MECHANISTIC PATHWAYS OF THE Si—H BOND — STEREOCHEMICAL STUDIES†

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INTRODUCTION

The first studies of the dynamic (reaction) stereochemistry of optically active acyclic R_3Si^*X were carried out in my laboratory about ten years ago by C. L. Frye. Since that time many enthusiastic collaborators have greatly expanded the field of organosilicon stereochemistry which now includes stereochemical studies of more than a hundred substitution reactions of R_3Si^*X. These studies have provided new insight into the nature of organosilicon reaction mechanisms. Indeed, it is perhaps appropriate to say here that the stereochemical data have afforded me many surprises and have compelled me to discard many of the mechanistic ideas which I held prior to 1958.

Our mechanistic conclusions concerning some of the reactions of *monofunctional* R_3SiX, based mainly on stereochemical data accumulated prior to 1964, but including also the implications of kinetic data when available, have been reviewed[1]. Those conclusions have received strong additional support from stereochemical work carried out during the past four years.

Perhaps the major mechanistic conclusions we have reached concerning R_3Si^*X may be stated as follows:

(1) The silicon atom is a highly sophisticated and sensitive reaction centre whose mechanism paths are many.

(2) With very few exceptions, nucleophilic substitution reactions of *monofunctional* acyclic organosilicon compounds do not involve expanded-octet (Si-V or Si-VI) intermediates, or else such intermediates, if formed, do not differ significantly in energy and structure from the rate-limiting transition state. In short, the stereochemical aspects of such reactions are consistent with the concept of such reactions as concerted processes involving essentially simultaneous bond-making and bond-breaking processes. This is not to say that expanded-octet mechanisms are unavailable to R_3SiX, but only that concerted displacement mechanisms in many (but not all) cases provide the path of lower free energy of activation. Perhaps the major evidence for this conclusion comes from the dependence of the stereochemistry of R_3Si^*X on the nature of the leaving group, X.

(3) The S_N2-Si Stereochemistry Rule[1, 2] for R_3Si^*X states that good leaving groups X, whose conjugate acids (HX) have pK_a less than ~ 6 undergo nucleophilic displacement from R_3Si^*X with inversion of configuration, regardless of the nature of the solvent, and providing only that the attacking reagent furnish an entering group Y that is more basic than X.
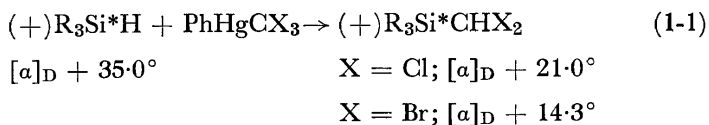
† This paper was presented *in absentia*.

(4) For poor leaving groups, X, whose conjugate acids have pK_a greater than ~ 10, the stereochemical path, inversion or retention of configuration, depends upon the nature of the reagent[3-5] and the nature of the solvent[6]. Stereochemistry crossover (from inversion to retention or vice versa) as a function of reagent or solvent change have recently[4, 6] provided important new support for our earlier conclusion[1] that poor leaving groups undergo nucleophilic displacement from R_3Si*X with retention of configuration by a quasi-cyclic mechanism designated[1] S_Ni-Si. The inversion reactions of good and poor leaving groups in R_3Si*X have been assigned an S_N2-Si mechanism which, except for the possibility of d-orbital participation, is similar to the S_N2 nucleophilic displacement mechanism for carbon. The phenomenon of stereochemistry crossover for poor leaving groups and the S_N2-Si stereochemistry Rule for good leaving groups strongly support the S_N2-Si mechanism as originally postulated.[1]

Although most of our earlier stereochemical work has concerned nucleophilic substitution reactions of R_3Si*X in homogeneous solution and has revealed that the S_N2-Si and S_Ni-Si mechanisms are quite common pathways for such reactions, the known chemistry of the Si—H bond has given us the opportunity to broaden the scope of our stereochemical studies to include reactions which do not fall into the category of homogeneous nucleophilic displacement reactions.

In this lecture I shall report some of our newer stereochemical studies of R_3Si*H (R_3Si*- is usually α-NpPhMeSi*-, α-naphthylphenylmethylsilyl). These studies concern homogeneous reactions with reagents not usually classified as nucleophilic, and reactions, both heterogeneous and homogeneous, involving catalysis by group VIII metals and their compounds.
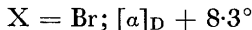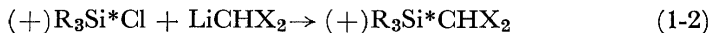
1. INSERTION REACTIONS WITH DIBROMOCARBENE AND DICHLOROCARBENE

Seyferth and co-workers have previously shown[7] that phenyl(trihalomethyl)-mercury compounds, $PhHgCX_3$, react smoothly with R_3SiH to give R_3SiCHX_2. We have recently completed a stereochemical study of this reaction. Using optically active R_3Si*H in refluxing benzene solvent during 24 hours gave the following results[8].

$$(+)R_3Si*H + PhHgCX_3 \rightarrow (+)R_3Si*CHX_2 \qquad (1\text{-}1)$$

$$[a]_D + 35 \cdot 0° \qquad\qquad X = Cl; [a]_D + 21 \cdot 0°$$

$$X = Br; [a]_D + 14 \cdot 3°$$

The problem of correlations of configuration between R_3Si*H and $R_3Si*CHX_2$ was recently overcome by preparation of the insertion products via independent syntheses involving reactions of known stereochemistry. These involved the use of organolithium reagents in coupling reactions with R_3Si*Cl, a class of reactions which follows the S_N2-Si Stereochemistry Rule of inversion of configuration for good leaving groups[9].

