(vs), 2010 (vs), 1990 (vs), 1950 cm^{-1} (w). Also present was a band of medium intensity at 1860 cm^{-1} due to some unreacted dicobalt octacarbonyl. The specific rotation of the solution was measured at 589 mμ on a JASCO Model ORD/uv-5 instrument in a 1-mm quartz cell using the initial concentration of the starting silane to calculate the concentration in grams per 100 ml of phenylneopentylmethylsilylcobalt tetracarbonyl assuming quantitative conversion. The specific rotation calculated in this manner was [α]D $-42.8°$ (c 16, toluene). The sign of the plain dispersion curve is opposite that of the starting silane as was the case in the α-NpPhMeSi* system. No attempt was made to isolate this material, but it was used directly in expt 6 below.

6. Exchange Reaction between (−)-Phenylneopentylmethyl-silylcobalt Tetracarbonyl and Triphenylsilane. Triphenylsilane, 6.3 g, was added directly to the stirred reaction mixture from experiment F5 above and immediate hydrogen evolution occurred, presumably due to reaction of triphenylsilane with the excess dicobalt octacarbonyl in solution. The reaction mixture was then stirred under nitrogen for 24 hr, at room temperature, after which time (+)-phenylneopentylmethylsilane, [α]D $+1.6°$ (c 10, pentane), [α]D $+6.2°$ (c 10, toluene), 1.0 g (62.5% yield), was distilled directly from the reaction flask through a micro Vigreux column, bp 42° (0.15 mm), showing that complete exchange had occurred with 100% retention of configuration at the optically active silicon cen-

ter. An infrared spectrum of the recovered silane was identical with that of the pure compound.[9]

The solid triphenylsilylcobalt tetracarbonyl precipitated out of the distillation pot as the flask cooled to room temperature. The toluene was decanted from the light brown solid and the material was washed with heptane. It was then taken up in benzene and crystallized at 8° yielding 1.10 g of a white, crystalline solid. The infrared spectrum of this compound was in complete agreement with that reported in the literature[9] for triphenylsilylcobalt tetracarbonyl; however, the melting point, 168–170°, was sharper and much higher than that reported by Chalk and Harrod, 135–140°.[9] The melting behavior was characteristic[9] of silylcobalt carbonyls, i.e., decomposition starting at 168° with gas evolution turning green at 175°, and finally blackening at high temperatures. As a further proof of structure, 0.40 g of the triphenylsilylcobalt tetracarbonyl was dissolved in 2.0 ml of benzene and 0.30 ml of methanol was added. The solution darkened, a gas was evolved, and a greenish solid precipitated. The mixture was filtered and 10 ml of pentane added to the light yellow filtrate. The solution was put in the freezer at −20° and an initial crop of 70 mg of triphenylsilanol, mp 155°, came out quickly. The solution was decanted into another flask and returned to the freezer. After 20 hr at −20°, 0.26 g (58% yield), of the white, crystalline triphenylsilylmethoxysilane, mp 54–56°, had fallen out of solution. An infrared spectrum of this material was completely consistent with the structure.

Stereochemistry of Asymmetric Silicon. XVI. Transition Metal Catalyzed Substitution Reactions of Optically Active Organosilicon Hydrides[1]

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Abstract: The stereochemistry of a general class of group VIII metal-catalyzed reactions of the Si–H bond has been studied. The reactions of a variety of reagents containing OH and NH functions with optically active α-NpPhMeSi*H were found to proceed with inversion of configuration at the silicon center in contrast to the non-catalytic cleavages of Si*–H with strong nucleophiles which proceed with retention. The effects of structure on reactivity as well as solvent and catalyst effects were examined. It was shown that substitution reactions were catalyzed by pure palladium metal and may best be regarded as examples of heterogeneous catalysis. A mechanistic interpretation involves initial coordination of α-NpPhMeSi*H with the reactive metal center followed by backside displacement of silicon from the metal surface with inversion.

The metals of group VIII and some of their salts are known to catalyze the cleavage of the silicon–hydrogen bond by a wide variety of nucleophilic reagents.[2,3] The most widely studied nucleophiles have been amines (1), alcohols (2), and carboxylic acids (3). This general

$$RNH_2 + R_3SiH \xrightarrow{M} RNHSiR_3 + H_2 \quad (1)$$

$$ROH + R_3SiH \xrightarrow{M} ROSiR_3 + H_2 \quad (2)$$

$$RCOOH + R_3SiH \xrightarrow{M} RCOOSiR_3 + H_2 \quad (3)$$

class of reactions constitutes a convenient method for the preparation of substances containing the silicon-oxygen and silicon-nitrogen bonds in high yields. Despite numerous studies which have greatly widened the

synthetic scope of these processes, little has been learned concerning the fundamental nature of the reactions.

The recent synthesis and correlation of configurations of a large number of optically active silylamines,[4,5] alkoxysilanes,[5,6] and silyl esters[6c,d,7] has made possible a systematic stereochemical study of the group VIII metal-catalyzed substitution reactions (1–3). Because of the profound effect that the metal surface may exert on the geometry of reaction, stereochemical data can be extremely useful in attempts to determine the mechanisms of heterogeneous catalysis. The mechanistic implica-

(1) (a) Support of this work by a grant from the National Science Foundation is gratefully acknowledged. (b) For the preceding paper in this series, see L. H. Sommer, et al., J. Am. Chem. Soc., **91**, 7051 (1969).

(2) L. H. Sommer and J. E. Lyons, ibid., **89**, 1521 (1967), and references cited therein.

(3) L. H. Sommer and J. D. Citron, J. Org. Chem., **32**, 2470 (1967).

(4) L. H. Sommer and J. D. Citron, J. Am. Chem. Soc., **89**, 5797 (1967).

(5) (a) A. G. Brook, et al., Can. J. Chem., **45**, 1231 (1967); (b) K. Ruhlman, et al., Z. Chem., **5**, 108 (1965).

(6) (a) L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, J. Am. Chem. Soc., **86**, 3271 (1964); (b) L. H. Sommer, C. L. Frye, and G. A. Parker, ibid., **86**, 3276 (1964); (c) L. H. Sommer, et al., ibid., **89**, 857 (1967); (d) L. H. Sommer, K. W. Michael, and W. D. Korte, ibid., **89**, 868 (1967); (e) L. H. Sommer and H. Fujimoto, ibid., **90**, 982 (1968).

