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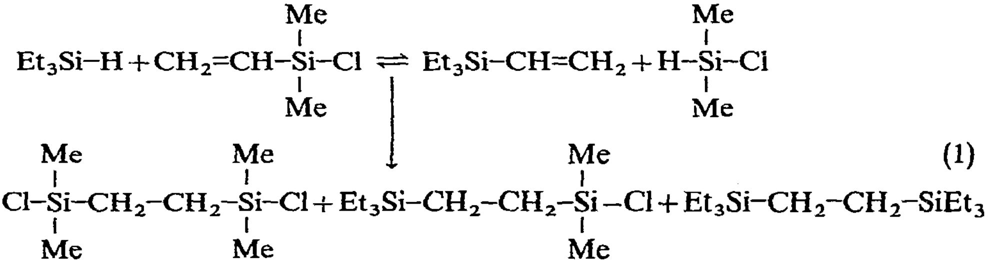
Vinyl-hydrogen ligand exchange on silicon

While the redistribution of electronegative groups attached to silicon is well documented and is of some synthetic import[1], there are scant examples of aryl or alkyl groups participating with hydrogen in ligand exchange reactions*. It has been shown that disproportionation of ethyl[2], phenyl[3], and aralkylsilanes[4] will occur at elevated temperatures and that platinum[3] and free radical sources[5] may act as catalysts. More recently two groups[6], working with derivatives of the unusually reactive silacyclobutane and 1,3-disilacyclobutane ring systems, reported examples of alkyl-hydrogen ligand exchange occurring under considerably milder conditions. In this communication we wish to describe the first example of vinyl-hydrogen ligand exchange at silicon, which occurred during the chloroplatinic acid-catalyzed hydrosilation of a vinylsilane. Some experimental observations relevant to the mechanism of this reaction are also noted.

As a potential synthesis of 1-(triethylsilyl)-2-(dimethylchlorosilyl)ethane, we chose to study the addition of triethylsilane to vinyldimethylchlorosilane catalyzed by chloroplatinic acid. The catalytic activity rapidly diminished[7] and it was necessary to add the chloroplatinic acid in portions to complete the reaction. Gas–liquid chromatography (GLC) showed the presence of four major products, which were separated by fractional distillation and identified as triethylvinylsilane (7%), 1,2-bis-(dimethylchlorosilyl)ethane (17%), 1-(triethylsilyl)-2-dimethylchlorosilyl)ethane (66%) and bis-1,2-(triethylsilyl)ethane (10%)**. All of these products may be satisfactorily explained by vinyl-hydrogen ligand exchange (eqn. 1). The extent of this exchange cannot be determined, since dimethylchlorosilane and triethylvinylsilane may react to give 1-(triethylsilyl)-2-(dimethylchlorosilyl)ethane as well as "abnormal addition products", but must be greater than 17%.



$$\mathrm{Et_3Si{-}H + CH_2{=}CH{-}SiMe_2{-}Cl \rightleftharpoons Et_3Si{-}CH{=}CH_2 + H{-}SiMe_2{-}Cl}$$
$$\downarrow$$
$$\mathrm{Cl{-}SiMe_2{-}CH_2{-}CH_2{-}SiMe_2{-}Cl + Et_3Si{-}CH_2{-}CH_2{-}SiMe_2{-}Cl + Et_3Si{-}CH_2{-}CH_2{-}SiEt_3} \qquad (1)$$

Vinyl-hydrogen ligand exchange can reduce the synthetic efficiency of the hydrosilation of vinylsilanes, and may constitute a termination process in the copolymerization of vinylsilanes and silicon hydrides[8].