Using previously reported procedures, dichloromethyllithium[10] and dibromomethyllithium[11] were prepared and reacted with R_3Si*Cl at low temperature in tetrahydrofuran solvent.
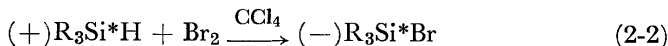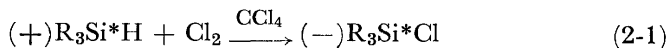
$$(+)R_3Si^*Cl + LiCHX_2 \rightarrow (+)R_3Si^*CHX_2 \qquad (1\text{-}2)$$

$[a]_D + 6\cdot3°$ $\qquad$ $X = Cl; [a]_D + 9\cdot3°$

$\qquad\qquad\qquad\qquad$ $X = Br; [a]_D + 8\cdot3°$

Since $(+)R_3Si^*Cl$ and $(+)R_3Si^*H$ have opposite configuration and since (1-2) proceeds with inversion of configuration, it follows that $(+)R_3Si^*H$, $(+)R_3Si^*CHCl_2$ and $(+)R_3Si^*CHBr_2$, all possess the same configuration. Thus, *the insertion of dichlorocarbene and dibromocarbene into the silicon-hydrogen bond proceeds with retention of configuration.*

The insertion products of R_3Si^*H and those obtained by the coupling reactions with R_3Si^*Cl had identical infrared and n.m.r. spectra and gave correct analyses for carbon, hydrogen and halogen. Probably due to racemization of R_3Si^*Cl by the formed LiX salts in tetrahydrofuran the optical purity of the coupling products was lower than that of the insertion products.

Seyferth and co-workers have reported kinetic evidence which supports the operation of a free carbene mechanism for the reaction of phenyl-(bromodichloromethyl) mercury with olefins to give gem-dichlorocyclopropanes[12]. This evidence plus our demonstration of a retention stereochemistry lead to (1-3) as a probable transition state for reactions (1-1).

$$(1\text{-}3)$$
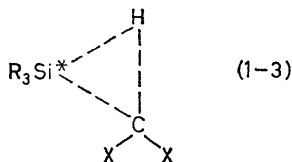
2. REACTIONS WITH CHLORINE AND BROMINE IN CARBON TETRACHLORIDE

$$(+)R_3Si^*H + Cl_2 \xrightarrow{CCl_4} (-)R_3Si^*Cl \qquad (2\text{-}1)$$

$$(+)R_3Si^*H + Br_2 \xrightarrow{CCl_4} (-)R_3Si^*Br \qquad (2\text{-}2)$$

Reactions (2-1) and (2-2) are highly stereospecific and proceed with retention of configuration[13].

For the reaction of triorganosilanes in general, R_3SiH, with chlorine and bromine in carbon tetrachloride, it was found that a second-order rate law was followed: rate $= k_2[R_3SiH] [X_2]$. Chlorination of R_3Si^*H had $k_2 = 2\cdot2 \times 10^2$ l. mole^{-1} min^{-1}. Bromination is also quite rapid. These reactions are not light-catalyzed and proceed much faster in carbon tetrachloride than in cyclohexane[14].

The fast reaction rates of R_3Si^*H with chlorine and bromine which are generally regarded as electrophilic reagents in polar (non-radical) reactions, serve to disprove any naïve generalization which assigns fast rates of displacement at silicon solely to the ability of silicon to act as an effective centre for nucleophilic attack. For polar reactions, two kinds of chemical driving force are important for organosilicon reactions: electrophilic attack on X, as well as nucleophilic attack on Si.

For reaction series involving wide structural variation in R_3SiH, it was found that chlorination and bromination both involve generation of considerable *positive charge* at the silicon atom in the rate-limiting transition state. Thus, the Taft reaction constant for chlorination and bromination was negative and large. For both reaction series, $\rho^* = -4.2$, and electron releasing substituents greatly facilitate rate.

Extensive studies of the mechanism of chlorination and bromination of R_3SiH in carbon tetrachloride solvent[14] yielded the information given above and also the very interesting facts indicated in (2-3) below.

$$(+)R_3Si^*H + BrCl \xrightarrow{CCl_4} (-)R_3Si^*Br \ (80\text{--}90\%)$$
$$+ (-)R_3Si^*Cl \ (10\text{--}20\%) \qquad (2\text{-}3)$$
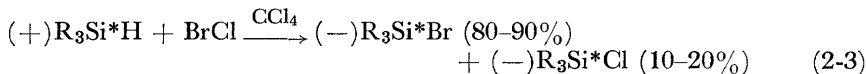
Bromination and chlorination with BrCl proceeded with high stereospecificity, better than 90 per cent retention of configuration. Furthermore, the same ratio of products was found for reaction of $(C_2H_5)_3SiH$ with BrCl, 80 to 90 per cent Et_3SiBr and 10 to 20 per cent Et_3SiCl.

There is no evidence that R_3SiBr is not the primary major product in the reactions of R_3SiH with BrCl. A solution of Et_3SiBr in carbon tetrachloride was saturated with anhydrous HCl, and conversely a solution of Et_3SiCl in carbon tetrachloride was saturated with anhydrous HBr. No halogen exchange was observed in either case. R_3Si^*H was reacted with an excess of BrCl and after the initial extremely fast reaction, no significant change in rotation occurred. Also, it has been shown[15] that BrCl reacts with Me_3SiCl to give $(BrCH_2)Me_2SiCl$ without conversion of Si–Cl to Si–Br.

The order of reactivity of the halogenation reagents towards R_3SiH is:

$$BrCl \ggg Cl_2 > Br_2$$
$$130 \qquad 8 \qquad 1$$
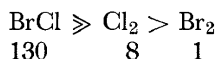
Taken together, all of the facts concerning reaction of R_3SiH with BrCl, Cl_2 and Br_2 suggest that the mechanism involves formation of a three-centre intermediate which decomposes rapidly to products with retention of configuration. This is shown in (2-4) for reaction with BrCl.