(7) L. H. Sommer, G. A. Parker, and C. L. Frye, ibid., **86**, 3280 (1964).

Table I. Palladium[a] and Nickel[b] Catalyzed Substitution Reactions of (+)-R₃Si*H[c]

| | | | Pd-catalyzed reactions | | | Ni-catalyzed reactions | | |
| | | | Yield, % | [α]D[d] | Predominant stereochemistry,[e] % inv | Yield, % | [α]D[d] | Predominant stereochemistry, % inv |
Reactant	Solvent	Product						
Water	CH₂Cl₂	(−)R₃Si*OH	91	−12	81	97	−17	94
Methanol	Xylene	(−)R₅Si*OCH₂	95	−16	97	94	−16.6	99
Methanol	Pentane	(−)R₃Si*OCH₃	93	−17	100	94	−17	100
Ethanol	Pentane	(−)R₃Si*OC₂H₅	87	−11	100			
n-Butyl alcohol	Pentane	(−)R₂Si*OC₄H₉	89	−9.3	100			
Benzyl alcohol	Pentane	(−)R₃Si*OCH₂Ph	91	−15	100			
2-Phenylethanol	Pentane	(−)R₃Si*OCH₂CH₂Ph	83	−6.0	≥97			
Cyclohexanol	CH₂Cl₂	(+)R₃Si*OC₆H₁₁	89	+6.7	87	98	+7.1	90
Cyclohexanol	Xylene[f]	(+)R₃Si*OC₆H₁₁	86	+3.9	72	95	+7.9	94
Cyclohexanol	Pentane	(+)R₃Si*OC₆H₁₁	90	+8.9	99	93	+8.4	96
1-Phenylethanol	Pentane	(+)R₃Si*OCH(CH₃)Ph[g]	95	+10[g]	>94			
(−)-Menthol	CH₂Cl₂	(−)R₃Si*OMen				99	−46	>95
t-Butyl alcohol	CH₂Cl₂	(+)R₃Si*OC(CH₃)₃	88	+21	88	91	+21	88
t-Butyl alcohol	Xylene	(+)R₂Si*OC(CH₃)₃				93	+22	90
Phenol	CH₂Cl₂	(−)R₃Si*OPh	92	−2	63	97	−8.7	92
Acetic acid	CH₂Cl₂	(−)R₃Si*OOCCH₃	79	−10	79	84	−12	83
Acetic acid	Pentane	(−)R₃Si*OOCCH₃	90	−12.5	86	90	−10	79
Benzoic acid	CH₂Cl₂	(−)R₃Si*OOCPh	85	−11	80	85	−12	83
Styrene oxide	CH₂Cl₂	(−)R₃Si*OCH₂CH₂Ph	75	+6	100			

[a] 10% Pd–C; Matheson Coleman and Bell. [b] No. 28 Raney active nickel catalyst in water, Raney catalyst Division, W. R. Grace & Co., Silver Springs, Md. (water removed at reduced pressure and stored under xylene or pentane). [c] The α-NpPhMeSi*H was optically pure; in several cases the (−) enantiomer was used and the sign of the product was therefore reversed. [d] Rotation (in degrees) taken in the solvent as reported in the literature.[5-8] [e] A predominant stereochemistry of 90% inversion indicates a reaction path that is 90% invertive and 10% retentive giving a product that is 80% optically pure. [f] Reaction mixture was heated at 80° for 1.5 hr. [g] Based on a value of [α]D +9.5° for optically pure R₃Si*OPh, from unpublished results of R. Mason; (−)R₃Si*H was used in this reaction.

tions of the stereospecific cleavage of the silicon–hydrogen bond by nucleophilic reagents in the presence of group VIII metals will be the subject of the present paper.

When optically active α-naphthylphenylmethylsilane (R₃Si*H) is treated with amines, alcohols, water, phenols, or carboxylic acids (Figure 1), hydrogen is evolved
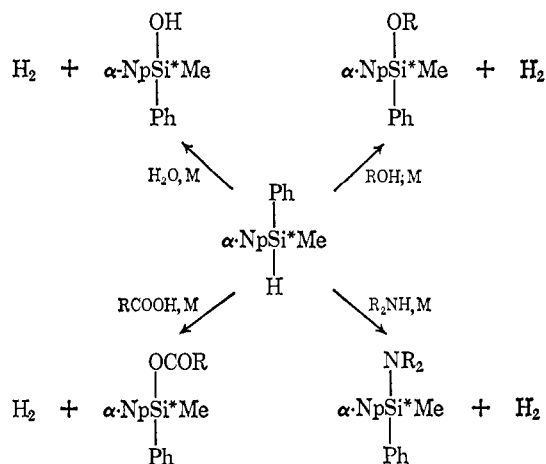

Figure 1.

and high yields of the corresponding optically active organosilicon compounds are obtained. The results of these reactions are reported in Tables I–III. In contrast to the hydrolsilation of olefins[1b,8] and Si*H–D exchange reactions[1b,9] which proceed with retention, group VIII metal-catalyzed substitution reactions of oxygen and

(8) L. H. Sommer, K. W. Michael, and H. Fujimoto, *J. Am. Chem. Soc.*, **89**, 1519 (1967).
(9) L. H. Sommer, J. E. Lyons, K. W. Michael, and H. Fujimoto, *ibid.*, **89**, 5483 (1967).

Table II. Metal-Catalyzed Methanolysis of R₃Si*H in Pentane

$$R_3Si^*H + CH_3OH \xrightarrow[C_6H_{12}]{catalyst} R_3Si^*OCH_3 + H_2$$

Catalyst	Reaction time, min	Yield, %	Predominant stereochemistry, % inv
10% Pd–C	30	93	100
Raney nickel	270	94	100
5% Rh–C[a]	120	90	58
5% Ru–C[b]	300	94	59
H₂PtCl₆·6H₂O[c]	50	91	(Racemic)
Ag (powder)	1140	94	(Racemic)
PdCl₂·2H₂O	3	93	(Racemic)
PdCl₂·2H₂O(Et₃N)[d]	390	99	98

[a] 5% Rh–C, Baker and Co., Inc. [b] 5% Ru–C, Engelhard Industries, Inc. [c] This reaction was run in methylene chloride. [d] Palladium(II) chloride to which triethylamine was added.

nitrogen nucleophiles with R_3Si^*H proceed with inversion of configuration at the silicon center.[10] The rate and stereospecificity of the reactions are dependent on the nature of the nucleophile, the organosilane, the solvent, and the catalyst system used.