When a mixture of 1-(triethylsilyl)-2-(dimethylchlorosilyl)ethane and tri-

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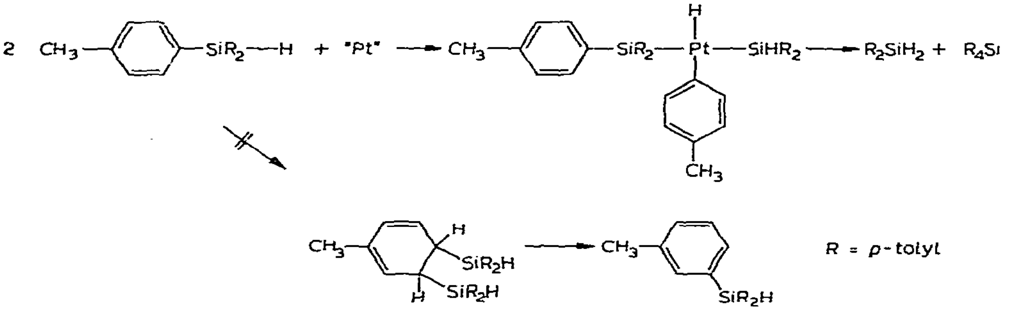
* The base and Lewis acid catalyzed disproportionation of aryl and alkylsilanes probably involves silicon alkoxides and halides respectively as intermediates, and consequently is not strictly an alkyl- or aryl-hydrogen ligand exchange.

** These figures were determined from the relative peak areas of GLC chromatograms.

ethylsilane was heated at 140° for 4 h in the presence of chloroplatinic acid, GLC indicated only unchanged starting materials were present. This would preclude the chloroplatinic acid-catalyzed dissociation of 1-(triethylsilyl)-2-(dimethylchlorosilyl)-ethane to dimethylchlorosilane and triethylvinylsilane as the mechanism of vinyl-hydrogen ligand exchange. In order to gain further insight into the mechanism of the ligand exchange of hydrogen and sp^2 hybridized carbon, the chloroplatinic acid-catalyzed disproportionation of tri-*p*-tolylsilane was examined. When tri-*p*-tolylsilane was heated at 240° for 12 h, GLC indicated the presence of di-*p*-tolylsilane (7%), tri-*p*-tolylsilane (58%) and tetra-*p*-tolylsilane (35%). After separation by distillation, NMR and infra-red analysis showed each of the three components was the *para* isomer. The NMR spectrum of tetra-*p*-tolylsilane showed an unidentified impurity absorbing at 442 cps (6% of total aromatic protons). However, the infrared spectra showed no absorption which could be attributed to *ortho*, *meta* or benzyl isomers[9]. When tri-*p*-tolylsilane was heated at 240° for 12 h, in the absence of chloroplatinic acid, no disproportionation occurred.

While not conclusive, the fact that no significant amounts of *m*-tolyl, *o*-tolyl or benzylsilanes are formed during the disproportionation of tri-*p*-tolylsilane suggests that an addition–elimination mechanism (eqn. 2) is of little consequence in this transformation. Similarly, π-bonded tolylplatinum intermediates are unlikely. Although a radical process is not ruled out by the absence of *ortho* and *meta* isomers[5], the chloroplatinic acid-catalyzed reactions of silicon hydrides are generally believed to be non-radical in character[7,10]. It appears that a σ-bonded *p*-tolylplatinum intermediate, formed by "platinum" cleavage[7] of the *p*-tolylsilicon bond, is best invoked to explain the observed results (eqn. 2). Vinyl-hydrogen ligand exchange may occur via an analogous intermediate.



(2)

EXPERIMENTAL

Gas–liquid chromatographic analyses were performed with an F and M model 300 instrument using a 6 ft. column of 5% SE 30 on Anakrome, with a helium flow rate of 75 ml/min. Infra-red spectra were obtained with a Perkin–Elmer Model 221 spectrophotometer. NMR spectra were obtained with a Varian A-60 spectrometer using tetramethylsilane as the internal standard. Melting points and boiling points are not corrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. All reactions were carried out under an atmosphere of pre-purified nitrogen.

Reagents. Triethylsilane and vinyldimethylchlorosilane were purchased from

Peninsular Chemresearch Inc. Tri-*p*-tolylsilane[11] was prepared from the reaction of *p*-tolylmagnesium bromide with trichlorosilane. 1,2-Bis(dimethylchlorosilyl)ethane[12] was prepared by addition of dimethylchlorosilane to vinyldimethylchlorosilane.