$$(2\text{-}4)$$
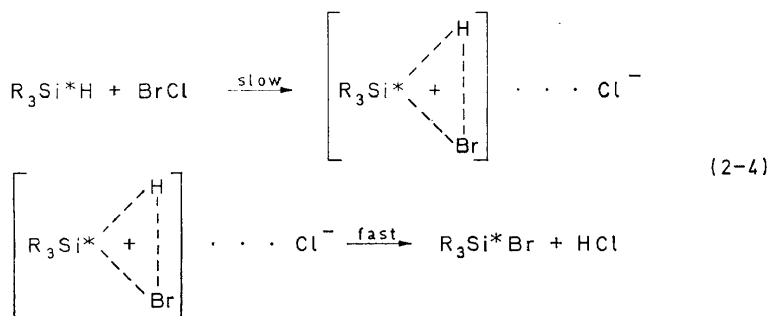
Because of the polarity in the Br—Cl molecule, $\overset{\delta+}{Br}$—$\overset{\delta-}{Cl}$, and its known mode of reaction as positive Br and negative Cl, a simple quasi-cyclic four-centre S_Ni-Si mechanism for reaction of R_3Si^*H with BrCl would be expected to yield mainly R_3SiCl. This is not observed.
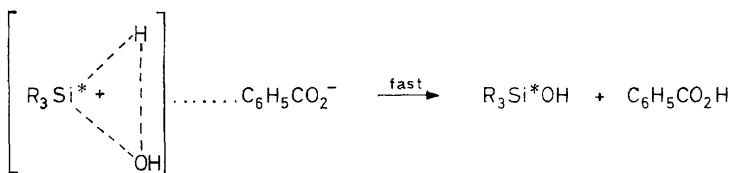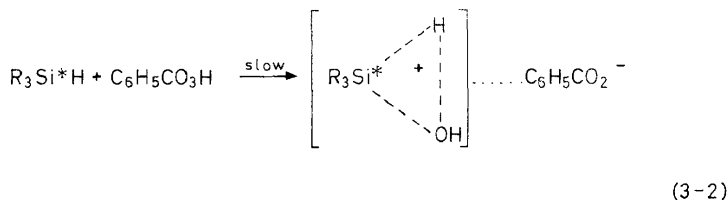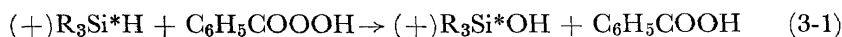
Mechanism (2-4) bears an obvious resemblance to (1-3) for insertion of dihalocarbenes into Si-H. However, unlike the latter, (2-4) gives a net result of substitution rather than insertion and (2-4) is rather difficult to classify. On a formal basis it involves *electrophilic* displacement at silicon and is an example of a three-centre S_Ei-Si mechanism. But the fact that $Br^{\oplus}$ like :CX_2, has an unshared pair of electrons available for donation to H in the postulated intermediate may contribute to the stability and formation of that intermediate. This is supported by the observation that R_3SiD does not undergo deuterium-hydrogen exchange with HBr in carbon tetrachloride solution during very long reaction times. The following intermediate does *not* form readily[14]:

$$\left[R_3Si \overset{+}{\underset{}{\diagup}} \begin{array}{c} H \\ \vert \\ \vert \\ D \end{array} \right] \cdots\cdots Br^-$$
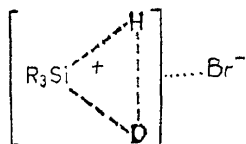
On balance, however, it seems best to designate the mechanism for reactions of R_3SiH with BrCl, Cl_2 and Br_2 in carbon tetrachloride solvent as S_Ei-Si. The postulated intermediate has the unit positive charge distributed over three atoms and is in accord with a large negative ρ^* for chlorination and bromination. It is certainly in accord with very clean retention of configuration. It is consistent with formation of R_3SiBr as the major product with BrCl. It is consistent with greatly increased rates for BrCl relative to Cl_2 and Br_2. It is consistent with second-order kinetics.

3. REACTION WITH PERBENZOIC ACID

Treatment of optically active R_3Si^*H with excess perbenzoic acid in benzene solvent at room temperature for 12 hours gave R_3Si^*OH in 40 per cent yield with retention of configuration and a stereospecificity of at least 90 per cent[16].

$$(+)R_3Si^*H + C_6H_5COOOH \rightarrow (+)R_3Si^*OH + C_6H_5COOH \qquad (3\text{-}1)$$

$$R_3Si^*H + C_6H_5CO_3H \xrightarrow{\text{slow}} \left[R_3Si^* \overset{+}{\underset{}{\diagup}} \begin{array}{c} H \\ \vert \\ \vert \\ OH \end{array} \right] \cdots\cdots C_6H_5CO_2{}^-$$

$$(3\text{-}2)$$

$$\left[R_3Si^* \overset{+}{\underset{}{\diagup}} \begin{array}{c} H \\ \vert \\ \vert \\ OH \end{array} \right] \cdots\cdots C_6H_5CO_2{}^- \xrightarrow{\text{fast}} R_3Si^*OH + C_6H_5CO_2H$$

It should be noted that this interesting reaction does *not* give the benzoxysilane as the primary product, despite the fact that perbenzoic acid is usually considered to be a source of $[C_6H_5CO_2]^-$ and $[OH]^+$ in polar reactions. Considerable experimentation[16] has shown that (3-1) correctly represents the reaction course.

The mechanism for (3-1) is doubtless similar to the $S_{E}i$-Si mechanism proposed for chlorination and bromination of R_3Si^*H (*cf.* 3-2).