Effect of the Nucleophile. The palladium and nickel catalyzed substitution reactions of R₃Si*H, Figure 1, are greatly affected by the bulk of the hydrocarbon portion of the attacking nucleophile. The order of reactivity of alcohols is in general primary > secondary > tertiary. Chain lengthening and branching in the alcohol result in lower reaction rates.[11] Carboxylic acids react

(10) Initial investigations into the reactions of amines with R₃Si*H[3] indicated that catalysis by 10% Pd–C led to racemic products. Subsequent work has shown that racemization was most probably due to acidic impurities in the commercial catalyst which may be removed (see Table III).
(11) Similar effects have been reported for the reaction of triethylsilane with alcohols using copper powder[11b] or chloroplatinic acid[11a] as the catalyst: (a) W. S. Miller, J. S. Peake, and W. H. Nebergall, *J. Am. Chem. Soc.*, **79**, 5604 (1957); (b) E. Lukevics and M. G. Voronkov, *Khim. Geterotsikl. Soedin.*, 171 (1965).
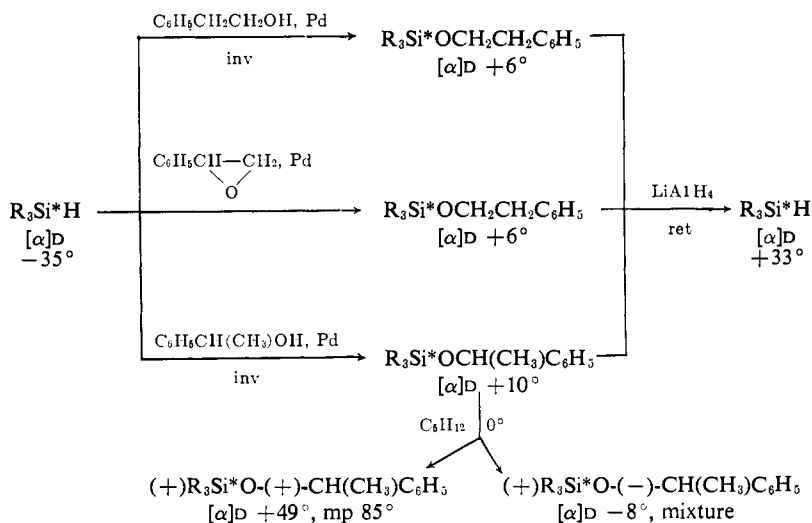
Figure 2. Palladium-catalyzed epoxide cleavage by $(-)R_3Si^*H$.

much more slowly than do alcoholic substrates and the stereospecificity is also noticeably lower. Amines react at a rate which is comparable to that of alcohols having a similar structure; however, the stereospecificity of these reactions is highly dependent on the nature of the catalyst surface (Table III). The following series

stereochemistry of this reaction since it bears a formal similarity to both the hydrosilation of olefins which occurs with retention,[1b,8] and to substitution reactions which proceed with inversion.[2,8]

We have found that R_3Si^*H reacts readily with styrene oxide in the presence of catalytic amounts of palladium

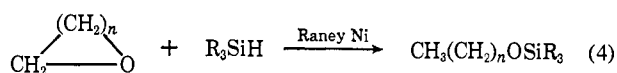Table III. Palladium-Catalyzed Reactions of $(-)R_3Si^*H^a$ with Amines

Reactant	Solvent	Catalyst[b]	Product	Yield, %	Prominant stereochemistry, % inv
Pyrrolidine	CH_2Cl_2	Pd–C	R_3Si^*Pyr	70	(Racemic)[c]
Pyrrolidine	C_5H_{12}	Pd–C	$(+)R_3Si^*Pyr$	90	65
Pyrrolidine	C_5H_{12}	Pd–CB	$(+)R_3Si^*Pyr$	89	100
i-BuNH₂	p-Xylene	Pd–C	R_3Si^*NHBu	76	(Racemic)[c]
i-BuNH₂	C_5H_{12}	Pd–CB	$(+)R_3Si^*NHBu$	92	97

[a] Optically pure $(-)R_3Si^*H$. [b] Pd–C is 10% Pd–C obtained from Matheson Coleman and Bell; Pd–CB is prepared by treating Pd–C with aqueous pyrrolidine, filtering and removing water and pyrrolidine at reduced pressure. [c] See ref 3.

demonstrates the relative reactivities of a representative group of nucleophiles toward R_3Si^*H in pentane using 10% Pd–C catalyst.
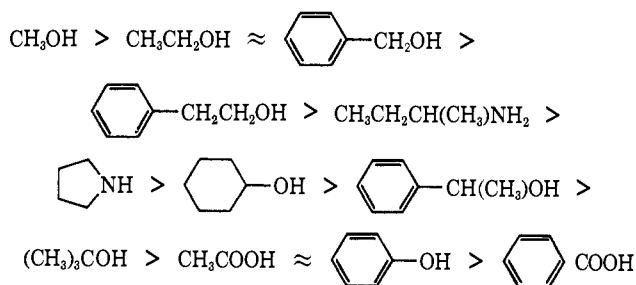
The recent synthesis of alkoxysilanes by the nickel-catalyzed cleavage of cyclic ethers with organosilanes[12] (4) demonstrates that the nucleophile need not bear an active hydrogen. It was of interest to determine the

on carbon. The major product of this reaction is (+)-α-naphthylphenylmethyl-2-phenylethoxysilane (1) and it is formed with *complete inversion at the optically active silicon center.* Figure 2 summarizes the reactions which establish the structure and relative configuration of (1),[13] and shows that the site of cleavage of the styrene oxide is the benzyl–oxygen bond. No α-naphthylphenylmethyl-1-phenylethoxysilane was detected in this reaction (see Figure 2).