Addition of triethylsilane to vinyldimethylchlorosilane. Triethylsilane (19.547 g, 0.1681 mole) was added dropwise to vinyldimethylchlorosilane (20.467 g, 0.1691 mole) containing 45 μl of chloroplatinic acid in isopropyl alcohol (36.9 mg/ml), stirring and refluxing the mixture. The temperature of the refluxing mixture rose from 84° to 144° during the course of the addition. After the further addition of two portions of the catalyst (20 μl each), the reflux temperature rose to 164° and then to 178°. At this time, GLC indicated the virtual absence of starting materials. Fractional distillation of the reaction mixture afforded the following pure compounds: *Triethylvinylsilane*, 2.448 g, b.p. 144–145°, n_D^{20} 1.4323. The structure was confirmed by comparison of the infra-red spectrum with that of an authentic sample. Reported[13] for triethylvinylsilane, b.p. 143.2°, n_D^{20} 1.4330. *Bis-1,2-(dimethylchlorosilyl)ethane*, 5.149 g, m.p. 36.5–37.5°. Mixture m.p., infra-red and NMR spectral comparison with an authentic sample[12] confirmed the structure of the product. *1-(Triethylsilyl)-2-(dimethylchlorosilyl)ethane*, 17.752 g, b.p. 76–77° (2.5 mm) ν_{max} (in CCl_4) 1140 cm^{-1} ($Si{-}CH_2{-}CH_2{-}Si$) (Found: C, 50.44; H, 10.49; Cl, 14.78; Si, 23.74; mol.wt. in $CHCl_3$, 240. $C_{10}H_{25}ClSi_2$ calcd.: C, 50.69; H, 10.63; Cl, 14.96; Si, 23.71%, mol.wt., 236.9.) *Bis-1,2-(triethylsilyl)ethane*, 2.5829 g, b.p. 77–80° (0.58 mm), ν_{max} (in CCl_4) 1140 cm^{-1} ($Si{-}CH_2{-}CH_2{-}Si$), n_D^{20} 1.4575. (Found: C, 64.87; H, 13.27; Si, 21.56. $C_{14}H_{34}Si_2$ calcd.: C, 65.03; H, 13.25; Si, 21.72%.) Reported[14] for bis-1,2-(triethylsilyl)ethane, b.p. 265-7°, n_D^{20} 1.4582.

Attempted reaction of 1-(triethylsilyl)-2-(dimethylchlorosilyl)ethane with triethylsilane. A mixture of 1-(triethylsilyl)-2-(dimethylchlorosilyl)ethane (612 mg) and triethylsilane (524 mg), containing 10 μl of chloroplatinic acid in isopropyl alcohol (52 mg/ml) was heated at 140° for 4 h. At this time GLC analysis showed that only unchanged starting materials were present.

Disproportionation of tri-p-tolylsilane. Tri-*p*-tolylsilane (6.0313 g) and 35 μl of chloroplatinic acid in isopropanol (46 mg/ml) were heated at 120° (18.5 h) and then at 160° (24 h). At this time GLC and infra-red analysis showed no significant disproportionation. After the reaction temperature was raised to 240° for 12 h, GLC analysis showed a mixture of ditolylsilane (7%), tritolylsilane (58%) and tetratolylsilane (35%). The reaction mixture was distilled to afford *di-p-tolylsilane*, 350 mg, b.p. 77–78° (0.03 mm), n_D^{20} 1.5706, ν_{max} (in CS_2) 1120(s), 940(s), 845(s), and 800(s) cm^{-1} (Found: C, 78.89; H, 7.58. $C_{14}H_{16}Si$ calcd.: C, 79.18; H, 7.59%.); *tri-p-tolylsilane*, 1.954 g, b.p. 148–51° (0.03 mm), identical (infra-red, m.p.) with unchanged starting material. The distillation residue was crystallized from benzene to give *tetra-p-tolylsilane*, 1.121 g, m.p. 232–233.5°, ν_{max} (in CS_2) 1110, 800 cm^{-1}. (Found: C, 85.78; H, 7.24. $C_{28}H_{28}Si$ calcd.: C, 85.66; H, 7.19%.) Reported[15] for tetra-*p*-tolylsilane, m.p. 228°. The mother liquor of crystallization afforded 2.065 g of a mixture of tri- and tetra-*p*-tolylsilane, shown by NMR and infra-red analysis to contain only the *para* isomers. The NMR spectra ($CDCl_3$) of all of the fractions isolated from the disproportionation showed a singlet at 140 cps (Ar-CH_3) and an AB quartet at 428, 435.5, 448, and 456.5 cps ($Si{-}\overset{|}{\underset{|}{C}}{-}CH{=}CH{-}\overset{|}{\underset{|}{C}}{-}CH_3$). Di- and tri-*p*-tolylsilane showed singlets at 296 and 329 cps. (Si-H) respectively. In addition to the anticipated absorption, both crystallized and uncrystallized samples of tetra-*p*-tolylsilane showed an unassigned singlet at 442 cps. (6% of total aromatic hydrogens).