4. STEREOSPECIFIC HOMOGENEOUS HYDROSILATION OF 1-OCTENE

The great importance of hydrosilation, illustrated in (4-1) below, as a laboratory and industrial process is well known and needs no elaboration.
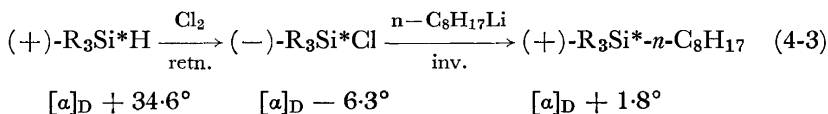
$$\equiv SiH + CH_2{=}CH{-}R \rightarrow \equiv SiCH_2CH_2R \qquad (4\text{-}1)$$

On the bases of considerable experimentation two research groups[17, 18] have concluded that hydrosilation catalyzed by chloroplatinic acid or Pt(II)-olefin complex, $((C_2H_4)PtCl_2)_2$, involves an intermediate in which silicon and alkyl are both bonded to a platinum centre, and that such intermediates may form adducts or revert to olefin which may be isomerized. The detailed mechanism advanced for homogeneous catalysis by Pt(II)-olefin is as follows[18].

$$(4\text{-}2)$$
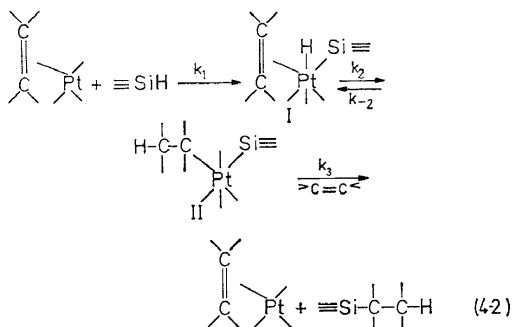
We have found that addition to 1-octene of R_3Si^*H proceeds with a high degree of stereospecificity with three catalyst systems: 5 per cent Pt-C, chloroplatinic acid, and $((C_2H_4)PtCl_2)_2$. Furthermore, all three catalysts give retention of configuration at the asymmetric silicon centre[19].

In view of previously assigned stereochemical paths for formation of R_3Si^*Cl from R_3Si^*H and for coupling of R_3Si^*Cl with RLi reagents[9], the stereochemical sequence given below shows that $(+)$-R_3Si^*H and $(-)$-R_3Si^*-n-C_8H_{17} have the same configuration.

$$(+)\text{-}R_3Si^*H \xrightarrow[\text{retn.}]{Cl_2} (-)\text{-}R_3Si^*Cl \xrightarrow[\text{inv.}]{n-C_8H_{17}Li} (+)\text{-}R_3Si^*\text{-}n\text{-}C_8H_{17} \qquad (4\text{-}3)$$

$$[\alpha]_D + 34{\cdot}6° \qquad [\alpha]_D - 6{\cdot}3° \qquad [\alpha]_D + 1{\cdot}8°$$

The infrared spectrum and elemental analysis of R_3Si^*-n-C_8H_{17} were completely consistent with the assigned structure, and the infrared spectra of the

hydrosilation products were identical with that of the authentic substance. Assuming that (4-3) gives optically pure product, the hydrosilation reactions proceeded with 90–100 per cent retention of configuration.

The finding of a highly stereospecific retention stereochemistry for asymmetric silicon in hydrosilation has some interesting mechanistic implications. For example, free silyl radicals or ions are clearly not involved, and the cleavage of the Si—H bond by the metal centre must proceed with virtually pure retention of configuration. Furthermore, the transfer of asymmetric silicon from the metal centre to olefinic carbon must also proceed with virtually pure retention of configuration.

There is a further stereochemical aspect of hydrosilation which has been explored previously. In a series of elegant studies, Benkeser and co-workers found that addition of Cl_3SiH to 1-alkynes in the presence of Pt-C or chloroplatinic acid proceeded in a *cis* manner to form *trans*-1-trichlorosilyl-1-alkenes[20]. Also, reaction of a large excess of Cl_3SiH with 1-methyl-d_3-cyclohexene in the presence of chloroplatinic acid gave *cis* addition to the ring[21]. More recently, it has been found[22] that addition of $MeHSiCl_2$ to 2-butyne in the presence of chloroplatinic acid proceeds in a *cis* manner with formation of *cis*-(2-methyldichlorosilyl)butene-2.

Retention of configuration at silicon and *cis* addition to olefin in hydrosilation are in harmony with mechanism sequence (4-2) if the following stereochemical processes are involved: (a) insertion of the platinum centre into the silicon-hydrogen bond proceeds with *retention* of configuration at silicon; (b) conversion of intermediate I to II results in *cis* addition of hydrogen and platinum to the double bond; (c) product formation from II takes place with *retention* of configuration at both silicon and carbon.

Retention of configuration in process (a) is reasonable, and *cis* addition of D_2 to fumaric acid, catalyzed by Ru(II), has been postulated to involve a process analogous to (b)[23]. Process (c) may be regarded as proceeding by a quasi-cyclic (S_Ni-Si) mechanism involving nucleophilic attack on silicon with *retention* of configuration, for which there is much precedent, and electrophilic attack on carbon with *retention* of configuration, which also has much precedent. A possible alternative to operation of (b) and (c) in hydrosilation is direct conversion of intermediate I to product *via* essentially concerted addition of Si* and H to olefin in a *cis* manner. However, intermediate II is almost certainly involved in olefin isomerization.

5. SYNTHESIS AND STEREOCHEMISTRY OF OPTICALLY ACTIVE $R_3Si^*Co(CO)_4$

Recent discovery of methods for the preparation of compounds containing the transition metal–silicon bond[18, 24, 25], together with the novel properties of these substances[26] has stimulated lively interest in this area of chemistry during the last three years. Because of the general interest in this new field and our own interest in the stereochemistry and mechanisms of reactions of R_3Si^*H catalyzed by transition metals, we have recently synthesized optically active $R_3Si^*Co(CO)_4$ by the method shown in (5-1)[24].
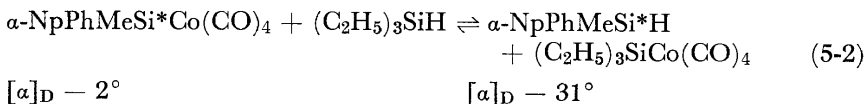
$$2\alpha\text{-NpPhMeSi}^*\text{H} + Co_2(CO)_8 \rightarrow 2\ \alpha\text{-NpPhMeSi}^*Co(CO)_4 + H_2 \quad (5\text{-}1)$$
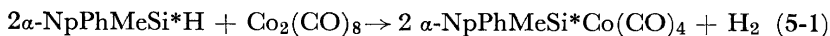
$[\alpha]_D - 35°$ $\qquad\qquad\qquad [\alpha]_D - 2°$