Effect of the Organosilane. Minor changes in the structure of the optically active silicon compound have no effect on the stereochemistry of the group VIII metal catalyzed substitution reactions. Thus when optically active neopentylphenylmethylsilane was treated with methanol in xylene using 10% palladium on carbon the product was formed with 98% inversion of configuration (5).

$$(+)\text{-neo-}C_5H_{11}C_6H_5CH_3Si^*H \xrightarrow[CH_3OH]{Pd-C}$$
$$(-)\text{-neo-}C_5H_{11}C_6H_5CH_3Si^*OCH_3 + H_2 \quad (5)$$

Structural changes in groups about the silicon do, on the other hand, have a marked effect on reaction rate

(12) W. D. English and L. H. Sommer, *Rev. Soc. Quím. Mex.*, **6**, (4), 114 (1962).

(13) For convincing evidence that reduction of alkoxysilanes with LiAlH₄ proceeds with retention of configuration, see ref 6b.

(Table IV). The time required for complete methanolysis of phenylmethylethylsilane (III) is approximately 60 times longer than for phenylmethylmethoxysilane (II) showing that *the presence of electronegative substituents on the silicon greatly enhances reaction rate.*

In a case where inversion of configuration is impossible, reaction rate is extremely slow. The methanolysis of silabicyclo[2.2.1]heptane (V) is many times slower than its acyclic analog, triethylsilane (IV). This is especially interesting in view of the fact that V undergoes base-catalyzed hydrolysis much more rapidly than does triethylsilane.[14] The following series indicates trends in reactivity of the organosilanes.

Effect of the Solvent. The reactions were run in a variety of organic solvents. For relatively unhindered nucleophiles such as methanol, cyclohexanol, and acetic acid, rates were fastest in aliphatic hydrocarbon solvents. The reaction rates followed the order aliphatics (pentane, heptane) > methylene chloride > aromatics (benzene, toluene, *p*-xylene). The faster rates in pentane than in polar or aromatic solvents are believed to be a result of the inability of saturated hydrocarbons to effectively poison the catalyst surface.[15] In addition it should be noted that both yields and predominant stereochemistry values are higher in pentane than in other solvents. For very hindered nucleophiles such as *t*-butyl alcohol rates appear to be faster in methylene chloride than in pentane. *Regardless of the solvent used, however, inversion of configuration is the predominant stereochemical path of the reaction.*

Effect of the Catalyst. The nature of the catalyst has a greater effect on the stereochemistry than does the solvent. Table II shows that while palladium and nickel catalyze methanolysis of R_3Si*H with nearly complete inversion, rhodium and ruthenium catalyze the reaction far less stereospecifically and platinum and silver catalysts lead to racemic products. Of the metals used in this study, *palladium was found to be by far the most versatile and effective catalyst.*

Table IV. Palladium[a] Catalyzed Methanolysis of Organosilanes in Pentane

Reactant	Product	Total reaction time, min	Yield, %
PhMe(MeO)SiH	PhMe(MeO)$_2$Si	0.4	99
PhMeEtSiH	PhMeEtSiOMe	25	98
Et$_3$SiH	Et$_3$SiOMe	30	100
α-NpPhMeSi*H	α-NpPhMeSi*OMe	30	93
⬡SiH	⬡SiOMe	≫60[b]	20[b]

[a] 10% Pd–C, Matheson Coleman and Bell. [b] Reaction was only 20% complete after 1 hr.

(14) (a) L. H. Sommer and O. F. Bennett, *J. Am. Chem. Soc.*, **81**, 251 (1959); (b) L. H. Sommer, O. F. Bennett, P. G. Campbell, and D. R. Weyenberg, *ibid.*, **79**, 3295 (1957).

(15) Voronkov has suggested that polar solvent molecules may inhibit the substitution reactions by poisoning the catalyst surface.[11b]

In this connection we felt it necessary to demonstrate that it was the palladium metal itself which was serving as the catalyst in these reactions. Finely divided palladium powder was generated according to the method of Nash and DeSieno,[16] by exploding a pure palladium wire in a reaction chamber containing an argon atmosphere. A solution of $(+)R_3Si*H$ in heptane was syringed into the chamber and then methanol (in excess) was added in a similar manner. Hydrogen was evolved and $(-)R_3Si*OCH_3$ was formed in high yield with pure inversion of configuration at the silicon (6). This is

$$(+)\alpha\text{-NpPhMeSi*H} + CH_3OH \xrightarrow[\text{inv}]{\text{Pd, heptane}}$$
$$[\alpha]_D +35°$$
$$(-)\alpha\text{-NpPhMeSiOCH}_3 + H_2 \quad (6)$$
$$[\alpha]_D -17°$$

evidence that *the alcoholysis of optically active silanes with inversion of configuration is indeed catalyzed by palladium metal* in the absence of supports or added impurities.

Palladium generated *in situ* from $PdCl_2$ has also been found to be an effective catalyst for the methanolysis of optically active silanes (Table II). In the absence of added amine this reaction gives totally racemic product. However, in the presence of a small amount of triethylamine the reaction proceeds with nearly complete inversion.

Racemization of R_3Si*H and $R_3Si*OCH_3$ in the presence of commercially available palladium on carbon occurs slowly. These processes are at least in part responsible for the lack of stereospecificity in reactions which proceed extremely slowly. Such racemization may be prevented by using a catalyst which has been washed with an aqueous solution of an amine, filtered, and dried in a vacuum desiccator. This suggests strongly that the racemizing agent is acidic in nature. Table III compares the stereospecificities of some substitution reactions using amine washed, Pd–CB, and untreated, Pd–C, catalysts.

Stereochemical Considerations

The stereochemical results presented in this paper have interesting mechanistic implications. For example, the high degree of stereospecificity observed for the group VIII metal catalyzed substitution reactions of R_3Si*H shows that *free* silyl radicals or ions are clearly not involved. The finding of *inversion* stereochemistry for reactions of oxygen and nitrogen nucleophiles argues against the operation of a four-center mechanism (7) on the catalyst surface.[17] This type of mechanism might

appear quite attractive in the absence of stereochemical data; however, it would be expected to lead to retention of configuration at the silicon center.

