixture with toluene results in the isolation of PPh_3 and III with the former subsequently separated from III by extraction with Et_2O; III was recrystallized from a minimum quantity of toluene.

It is difficult to distinguish between homologous polysilanes by analytical composition alone as is apparent from the data contained in Table I. The characterization of III as $Si_8Ph_{16}Cl_2$, as compared to the homologue Si_6, Si_7, Si_9 species, is based on the Cl analysis and the solution molecular weight determination. (III was found to be nonvolatile, prior to decomposition, in the mass spectrometer). The oxidative hydrolysis of III is ideally summarized by eqn. 1 with the observed

$$Si_8(C_6H_5)_{16}Cl_2 + 14H_2O + 2OH^- \longrightarrow 8(C_6H_5)_2Si(OH)_2 + 7H_2 + 2Cl^- \quad (1)$$

dihydrogen evolved equal to 6.9 moles per mole III. Hydridosilanes also afford H_2 on hydrolysis, however, absence of the SiH moiety is assured based on both infrared and ^1H NMR studies.

Neither the infrared nor ^1H NMR spectrum of III are particularly informative with regard to structural characterization, however, both are consistent with the absence of the SiH moiety. The infrared spectrum of III, reproduced in Fig. 1, clearly indicates the absence of νSiH at *ca.* 2100 cm^{-1}. For example, we observed this absorption at 2108 cm^{-1} (s) for 1,4-dihydridooctaphenyltetrasilane, 1,4-$H_2Si_4Ph_8$, and at 2100 cm^{-1} (m) for 1-chloro-4-hydridooctaphenyltetrasilane, $HClSi_4Ph_8$. The principal differences between the infrared spectra of 1,4-dichlorooctaphenyltetrasilane and III are in the low energy region. The former exhibits absorptions at 551, 527, 478, 441, 387, 331, and 317 cm^{-1} while III show absorptions

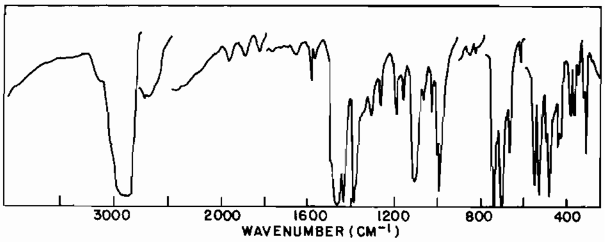

Fig. 1. Infrared Spectrum of 1,8-dichlorohexadecaphenyloctasilane, $Cl_2Si_8Ph_{16}$, in nujol.

TABLE I. Analytical Data Associated with α, ω Dichloropolyphenylpolysilanes.

Compound	m.p. °C	Mol. Wt.	%Si	%Cl	%H	%C	$\left(\frac{\text{mmol } H_2 \times 10^3}{g}\right)^a$
$Cl_2Si_5Ph_{10}$ [5]	179–180	981.95	14.3	7.23	5.09	73.38	4.07
$Cl_2Si_6Ph_{12}$ [6]	239–241	1164.26	14.50	6.09	5.15	74.27	4.29
$Cl_2Si_7Ph_{12}$^{b}	–	1346.4	14.60	5.26	5.20	74.93	4.45
$Cl_2Si_8Ph_{16}$^{b}	–	1528.6	14.70	4.46	5.24	75.43	4.58
$Si_2Si_9Ph_{18}$^{b}	–	1710.8	14.78	4.14	5.26	75.82	4.67
III	230	1529	14.94	4.32	5.47	75.37	4.49

^{a}Dihydrogen evolved as a result of oxidative cleavage of Si–Si bonds. ^{b}Unknown to date. [4, 5].

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at 547, 522, 471, 418, 412, 384, 360, and 317 cm^{-1}. The ^1H NMR spectrum is also consistent with the absence of SiH bonds in that no absorption is observed in the range 4.5–5.5 τ. For example, we observed that $H_2Si_4Ph_8$ contain the SiH related absorption at 5.14 τ.