Optically active α-naphthylphenylmethylsilylcobalt tetracarbonyl, R_3Si^*-$Co(CO)_4$, I, was prepared in hydrocarbon solvent. It is a white, crystalline compound, m.p. 102–104·5°, which may be purified by fractional crystallization from pentane and heptane. *Anal.* Calcd. for $C_{21}H_{15}O_4CoSi$: C, 60·29; H, 3·61. Found: C, 60·39; H, 3·51. The infrared spectrum exhibits all the bands related to the α-NpPhMeSi*-moiety as well as the following absorptions which are characteristic of silylcobalt carbonyls: 2095 (s), 2040 (s), 2010 (vs), 1995 (vs, sh), 1960 (w). The sign of the plain optical rotatory dispersion curve of I is opposite that of the starting silane Specific rotations in heptane at a number of wavelengths are as follows: − 2° (589), + 5° (510), + 10° (490), + 50° (420), + 100° (388), + 200° (360). At 360 mμ the molecular rotation of I is approximately double that of optically pure $(−)R_3Si^*H$ and of opposite sign.

The original optically active silane, $(−)R_3Si^*H$, may be regenerated from I by Si*Co-SiH exchange with excess triethylsilane The optical rotation of the $(−)R_3Si^*H$ obtained in (5-2) indicates that the $R_3Si^*Co(CO)_4$ had a minimum optical purity of 88 per cent.

$$\alpha\text{-NpPhMeSi}^*Co(CO)_4 + (C_2H_5)_3SiH \rightleftharpoons \alpha\text{-NpPhMeSi}^*H$$
$$+ (C_2H_5)_3SiCo(CO)_4 \qquad (5\text{-}2)$$

$[\alpha]_D − 2°$ $\qquad\qquad\qquad\qquad\qquad [\alpha]_D − 31°$
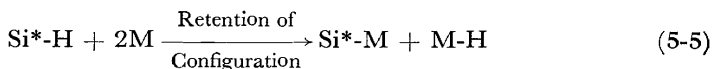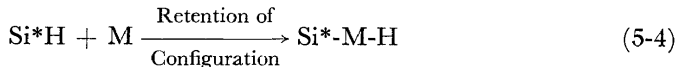
The overall stereochemical result of (5-1) and (5-2) is retention of configuration at the silicon centre.

Treatment of I with methanol, on the other hand, leads to $(+)R_3Si^*OCH_3$ having the opposite configuration from $(−)R_3Si^*H$.

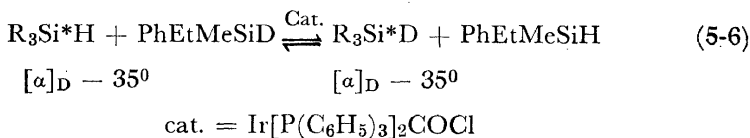$$R_3Si^*Co(CO)_4 + CH_3OH \rightarrow R_3Si^*OCH_3 \qquad (5\text{-}3)$$

$[\alpha]_D − 2°$ $\qquad\qquad\qquad\qquad\qquad [\alpha]_D + 8°$
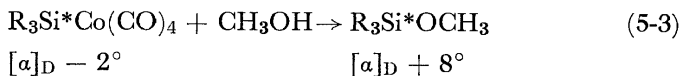
Since $HCo(CO)_4$ is an acid of approximately the same strength as HCl[27,] the $−Co(CO)_4$ group is a good leaving group and should be displaced from silicon with inversion of configuration according to the S_N2-Si Stereochemistry Rule. Inversion for (5–3) leads to assignment of retention of configuration to (5-1) and to (5-2). Thus, (5-1) and the formation of intermediate I in mechanism (4-2) for hydrosilation both *involve reaction of Si*-H with a transition metal centre to give Si*-M with retention of configuration.* In general terms, these processes may be formulated (M = transition metal centre):

$$\text{Si}^*\text{H} + \text{M} \xrightarrow[\text{Configuration}]{\text{Retention of}} \text{Si}^*\text{-M-H} \qquad (5\text{-}4)$$

$$\text{Si}^*\text{-H} + 2\text{M} \xrightarrow[\text{Configuration}]{\text{Retention of}} \text{Si}^*\text{-M} + \text{M-H} \qquad (5\text{-}5)$$

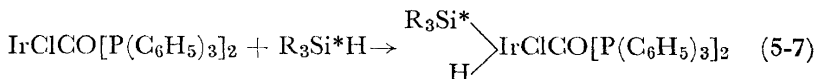*We believe that (5-4) and (5-5) have great, general significance for homogeneous as well as heterogeneous reactions of Si—H catalyzed by reactive transition metal centres.*
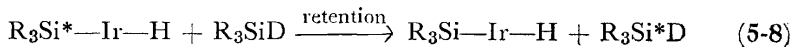
We have recently found that bis(triphenylphosphine)carbonylchloroiridium (I) is a catalyst for Si*H-SiD exchange in homogeneous solution and that such exchange proceeds with complete retention of configuration at the asymmetric silicon centre.

$$R_3Si^*H + PhEtMeSiD \underset{}{\overset{Cat.}{\rightleftharpoons}} R_3Si^*D + PhEtMeSiH \qquad (5\text{-}6)$$

$$[\alpha]_D - 35^0 \qquad\qquad [\alpha]_D - 35^0$$

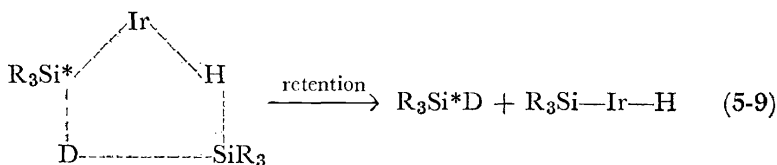$$cat. = Ir[P(C_6H_5)_3]_2COCl$$

In accord with general mechanism (5-4) we propose that (5-6) proceeds *via* the intermediate shown in (5-7) which is optically active and further that its formation as well as subsequent exchange processes occur with complete retention at the silicon centre.
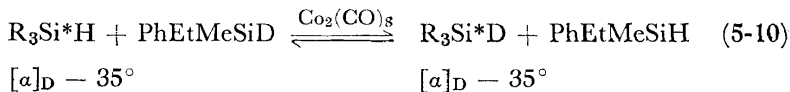
$$IrClCO[P(C_6H_5)_3]_2 + R_3Si^*H \rightarrow \begin{array}{c} R_3Si^* \\ \diagdown \\ H \diagup \end{array}\!\!\!IrClCO[P(C_6H_5)_3]_2 \quad (5\text{-}7)$$