Retention of configuration is, in fact, the most common stereochemical path for nucleophilic substitution

(16) C. P. Nash and R. P. DeSieno, *J. Phys. Chem.*, **69**, 2139 (1965).

(17) E. Lukevics and M. G. Voronkov, *Khim. Geterotsikl. Soedin.*, 171 (1965). The authors have proposed a mechanism similar to (7) for reactions of alcohols with triethylsilane in the presence of chloroplatinic acid which is reduced to metallic platinum during the reaction.

reactions of R₃Si*H in the absence of transition metals. Base-catalyzed hydrolysis and alcoholysis as well as reactions with lithium aluminum hydride, alkyl-, and aryllithium reagents all occur with retention of configuration.[6,18] The mechanisms of such reactions are best described as proceeding through quasi-cyclic rate-controlling transition states and fall into the general category, SNi–Si. In contrast to this, *the group VIII metal catalyzed substitutions are the first general class of reactions of R₃Si*H which have been found to yield optically active products of opposite configuration to the starting silane.*

A mechanism analogous to the one presented for the group VIII metal catalyzed hydrosilation of olefins (8) suffers from the same drawbacks as does (7). Collapse of the intermediate to product in an intramolecular fashion in (8) should occur with retention. This would require that initial reaction of the optically active silane with the metal occur with inversion. The evidence pre-

$$R_3Si^*H \quad + \quad$$

$$\longrightarrow \quad R_3Si^*OR \quad (8)$$
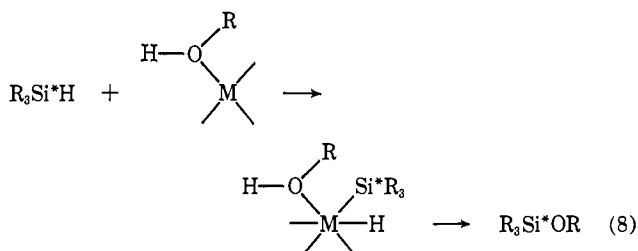
sented in a previous paper[9] makes this alternative seem highly improbable. It appears doubtful, therefore, that the metal atom which coordinates silicon is also bonded to the attacking nucleophile.

It should be noted at this point that, in contrast to the hydrosilation of olefins and SiH(D) exchange reactions, we have found no evidence to date of a stereospecific group VIII metal-catalyzed substitution reaction in homogeneous solution. Furthermore, pure palladium powder, generated by exploding a wire in an inert argon atmosphere, is an efficient catalyst for the substitution reaction. This suggests strongly that the reactions discussed in this paper should be regarded as examples of *heterogeneous* catalysis.

A plausible mechanism for the substitution reactions involving oxygen and nitrogen nucleophiles is one in which interaction of the optically active silane with the reactive transition metal center occurs with *retention* and the displacement of the silicon from the metal occurs with *inversion* (9). The surface intermediate (VI)

$$R_3Si^*H \xrightarrow[\text{ret}]{(M)} [R_3Si^*H(M)] \xrightarrow[\text{inv}]{ROH} R_3Si^*OR \quad (9)$$
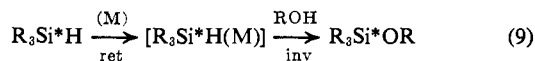
may contain a metal–silicon bond (VIa) or may be a complex (VIb) in which the Si–H bond is not broken but merely activated by the metal. In either case back-

VIa   VIb

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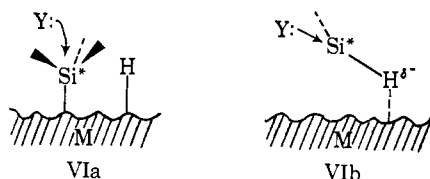
(18) Exceptions to this generalization have been reported. For example, benzhydryllithium reacts with R₃SiH*H to form R₃SiCH(Ph)₂ with 60% inversion: L. H. Sommer and W. D. Korte, *J. Am. Chem. Soc.*, 89, 5802 (1967).

side attack by a nucleophile, Y:, would lead to an optically active product with inverted configuration.

A previous study[3] has shown that optically active R₃Si*H reacts with hydrogen chloride (10) in the presence of palladium catalysts to give good yields of optically active R₃Si*Cl. In contrast to reactions of oxygen and nitrogen nucleophiles, HCl reacts with

$$R_3Si^*H + HCl \xrightarrow{Pd} R_3Si^*Cl + H_2 \quad (10)$$
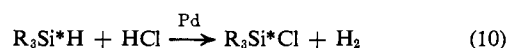
R₃Si*H with predominant *retention* of configuration. For reasons which are not clearly understood the mode of absorption of reactants in this case may be similar to that shown in mechanism 7.

Another alternative is that the palladium metal and HCl may react to form an intermediate capable of displacing H from silicon with retention. Tsuji and Ohno[19] have suggested that oxidative addition of HX to palladium metal may occur to yield species of the type H–Pd–X (11). It is not unreasonable that if a species such as H–Pd–Cl were an intermediate in this process it

$$HX + Pd + nL \rightleftharpoons H\overset{\overset{\displaystyle Ln}{|}}{Pd}X \quad (11)$$
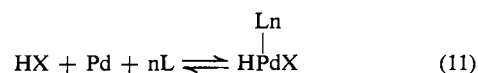
could react with R₃Si*H with retention of configuration at silicon (12). When, in fact, palladium(II) chloride is

added to a solution of R₃Si*H in pentane, optically active R₃Si*Cl is formed rapidly in high yield with retention of configuration (13). The insolubility of the

$$2R_3Si^*H + PdCl_2 \xrightarrow{ret} Pd + H_2 + 2R_3Si^*Cl \quad (13)$$
$$[\alpha]D\ -35° \qquad\qquad\qquad\qquad [\alpha]D\ +5.8°$$
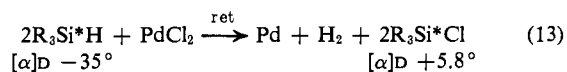
polymeric palladium (II) chloride in pentane makes this system a reasonably good model for a heterogeneous catalyst containing Cl bonded to the metal surface.