With regard to the reaction mechanism associated with formation for III, we have succeeded in the isolation of $[(PPh_3)_3RuHCl]_2$ [3] from the reaction of $(PPh_3)_4RuH_2$ with $Cl_2Si_4Ph_8$ with the implication that ligand exchange takes place to afford *in situ* HSi_4Ph_8Cl. Furthermore, $(PPh_3)_4RuH_2$ has been shown to oxidatively add hydrido silanes to afford seven coordinate trihydrido species, *e.g.* $(PPh_3)_4RuH_3SiR_3$ [6–8]. We propose $(PPh_3)_3RuH_2$ reacts with *in situ* HSi_4Ph_8Cl to afford a cationic ruthenium complex and $Si_4Ph_8Cl^-$. The latter subsequently functions as a nucleophile toward $Cl_2Si_4Ph_8$ to afford III and Cl^-.

We shall soon report the results of additional investigations concerning the intermediates involved in the reactions of $(PPh_3)_4RuH_2$ with $Cl_2Si_4Ph_8$.

Experimental

Equipment

Standard vacuum line techniques were employed to carry out the reactions described in the study. Manipulation of non-volatile materials was performed in a modified Kewanee Scientific (Adrian, Michigan) inert atmosphere box. Oxygen was removed with Ridox Oxygen Scavenger (Fisher Scientific). Filtrations were carried out, *in vacuo*, employing an apparatus consisting of Kontes teflon stopcocks, a medium porosity glass frit and Fusion-Urry O-ring joints sealed with Viton-A O-rings. Melting points, determined with a Mel-Temp apparatus, sealed under N_2, are reported uncorrected.

Molecular weight measurements were determined with a Model 301A vapor Pressure Osmometer, Mechrolab, Incorporated. Infrared spectra were recorded with a Perkin-Elmer 457 spectrophotometer. Solids were examined as nujol and Fluorolube muls between KBr of CsI plates. Mulling agents were dried with Linde 4A molecular sieves. ^1H NMR spectra were recorded with a EM-360 spectrometer. Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elback, West Germany.

Hydrolyses were carried out employing a variation of the lit. procedure [9]. The sample was dissolved in benzene followed by treament with 1 ml H_2O and 10 ml piperidine. Dihydrogen was collected in a calibrated Toepler pump and subsequently identified by its complete combustion, over CuO at 300 °C, to CO_2 and H_2O.