Formation of the proposed complex in (5-7) is in accord with the reported[13] isolation of stable Ir (I) complexes formed from silanes in which silicon is bonded to highly electronegative groups, *i.e.*, from Cl_3SiH and $(RO)_3SiH$. At present we have no definitive mechanistic information concerning (5-8) except for a knowledge of the dynamic stereochemistry.
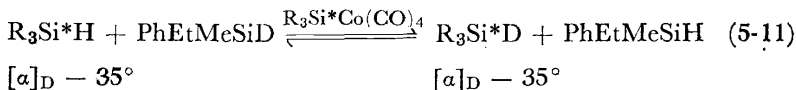
$$R_3Si^*—Ir—H + R_3SiD \xrightarrow{\text{retention}} R_3Si—Ir—H + R_3Si^*D \qquad (5\text{-}8)$$

One possibility for (5-8) is a quasi-cyclic 5-centre mechanism:

$$\begin{array}{c} \text{Ir} \\ R_3Si^* \diagup\quad\diagdown H \\ | \qquad\qquad | \\ D\text{------------}SiR_3 \end{array} \xrightarrow{\text{retention}} R_3Si^*D + R_3Si—Ir—H \qquad (5\text{-}9)$$

We have recently found that dicobalt octacarbonyl is a catalyst for Si*H—Si*D exchange in homogeneous solution and that exchange takes place with complete retention of configuration at the asymmetric silicon centre.

$$R_3Si^*H + PhEtMeSiD \underset{}{\overset{Co_2(CO)_8}{\rightleftharpoons}} R_3Si^*D + PhEtMeSiH \qquad (5\text{-}10)$$

$$[\alpha]_D - 35° \qquad\qquad [\alpha]_D - 35°$$

In accord with general mechanism (5-5), we proposed that optically active $R_3Si^*Co(CO)_4$ is an intermediate in (5-10), and that its formation and subsequent exchange proceed with complete retention of configuration. If this mechanistic hypothesis is correct, $R_3Si^*Co(CO)_4$ should function as an effective catalyst for Si*H—Si*D exchange with retention of configuration. This prediction was confirmed by experiment, which gave reaction (5-11).

$$R_3Si^*H + PhEtMeSiD \underset{}{\overset{R_3Si^*Co(CO)_4}{\rightleftharpoons}} R_3Si^*D + PhEtMeSiH \qquad (5\text{-}11)$$

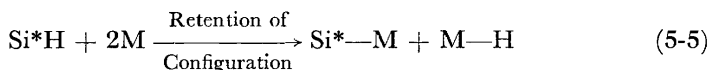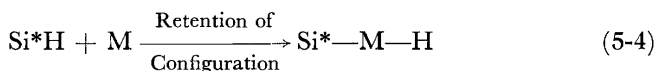$$[\alpha]_D - 35° \qquad\qquad [\alpha]_D - 35°$$

Reaction of $R_3Si^*Co(CO)_4$ with R_3SiD may proceed *via* a quasi-cyclic 4-centre mechanism, (5-12), although no mechanistic information other than its dynamic stereochemistry is presently known.

$$R_3Si^* \underset{D}{\overset{Co}{\diamond}} SiR_3 \xrightarrow{\text{retention}} R_3Si^*D + R_3Si\text{—}Co \qquad (5\text{-}12)$$
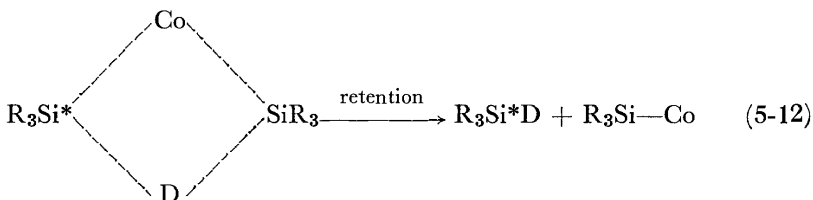
6. REACTIONS OF R_3Si^*H CATALYZED BY REACTIVE TRANSITION METAL CENTRES

We have recently formed the opinion that *reactive* transition metal centres give reactions of R_3Si^*H which involve first steps approximated in general terms by mechanisms (5-4) and (5-5) above and repeated here for emphasis.

$$Si^*H + M \xrightarrow[\text{Configuration}]{\text{Retention of}} Si^*\text{—}M\text{—}H \qquad (5\text{-}4)$$

$$Si^*H + 2M \xrightarrow[\text{Configuration}]{\text{Retention of}} Si^*\text{—}M + M\text{—}H \qquad (5\text{-}5)$$

We believe that (5-4) and (5-5) are important for general reactions of silicon-hydrogen bonds with *reactive* transition metal centres whether these are present in compounds such as $Co_2(CO)_8$, $((C_2H_4)PtCl_2)_2$, $IrClCO[P\text{-}(C_6H_5)_3]_2$, or in "heterogeneous" catalysts which *may or may not* comprise pure metal particles deposited on a carrier such as charcoal. Except for some of the homogeneous transition metal catalyzed reactions discussed in sections 4 and 5, detailed mechanisms cannot be proposed for the reactions whose stereochemistry is presented in this section. However, we believe that all of the reactions have the common feature of (5-4) or (5-5) as a first step.