Despite the fact that –H is a poor leaving group from silicon, and consequently the stereochemistry of the Si–H bond is largely that of retention, the vast majority of substitution reactions which we have investigated proceed with inversion in the presence of reactive transition metal centers. The marked effect of the metal surface on the stereochemistry of reactions is not unique in organic chemistry. The hydrogenolysis of optically active benzyl alcohols and ethers proceeds with inversion over palladium or platinum catalysts and with retention on the surface of nickel or cobalt, whereas optically active sulfones are reduced with inversion over nickel.[20] Thus, there is a dramatic difference in the nature of surface species depending on the metal used and on the chemical function which is bonded to it. Information which is rapidly accumulating concerning the nature of adsorbed species will eventually lead to a more precise picture of surface reactions.

(19) J. Tsuji and K. Ohno, *J. Am. Chem. Soc.*, 90, 94 (1967).
(20) (a) S. Mitsui, Y. Senda, and K. Konno, *Chem. Ind.* (London), 1354 (1963); (b) S. Mitsui and Y. Kato, *ibid.*, 381 (1965); (c) S. Mitsui and Y. Nagahisa, *ibid.*, 1975 (1965); (d) A. M. Khan, I. J. McQuillan, and I. Jardine, *Tetrahedron Lett.*, 24, 2649 (1966); (e) W. A. Bonner, *J. Am. Chem. Soc.*, 74, 1033 (1952); (f) D. J. Cram and J. Alinger, *ibid.*, 76, 4516 (1954).

Experimental Section

Pd- and Ni-Catalyzed Substitution Reactions of (+)R₃SiH. Reactions with alcohols or carboxylic acids summarized in Table I were carried out by first dissolving 0.62 g (2.5 mmol) of optically active α-naphthylphenylmethylsilane, $[\alpha]D$ +35° (c 2.1, pentane), in 6 ml of the carefully dried solvent. The desired catalyst, 0.06 g, was mixed with the solution of silane. An equimolar amount of the nucleophilic reagent (2.5 mmol) was then admitted to the reaction vessel through a syringe. Liquid reagents were added neat. Solid nucleophiles were admitted in a minimum of the reaction solvent. In these cases the amount of solvent initially used to dissolve the silane was adjusted so that the total volume of solvent used was 6 cc. In most cases immediate bubbling occurred; however, short induction periods of 5–15 min preceded several of the reactions. The reaction was allowed to proceed at room temperature in an atmosphere of dry nitrogen until bubbling had ceased. The mixture was then stirred for an additional 30 min and the solution filtered free of catalyst. Methanol was the most reactive nucleophile requiring 0.5–4 hr for complete reaction and benzoic acid was the least reactive requiring 2–4 days. The solvent was removed at reduced pressure and the resulting alkoxysilane or silyl ester was purified by column chromatography.[7] Pure, optically active products were isolated in high yields (75–95%) and identified by comparison of infrared spectra with those of authentic samples.[5,7,8] Specific rotations of the products were determined in solvents at concentrations reported in the literature.[1b,5,7,8] The predominant stereochemistries listed in Table I were reproducible to within ±2%.

Palladium-Catalyzed Reactions of (−)R₃Si*H with Amines. Optically active α-naphthylphenylmethylsilane, $[\alpha]D$ −35° (c 2.1, pentane), 0.62 g (2.5 mmol) was dissolved in 6 ml of dry pentane and 0.06 g of the desired catalyst was added. An equimolar amount of the amine (2.5 mmol) was syringed into the mixture and after a short induction period hydrogen was evolved and the reaction was allowed to proceed at room temperature under nitrogen. In some cases hydrogen evolution ceased before all the silane was reacted and addition of a small amount of fresh catalyst at this point was necessary to ensure complete reaction. The solution was filtered free of catalyst and evaporation of solvent at 10⁻² mm left the optically active aminosilane which was identified by its infrared spectrum.[4] When the catalyst used was 10% Pd–C from Matheson Coleman and Bell, stereospecificity was poor. If the commercial catalyst was shaken with an aqueous solution of the amine, filtered, and dried in a vacuum desiccator (Pd–CB) prior to use, the reaction was completely stereospecific. Rates were much slower when Pd–CB was used.

Palladium-Catalyzed Methanolysis of Organosilanes in Pentane. a. Preparation and Methanolysis of Phenylmethylmethoxysilane. A solution was prepared containing 4.00 g (0.125 mol) of methanol. 11.1 g (0.11 mol) of triethylamine, 200 ml of pentane, and 50 ml of ethyl ether. Solvents and reagents had been thoroughly dried and distilled prior to use. To the stirred solution under nitrogen 15.65 g (0.100 mol) of phenylmethylchlorosilane in 20 ml of pentane was added dropwise over a 1-hr period. The mixture was stirred 10 hr, filtered free of triethylamine hydrochloride, and solvent was stripped off using a water aspirator. The crude product was fractionated on a spinning band column. A total of 9.6 g (64% yield) of phenylmethylmethoxysilane distilled at 63° at 12 mm, $n^{22.5}D$ 1.4888. Infrared and nmr spectra were completely consistent with the assigned structure.

Anal. Calcd for C₈H₁₂OSi: C, 63.10; H, 7.94. Found: C, 63.16; H, 7.95.