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1 K. MOEDRITZER, *Organometal. Chem. Rev.*, 1 (1966) 179.
2 G. FRITZ, *Z. Anorg. Allgem. Chem.*, 273 (1953) 275.
3 H. GILMAN AND D. H. MILES, *J. Org. Chem.*, 23 (1958) 326.
4 H. GILMAN, R. A. TOMASI AND D. WITTENBERG, *J. Org. Chem.*, 24 (1959) 821.
5 L. E. NELSON, N. C. ANGELOTTI AND D. R. WEYENBERG, *J. Am. Chem. Soc.*, 85 (1963) 2662.
6 N. S. NAMETKIN, V. M. VDOVIN AND P. L. GRINDBERG, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1964) 1133; D. R. WEYENBERG AND L. E. NELSON, *J. Org. Chem.*, 30 (1965) 2618.
7 A. J. CHALK AND J. F. HARROD, *J. Am. Chem. Soc.*, 87 (1965) 16.
8 R. K. INGHAM AND H. GILMAN, in F. G. A. STONE AND W. A. G. GRAHAM, *Inorganic Polymers*, Academic Press, New York, 1962, pp. 335–337.
9 H. A. CLARK, A. F. GORDON, W. C. YOUNG AND M. J. HUNTER, *J. Am. Chem. Soc.*, 73 (1951) 3798; M. L. JOSIEN AND J. M. LEBAS, *Bull. Soc. Chim. France*, 23 (1956) 53.
10 C. EABORN, *Organosilicon Compounds*, Butterworth, London, 1960, pp. 51–55.
11 R. A. BENKESER AND F. J. RIEL, *J. Am. Chem. Soc.*, 73 (1951) 3472.
12 W. A. PICCOLI, G. G. HABERLAND AND R. L. MERKER, *J. Am. Chem. Soc.*, 82 (1960) 1883.
13 M. KANAZASHI, *Bull. Chem. Soc. Japan*, 26 (1953) 493.
14 A. V. TOPCHIEV, N. S. NAMETKIN AND A. A. SHCHERBAKOVA, *Dokl. Akad. Nauk SSSR*, 86 (1952) 559.
15 H. GILMAN AND G. N. R. SMART, *J. Org. Chem.*, 15 (1950) 720.

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Dicyclopentadienyltitanium(IV) halide species in acetone solutions

In a paper on the kinetics of dicyclopentadienyltitanium(IV) complexes Langford and Aplington[1] elude a proposal by Jensen[2,3] that such compounds are dimerized in acetone solution. Also, objections have been raised to the introduction of more intermediates despite the local inconsistencies in the parameters from different experiments[4]. Multicomponent mixtures are liable to great freedom in interpretation[5], and a global approach[6] in handling the experimental data is needed in order to bring such freedom under reasonable control.

This note is an attempt to mediate between the crowded model of Jensen and the simplified reaction scheme of Langford and Aplington[1], in which—after deduction of the influence of the water content—a single parameter should characterize the exchange of one ligand for another. We have used Jensen's data for the LiSCN/LiCl system, see Table 1, because for these ligands we may neglect the aquation effects, which seem to be competitive in case of LiBr.