Reagents

Benzene, Anal. Reagent, Mallinckrodt Chemical Works, was dried over lithium aluminum hydride and distilled from the hydride just prior to use. *Chloroform*, Certifie A.C.S., Fisher Scientific Co., was dried over lithium aluminum hydride. *Piperidine*, 99.2%, Fisher Scientific Company, was dried over Linde 4x Molecular Sieves, and distilled under vacuum just prior to use. *Tetrahydrofuran*, Certified, Fisher Scientific Company, was dried over lithium aluminum hydride. *Tetramethylsilane*, PCR, Inc., was used as received. *Toluene*, Certified A.C.S., Fisher Scientific Company, was dried over lithium aluminum hydride and distilled just prior to use. *Triethylamine*, Matheson, Coleman and Bell, was stored over lithium aluminum hydride and distilled just before use. *1,4-dichlorooctaphenyltetrasilane* was prepared by the lit. method [10, 11]. The product had a mp 182 °C, lit. 182–183 [10] and exhibits infrared absorptions at 3075 m, 3055 m, 1962 w, 1895 w, 1824 w, 1774 vw, 1660 vs(br), 1587 m, 1568 w, 1487 m, 1431 vs, 1335 vw, 1310 m, 1262 m, 1190 m, 1156 m, 1100 vs, 1065 m(sh), 1026 m, 997 s, 971 vw, 922 vw, 856 vw, 845 vw, 748 vs(sh), 687 vs, 650 vs, 617 m, 551 s, 527 s, 478 s, 441 s, 387 s, 331 s, and 317 s, cm^{-1}. *1,4-dihydridooctaphenyltetrasilane* was prepared by $LiAlH_4$ reduction of $Cl_2Si_4Ph_8$ in tetrahydrofuran and was purified by fractional recrystallization with petroleum ether from benzene, mp 160–162 °C, lit. [10] 161–162 °C. The infrared spectrum of 1,4-$H_2Si_4Ph_8$ exhibits absorptions at 3060 w, 3040 w, 2108 s, 1958 vs(b), 1885 vw(b), 1815 vw(b), 1581 w, 1480 m, 1427 s, 1300 w, 1260 w, 1189 w, 1155 w, 1115 m(sh), 1098 s, 1025 w, 996 w, 970 vw, 804 vw(sh), 790 s, 757 s, 735 s(sh), 730 s, 720 vs, 694 vs, 600 vs(sh), 510 w, 468 m, 460 m(sh), 420 w, 375 w, 345 vw, 290 m, and 280 w(sh), cm^{-1}. *1-chloro-4-hydridooctaphenyltetrasilane* was prepared as described in the lit. [12]. After recrystallization from benzene–petroleum ether, the white crystalline solid had a melting point of 161 °C, lit [12] 161–163 °C. The product exhibits infrared absorptions at 3044 m, 2100 m, 1965 w(br), 1894 w(br), 1825 w(br), 1775 vw(br), 1568 w, 1489 s, 1434 vs, 1309 m, 1264 m, 1192 m, 1158 w, 1100 s, 1078 m(sh), 1028 m, 999 m, 973 vw, 920 vw, 858 vw, 848 vw, 788 s, 766 s, 740 vs, 726 vs, 700 vs, 620 w, 568 m, 542 s, 527 s, 478 vs, 439 s, 388 s, 355 vw, 342 w, 305 s, and 278 vw, cm^{-1}. *Dihydridotetrakis(triphenylphosphine)ruthenium(II)* was prepared by the lit. method [13, 14].

Preparation of 1,8-dichlorohexadecaphenyloctasilane, $Cl_2Si_8Ph_{16}$

A solution of 0.48 g $Cl_2Si_4Ph_8$ (0.60 mmol) in 20 ml of benzene was added to a suspension of 0.70 g $(Ph_3P)_4RuH_2$ (0.61 mmol) in 25 ml of benzene and 1 ml Et_3N. The reaction is accompanied by an immediate solution color change to red and H_2 evolution, 0.29 mmol total. The reaction residue, after solvent and NEt_3 removal, was treated with toluene and filtered to afford a soluble mixture of PPh_3 and $Cl_2Si_8Ph_{16}$. Next PPh_3 was removed by washing with Et_2O and the remaining $Cl_2Si_8Ph_{16}$ recrystallized from a minimum quantity of toluene, mp 230 ℃; yield, 90%. Anal. results are contained in Table I.

III exhibits infrared absorptions at 3041 m(sh), 2035 vw(br), 1957 vw(br), 1890 vw(br), 1813 vw(br), 1650 vw(br), 1585 m, 1567 w, 1478 m(sh), 1428 s, 1307 w, 1260 w, 1181 w, 1155 w, 1115 m(sh), 1096 s(sh), 1087 s, 1027 m, 997 m, 739 vs, 698 vs, 678 s(sh), 617 w, 547 m, 522 m, 471 s, 418 m, 412 m, 384 w, 360 w, and 317 m, cm^{-1}.

Hydrolysis of III

A 27.6 mg sample of (0.00181 mmol) was dissolved in 20 ml of benzene and the solution treated with 10 ml of piperidine and 1 ml of H_2O at 25 ℃. After stirring overnight, 0.124 mmol of H_2 was collected.

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