Phenylmethylmethoxysilane, 1.5200 g (1.00 × 10⁻² mol), was dissolved in 15 ml of dry pentane and 0.131 g of 10% Pd–C was added. This mixture was stirred under nitrogen for 1 min and then 0.40 g (1.23 × 10⁻² mol) of methanol was added rapidly through a syringe. Rapid hydrogen evolution occurred over a period of 25 sec after which time bubbling had completely stopped. The reaction mixture was immediately filtered free of catalyst and the pentane evaporated using a water aspirator leaving behind 1.80 g (99% yield) of a clear colorless liquid having an infrared spectrum consistent with the expected product. The crude reaction product was distilled through a small Vigreux column yielding 1.50 g of phenylmethyldimethoxysilane boiling at 96° (21 mm), $n^{25}D$ 1.4778 (lit.[21] bp 91° (15 mm), $n^{25}D$ 1.4778).

b. Methanolysis of Phenylmethylethylsilane. The palladium-catalyzed methanolysis of phenylmethylethylsilane was carried out on the same scale as with phenylmethylmethoxysilane and under identical conditions. In this case hydrogen was evolved for a period of 25 min. After this time bubbling had stopped and the reaction mixture was immediately filtered free of catalyst, pentane evaporated, and an infrared spectrum of the crude product was taken. The spectrum exhibited bands characteristic of the PhMeEtSi system[22] and in addition showed intense new absorptions at 3.54, 8.43, and 9.2 μ related to the SiOCH₃ moiety. Complete absence of the Si–H absorption at 4.75 μ showed that reaction was complete. The crude product, 1.8 g (99% yield), was fractionated on a semimicro spinning band column yielding phenylmethylethylmethoxysilane, 1.2 g, which distilled at 110° (23 mm), $n^{22.5}D$ 1.4884.

Anal. Calcd for C₁₀H₁₆OSi: C, 66.61; H, 8.94. Found: C, 66.67; H, 8.85.

c. Methanolysis of Triethylsilane. Triethylsilane, 0.1834 g (1.58 mmol), in 3.6 cc of pentane was treated with 0.080 g (2.72 mmol) of methanol using 0.019 g of 10% Pd–C as a catalyst in the manner of previous reactions. Rapid hydrogen evolution occurred, slowing noticeably after 6 or 7 min and terminating after 30 min. The reaction mixture was filtered immediately and the product recovered as before. Triethylmethoxysilane was produced in quantitative yield (0.23 g).

d. Methanolysis of 1-Silabicyclo[2.2.1]heptane. The bridgehead silane,[23] 0.1690 g (1.51 mmol), in 3.4 cc of pentane was treated as before with 0.080 g (2.72 mmol) of methanol using 0.020 g of 10% Pd–C as the catalyst. Very slow bubbling occurred and continued for 1 hr after which time the reaction mixture was filtered free of catalyst. An infrared spectrum of the reaction mixture showed a broad band at 3300 cm⁻¹ indicating the presence of a large amount of methanol, an intense absorption at 2150 cm⁻¹ due to the Si–H moiety at the bridgehead, and demonstrating the presence of a large amount of unreacted 1-silabicyclo[2.2.1]heptane, V, and a weak band at 9.2 μ presumably due to a minor amount of 1-methoxy-1-silabicyclo[2.2.1]heptane,[24] VII. Other characteristic absorptions of the bridgehead silicon system were also present. From the relative intensities of the Si–H and Si–OCH₃ bands in the infrared, the extent of reaction after 1 hr was estimated to be approximately 20%. Fractional sublimation of the mixture afforded 0.056 g of pure V[23] and 0.065 g of a material whose infrared spectrum was consistent with a mixture of V and VII. It was not possible to isolate pure VII by this method. Losses during sublimation were great due to the volatility of the bridgehead silane.

Palladium-Catalyzed Reaction of (−)R₃Si*H with Styrene Oxide. Optically active (−)R₃Si*H, $[\alpha]D$ −35° (c 2.1, pentane), 2.49 g (10 mmoles), was dissolved in 7.0 ml of pure, dry methylene chloride and 0.25 g of 10% Pd–C was added. Freshly distilled styrene oxide, 2.40 g (20 mmoles), was added and the mixture stirred under nitrogen for 17 hr. The reaction mixture was filtered free of catalyst. Volatile materials consisting of methylene chloride, unreacted styrene oxide, and 0.2 g of phenylacetaldehyde (isolated and identified as its 2,4-dinitrophenylhydrazone, mp 120–121°) were distilled into a chilled trap at reduced pressure. The pot residue consisted of 1.2 g of a waxy substance which was insoluble in pentane and 3.6 g of pentane soluble material which was purified by chromatography through silica gel using 1:1 benzene-pentane as the eluent. Evaporation of the solvent left 2.6 g (70% yield) of a clear, colorless oil identified by its infrared and nmr spectra as (+)-α-naphthylphenylmethyl-2-phenylethoxysilane (VIII). An infrared spectrum of the neat liquid showed the expected R₃Si* system absorptions[6] plus new bands at 3.3 (s), 3.4 (s), 3.5 (s), 6.35 (w), 6.7 (s), 6.9 (s), 7.25 (m), 9.2 (vs), 9.35 μ (vs), apparently related to the –SiOCH₂CH₂Ph moiety. The proton magnetic resonance spectrum of VIII exhibited triplets at δ 3.68 (two protons) and 2.62 (two protons) due to the two sets of methylene protons, a singlet at 0.45 (three protons) due to the methyl group on silicon and complex multiplets (total of 17 protons) due to the aromatic hydrogens. The specific rotation of VIII was determined in pentane, $[\alpha]D$ +6.8° (c 11.1, pentane), $n^{22}D$ 1.6155.

Anal. Calcd for C₂₅H₂₄OSi: C, 81.48; H, 6.59. Found: C, 81.63; H, 6.98.

(21) This material is commercially available. Properties are listed in "Selection Guide to Dow Corning Reactive Organosilicon Chemicals," Dow Corning Corp. Form No. 03-017, Product No. Z-6073.

(22) K. W. Michael, Ph.D. Thesis, The Pennsylvania State University, 1963, and ref 6d.

(23) O. F. Bennett, Ph.D. Thesis, The Pennsylvania State University, 1958, and ref 15.

(24) M. C. Musolf, Ph.D. Thesis, The Pennsylvania State University, 1960.

Reduction of VIII with LiAlH₄[5b] gave (+)-α-naphthylphenyl-methylsilane, [α]D +33° (c 2.1, pentane).