It has long been known that the group VIII metals (as well as metal halides) catalyze the reactions of organosilicon hydrides with compounds containing the hydroxyl function[28].

$$R_3SiH + ZOH \xrightarrow{M} R_3SiOZ + H_2 \qquad (6\text{-}1)$$

$$Z = H, \text{ alkyl, aryl, acyl, etc.}$$
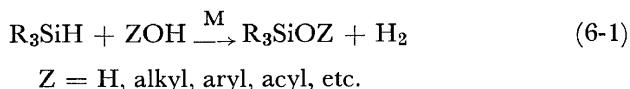
We have found that reactions (6-1) carried out with 10 per cent palladium on charcoal and Raney nickel catalysts are highly stereospecific and proceed with *inversion* of configuration. This finding of inversion is in harmony with our postulate of formation of a silicon–metal bond as a first step followed by invertive displacement of the silicon, as was the case for the reaction of $R_3Si^*Co(CO)_4$ with methanol in reaction (5-3). Data are presented in *Tables 1 and 2.*

Table 1. Palladium catalyzed[a] substitution reactions of $(-)$-R_3Si*H[b]

Reactant	Solvent	Product	Yield, %	$[\alpha]_D$[c]	Stereo specificity[d]
Water	CH_2Cl_2	$(+)$-R_3Si*OH	91	$+ 12$	81% invn
Methanol	p-Xylene	$(+)$-$R_3Si*OCH_3$	95	$+ 16$	97% invn
Cyclohexanol	CH_2Cl_2	$(-)$-$R_3Si*OC_6H_{11}$	89	$- 6.7$	93% invn
Cyclohexanol	p-Xylene[e]	$(-)$-$R_3Si*OC_6H_{11}$	86	$- 3.9$	75% invn
t-Butyl alcohol	CH_2Cl_2	$(-)$-$R_3Si*OC(CH_3)_3$	86	$- 11$	70% invn
Phenol	CH_2Cl_2	$(+)$-$R_3Si*OPh$	92	$+ 2$	63% invn[f]
Acetic acid	CH_2Cl_2	$(+)$-$R_3Si*OOCCH_3$	79	$+ 10$	79% invn
Benzoic acid	CH_2Cl_2	$(+)$-$R_2Si*OOCPh$	85	$+ 11$	80% invn

[a] 10% Pd-C; Matheson Coleman and Bell. [b] The $[\alpha]_D$ of the $(-)$-R_3Si*H used was $- 33.6°$. [c] Rotations (in degrees) taken in the solvent as reported in the literature. [d] A stereospecificity of 90%, for example, corresponds to a product which is 80% optically pure (20% racemic). Since the $(-)$-R_3Si*H used in this reaction series was not optically pure, these values are adjusted correspondingly. [e] Reaction mixture was heated at 80° for 1·5 hr. [f] based on a value of $[\alpha]_D + 9.5°$ for optically pure $R_3Si*OPh$, from unpublished results of R. Mason.

Table 2. Raney nickel[a] catalyzed substitution reactions of $(+)$-R_3Si*H[b]

Reactant	Solvent	Product	Yield, %	$[\alpha]_D$[c]	Stereo specificity[d]
Water	CH_2Cl_2	$(-)$-R_3Si*OH	97	$- 17$	94% invn
Methanol	p-Xylene	$(-)$-$R_3Si*OCH_3$	94	$- 16.6$	99% invn
Cyclohexanol	CH_2Cl_2	$(+)$-$R_3Si*OC_6H_{11}$	98	$+ 7.1$	95% invn
Cyclohexanol	p-Xylene	$(+)$-$R_3Si*OC_6H_{11}$	95	$+ 7.9$	99% invn
t-Butyl alcohol	CH_2Cl_2	$(+)$-$R_3Si*OC(CH_3)_3$	91	$+ 21$	88% invn
t-Butyl alcohol	p-Xylene	$(+)$-$R_3Si*OC(CH_3)_3$	93	$+ 22$	90% invn
Phenol	CH_2Cl_2	$(-)$-$R_3Si*OPh$	97	$- 8.7$	92% invn
Acetic Acid	CH_2Cl_2	$(-)$-$R_3Si*OOCCH_3$	84	$- 12$	83% invn
Benzoic Acid	CH_2Cl_2	$(-)$-$R_3Si*OOCPh$	85	$- 12$	83% invn

[a] No. 28 Raney Active Nickel Catalyst in Water, Raney Catalyst Division, W. R. Grace & Co. (water removed at reduced pressure and stored under xylene). [b] The α-NpPhMeSi*H used for this series was optically pure. [c] Rotation (in degrees) taken in the solvent as reported in the literature. [d] A stereospecificity of 90%, for example, refers to a product which is 80% optically pure (20% racemic). [e] Based on a value of $[\alpha]_D + 9.5°$ for optically pure $R_3Si*OPh$ from unpublished results of R. Mason.

The desired catalyst, 0·06 g, was mixed with a solution of 0·62 g of optically active R_3Si*H in 6 ml of the designated solvent. An equimolar amount of the reagent was added and the reaction was allowed to proceed at room temperature in an atmosphere of dry nitrogen. After evolution of hydrogen had ceased, products were isolated in good yields and identified by comparison of infrared spectra with those of authentic samples. With both catalysts, methanol was the most reactive, requiring 1–3 hours for complete reaction, and benzoic acid was the least reactive, requiring 2–4 days for complete reaction. Stereospecificity is generally better with nickel than with palladium on carbon, and reaction rates are not greatly different.

We have found[29] that (a) a wide variety of hydrosilation and substitution catalysts promote Si*H-Si*D exchanges that are much faster than either hydrosilation or substitution; and (b) *such exchanges proceed with nearly complete retention of configuration at the asymmetric centre in* (6-2).
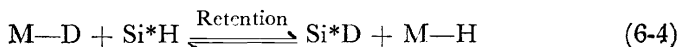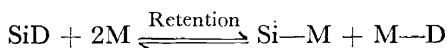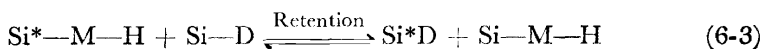
$$R_3Si*H + PhMeEtSiD \overset{cat.}{\rightleftharpoons} R_3Si*D + PhMeEtSiH \qquad (6-2)$$
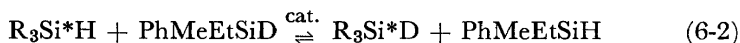
The data are summarized in *Table 3*.

Table 3. Transition metal catalyzed exchange reactions of $(+)$-R_3Si*H and $PhMeEtSiD$

Catalyst	Solvent	Contact time, min	$[a]^{25}_D$ of $R_3Si*H,D,$ deg	$[R_3Si*H]/$ $[R_3Si*D]$	$[PhMeEtSiH]/$ $[PhMeEtSiD]$	% ex change	Stereo-specificity
10% Pd-C[a]	CH_2Cl_2	1020	$+ 31.0$	1.0	1.1	100	95 %retn
10% Pd-C[a]	CH_2Cl_2	10	$+ 33.2$	1.0		100	98% retn
RaNi[b]	CH_2Cl_2	10	$+ 34.5$	1.1		>90	100% retn
5% Pt-C[c]	CH_2Cl_2	420	$+ 34.5$	1.2	1.4	100	100% retn
5% Pt-C[c]	CH_2Cl_2	15	$+ 34.6$	1.8		71	100% retn
10% Pd-C[a]	n-C_5H_{12}	60	$+ 34.2$	1.0	1.0	100	99% retn
10% Pd-C[a]	n-C_5H_{12}	10	$+ 34.0$	1.0	1.0	100	99% retn
Ra Ni[b]	n-C_5H_{12}	180	$+ 33.3$	1.2	1.4	100	98% retn
Ra Ni[b]	n-C_5H_{12}	10	$+ 33.6$	1.0	1.0	100	98% retn
5% Pt-C[c]	n-C_5H_{12}	30	$+ 33.4$	2.2	0.515	67	98% retn
H_2PtCl_6	CH_2Cl_2	180	$+ 34.5$	1.1		100	100% retn
Pt(II)[d]	C_6H_6	280	$+ 34.3$	1.0	1.0	100	100% retn

[a] 10% Pd-C, Matheson Coleman and Bell. [b] No. 28 Raney active nickel in water, Raney Catalyst Division, W. R Grace & Co. (water removed at reduced pressure and stored under pentane). [c] 5% Pt-C, Matheson Coleman and Bell. [d] $((C_2H_4)PtCl_2)_2$.

This finding of retention of configuration is in accord with formation of a silicon-metal bond as a first step followed by retentive exchange of Si*-M and Si-D as in reaction (5-2), but there are other mechanistic possibilities which may operate instead, for example (6-3) or (6-4).

$$Si*\text{—}M\text{—}H + Si\text{—}D \xrightleftharpoons{\text{Retention}} Si*D + Si\text{—}M\text{—}H \qquad (6\text{-}3)$$

$$SiD + 2M \xrightleftharpoons{\text{Retention}} Si\text{—}M + M\text{—}D$$

$$M\text{—}D + Si*H \xrightleftharpoons{\text{Retention}} Si*D + M\text{—}H \qquad (6\text{-}4)$$

If (6-4) is a realistic mechanism pathway, then H_2 and R_3Si*D should give isotopic exchange with retention of configuration in the presence of suitable catalysts. We have found that this is indeed the case. Data are presented in *Table 4.*

$$R_3Si*D + H_2 \xrightarrow{\text{cat.}} R_3Si*H + HD \qquad (6\text{-}5)$$
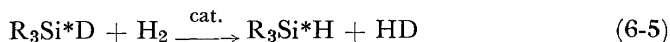
Table 4. Transition metal catalyzed reactions of $(+)$-R_3Si*D with H_2

Catalyst	$[a]^{25}_D$ of starting material deg	Contact time min	H_2 $\dagger$ ressure atm	$[a]^{25}_D$ of product, deg	% reaction	Stereo-specificity
10% Pd-C	$+ 33.2$	60	1.8	$+ 33.2$	100	100% retn
Ra Ni	$+ 33.2$	60	1.8	$+ 32.5$	100	98% retn
5% Pt-C	$+ 33.3$	60	1.8	$+ 33.3$	14	100% retn

The SiH–SiD exchange reactions were carried out by mixing the desired catalyst with a solution of 0.248 g (1 mmole) of optically active a-naphthyl-phenylmethylsilane and 0.151 g (1 mmole) of racemic phenylmethylethyl-

deuteriosilane in 5 ml of the designated solvent and stirring the mixture in an atmosphere of dry nitrogen. Scrambling of hydrogen and deuterium between the two available silanes was complete in 10 minutes at room temperature over palladium or nickel but took considerably longer when 5 per cent platinum on carbon was used. Infrared spectroscopy was used to determine the extent of exchange by comparing the relative intensities of the SiH band, $\sim 4 \cdot 75\ \mu$, and the SiD band, $\sim 6 \cdot 25\ \mu$, in each of the products.

Rapid exchange of deuteriosilane with hydrogen gas also occurred at room temperature. Optically active α-naphthylphenylmethyldeuteriosilane, 0·25 g, in 2·5 ml of pentane was shaken in a Parr hydrogenator under 1–2 atm of hydrogen gas in the presence of 25 mg of the designated catalyst, and the deuterium was rapidly replaced with hydrogen. Reaction was slower with platinum on carbon than when nickel or palladium catalysts were used. Retention stereochemistry was observed in all cases.

It has been reported[30] that each act of isotopic exchange between (+)-3-methylhexane and deuterium at position 3 of the hydrocarbon proceeds with *racemization*, in striking contrast to *retention* for R_3Si^*H.

Although a great deal of work remains to be done before the detailed mechanisms of reactions (6-1), (6-2) and (6·5) are elucidated, the stereo-chemical studies already prove that free silicon radicals or ions are not involved as intermediates in those reactions, and we feel that (5-4) and (5-5) probably represent important mechanistic pathways for Si—H and reactive transition metal centres.

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