To establish that VII was formed exclusively, VIII and (+)-α-naphthylphenylmethyl-1-phenylethoxysilane (IX) were each prepared by the catalytic method in pentane, see Table I. The product formed from 2-phenylethanol and (−)R₃Si*H was identical in every respect with the product of the styrene oxide cleavage. The product formed from 1-phenylethanol (IX), [α]D +10.1 (c 6, cyclohexane), had the characteristic nmr spectrum of a 1:1 mixture of the diasteriomeric α-naphthylphenylmethyl-1-phenylethoxysilane[25] and was resolvable into (+)-α-naphthylphenylmethyl-(+)-1-phenylethoxysilane, [α]D +49.2° (c 3.2, cyclohexane), mp 85°, (lit.[25] [α]D +47.2°), and (+)-α-naphthylphenylmethyl-(−)-1-phenylethoxysilane, [α]D −8.0° (c 3.0, cyclohexane), viscous oil. No attempt was made to resolve completely the (+, −) diasteriomer. Resolution was carried out by fractional crystallization from a 1:1 pentane-hexane solution.

Methanolysis of (+)R₃Si*H Using an Exploded Wire Catalyst.[16] A reaction chamber was constructed from two vacuum desiccator bottoms sealed together with a rubber "O" ring. Large electrodes were implanted into the top section of the chamber and an outlet for connection to a vacuum line was built into the side of the vessel. Pure palladium wire 70 mg, No. 30 (California Fine Wire) was connected across the electrodes and was outgassed at red heat electrically with a chamber pressure of 10⁻⁴ mm for 12 hr. The wire was allowed to cool and pure argon, 650 mm, was then admitted to the system, and the chamber was closed off and removed from the vacuum line. The wire was exploded electrically[16, 26] creating a dense black aerosol of palladium metal which settled to the bottom of the vessel after 2 hr. Argon was then admitted to the system until a chamber pressure of 800 mm was reached. A solution of 1.35 g of (+)R₃Si*H, [α]D +34.2 (c 2.1, pentane), in 14 ml of dry heptane was syringed into the vessel while an overpressure of argon was maintained. The mixture was magnetically stirred for 1 min and then 1.0 ml of dry methanol was injected into the reaction chamber. Bubbling started immediately and continued for 8 hr

during which time the chamber pressure was relieved periodically. The reaction mixture was then filtered free of catalyst and solvent evaporated leaving white, crystalline (−)-α-naphthylphenylmethyl-methoxysilane, 1.28 g (85% yield), [α]D −17.1 (c 2.42, pentane).

Palladium(II) Chloride Catalyzed Reactions. a. Optically active (−)R₃Si*H, [α]D −35° (c 2.1, pentane), 0.54 g, was dissolved in 5.4 ml of dry pentane. A suspension of palladium(II) chloride, 6 mg, in 0.33 ml of methanol was syringed into the solution of silane. Rapid gas evolution occurred accompanied by precipitation of metallic palladium. Reaction was over in 3 min and the mixture was filtered free of palladium. Evaporation of pentane at reduced pressure yielded racemic α-naphthylphenylmethylmethoxysilane, 0.55 g (93% yield).

b. A saturated solution of palladium(II) chloride in methanol was prepared by stirring PdCl₂·2H₂O, 20 mg, with 1 cc of methanol for 30 min and allowing the undissolved powder to settle on standing. Triethylamine, 20 μl, was added and 0.3 ml of the clear yellow supernate syringed into a stirred solution of 0.63 g of (−)R₃Si*H in 6.3 ml of pentane. The solution remained homogeneous for 25 sec then palladium metal began to precipitate and hydrogen was evolved. Bubbling continued for 6.5 hr after which the reaction mixture was filtered and solvent removed. A total of 0.68 g (99% yield) of white, crystalline R₃Si*OCH₃, [α]D +16° (c 3.1, pentane), was isolated. The palladium metal, 0.4 mg, which was recovered from the reaction mixture was shown to be an active catalyst for the methanolysis of R₃Si*H.

Reaction of Palladium(II) Chloride with R₃Si*H. PdCl₂ powder (0.88 g, 0.05 mole) was added to a solution of (−)R₃Si*H, [α]D −35° (2.24 g, 0.09 mole), in 25 cc of dry pentane. The reaction mixture was stirred under dry nitrogen. Vigorous bubbling occurred and the red solid PdCl₂ was converted to the black metal. Bubbling ceased after 30 min and the reaction mixture was filtered and solvent evaporated at reduced pressure yielding white, crystalline α-NpPhMeSi*Cl, mp 62–64°, [α]D −5.8° (c 10, cyclohexane).

(25) A. G. Brook, C. M. Warner, and W. W. Limburg, Can. J. Chem., 45, 1231 (1967).

(26) The condenser bank used employed 28.4 μF at a voltage of 10 kV in a circuit having an inductance of 0.3 μH.

Stereochemistry of Asymmetric Silicon. XVII. Synthesis, Resolution, and Stereochemistry of the 1,2,2,2-Tetraphenyl-1-methyldisilane System[1–3]

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Abstract: An entirely new route to optically active functionally substituted organosilicon compounds has been developed, by which the 1,2,2,2-tetraphenyl-1-methyldisilane system has been synthesized and resolved. Whereas previously studied systems PhMeRSi*X (R = α-naphthyl, neopentyl, benzhydryl, or ethyl) have nonreacting groups bonded to asymmetric silicon via carbon atoms exclusively, the new system has a nonreacting group bonded to asymmetric silicon via a metalloid–metalloid linkage. Thus far, replacement of an organic R group in PhMe-RSi*X by Ph₃Si has not resulted in a reversal of functional group stereochemistry, according to chemical evidence. This extends the validity of earlier stereochemical generalizations for R₃Si*X, and reinforces their nondependence on the nature of the nonreacting groups.

The α-naphthyl systems (*i.e.*, the α-naphthylphenyl-methylsilane system, α-NpPhMeSi*X) has afforded a practical route to other systems, where R equals benz-

hydryl, neopentyl, or ethyl, by the following method[4] (reactions 1–3). Conservation of optical activity has been shown to be very high in the above conversions,

(1) For the preceding paper in this series, see L. H. Sommer and J. E. Lyons, J. Am. Chem. Soc., 91, 7061 (1969).

(2) For a preliminary communication, see L. H. Sommer and K. T. Rosborough, ibid., 89, 1756 (1967).

(3) We are pleased to acknowledge vital support of this work by the National Science Foundation.

(4) L. H. Sommer, K. W. Michael, and W. D. Korte, J. Am. Chem. Soc., 89, 868 (1967).