silane (0.0280 *M*) and hydrogen chloride (0.08 *M*) at 24.4° was followed as a function of time. From the magnitude of the initial positive rotation and from the linearity of the resulting first-order rate plot, it was clear that the methoxysilane was essentially completely racemic before the first reading could be taken (~1 min).

Acid-Catalyzed Reaction of R_3Si^*F with MeOH in the Presence of $Th(NO_3)_4$. To a 25-ml glass-stoppered flask were added R_3Si^*F (0.250 g, 0.940 mmol), thorium nitrate (1.30 g, 2.61 mmol), 10 ml of carbon tetrachloride, 8.6 ml of dry methanol, and 1.4 ml of a 1.45 *M* solution of hydrogen chloride in methanol. After mixing thoroughly, the resulting solution was allowed to stand for 90 min. At the end of the reaction period, the solution was diluted with ether (50 ml) and washed well with water, then dried over anhydrous sodium sulfate. Volatiles were removed at reduced pressure, the residue was dissolved in 2 ml of carbon tetrachloride, and an infrared spectrum was taken. Comparison of this spectrum with those of known mixtures showed the reaction product to consist of about 70% methoxysilane and 30% fluorosilane. Both were racemic.

Racemization of R_3Si^*F Catalyzed by *c*-$C_6H_{11}NH_3F$. Standard methanolic solutions of cyclohexylammonium fluoride were prepared. The variation of the pseudo-first-order rate constant for the racemization of (−)-fluorosilane (0.0470 *M*) at 24.4° in 5% methanol in carbon tetrachloride was studied as a function of cyclohexylammonium fluoride concentration.

Racemization of R_3Si^*F in ROH/CCl_4 Solvent Mixtures. In this series of experiments, the rate of racemization of (+)-fluorosilane (0.0470 *M*) was determined in mixtures of different alcohols in carbon tetrachloride at 24.4°, all at equivalent concentrations. The procedure was the same as that already described.

Stereochemistry of Asymmetric Silicon. XV. Stereospecific Hydrosilation and Exchange Reactions of $R_3Si^*H(D)$ Catalyzed by Group VIII Metal Centers[1,2]

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Contribution from the Department of Chemistry, University of California at Davis, Davis, California 95616. *Received May 23, 1969*

Abstract: The addition of R_3Si^*H to olefins (hydrosilation) catalyzed by transition metal centers proceeds with *retention* of configuration as do Si*H–Si*D isotopic-exchange reactions. The data are accommodated by the general mechanistic conclusion that the initial process in these reactions involves stereospecific *retentive* interaction of the Si*–H bond with the reactive transition metal center to form a metal-silicon bond which then reacts in a variety of ways with complete retention of configuration in hydrosilation and isotopic exchange reactions.

The first example of hydrosilation, addition of a silicon hydride to an olefin, involved reaction of trichlorosilane with 1-octene in the presence of diacetyl peroxide and was reported in 1947.[3] During the next two decades hydrosilation became an exceedingly important laboratory and industrial process, and it was discovered that platinum–charcoal and chloroplatinic acid are very effective catalysts.[4]

$$\equiv SiH + CH_2{=}CHR \xrightarrow[\text{or}\ H_2PtCl_6]{Pt\text{-}C} \equiv SiCH_2CH_2R \qquad (1)$$

Beginning with the observation that primary alkylsilanes often result from reactions involving nonterminal olefins, as in reaction 2,[5] Speier and coworkers

$$Cl_2(CH_3)SiH + CH_3CH{=}CHCH_2CH_3 \xrightarrow{H_2PtCl_6} CH_3(CH_2)_3CH_2Si(CH_3)Cl_2 \qquad (2)$$

have engaged in an intensive study of the mechanism of reactions 1.[6] This work revealed that platinum-catalyzed hydrosilation is often accompanied by olefin isomerization which is significantly altered by the presence of silane,[6a–c] and that hydrosilation carried out with Cl_3SiD results in extensive exchange between Si–D and C–H of the olefin plus the formation of adducts having deuterium widely distributed in their structures as in reaction 3.[6c] It was also demonstrated that the silicon-hydrogen bond is extremely labile in the presence of platinum[7] and chloroplatinic acid,[6c] resulting in SiH–SiD exchange at room temperature (4).

$$3.56Cl_3SiD + CH_2{=}C(CH_3)_2 \xrightarrow{H_2PtCl_6} Cl_3SiC_4H_{6.5}D_{2.5} + 1.5Cl_3SiH + Cl_3SiD \qquad (3)$$

$$R_3SiD + R_3'SiH \underset{\text{or}\ H_2PtCl_6}{\overset{Pt\text{-}C}{\rightleftharpoons}} R_3SiH + R_3'SiD \qquad (4)$$

In a significant extension of the above studies, Chalk and Harrod[8] have reported that a Pt(II)–olefin complex, $((C_2H_4)PtCl_2)_2$, provides homogeneous catalysis of hydrosilation and concurrent olefin isomerization, and that the presence of silane markedly affects the olefin isomerization profile. It is also found[8] that the Pt(II)–olefin catalyst gave results very similar to those obtained with chloroplatinic acid. In addition, it was reported that a phosphine complex of iridium(I) cleaved a variety of

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(1) For the preceding paper in this series, see L. H. Sommer and D. L. Bauman, *J. Am. Chem. Soc.*, **91**, 7045 (1969).

(2) In its initial stages this work was supported by a grant from Dow Corning Corp. and carried out in part at the Pennsylvania State University.

(3) L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, *J. Am. Chem. Soc.*, **69**, 188 (1947).

(4) For an excellent review up to about 1959, see C. Eaborn, "Organosilicon Compounds," Academic Press, New York, N. Y., 1960, pp 45–64.

(5) J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Am. Chem. Soc.*, **79**, 974 (1957).

(6) (a) J. L. Speier and J. C. Saam, *ibid.*, **80**, 4104 (1958); (b) *ibid.*, **83**, 1351 (1961); (c) J. W. Ryan and J. L. Speier, *ibid.*, **86**, 895 (1964); (d) M. C. Musolf and J. L. Speier, *J. Org. Chem.*, **29**, 2519 (1964); (e) J. W. Ryan and J. L. Speier, *ibid.*, **31**, 2698 (1966).

(7) V. A. Ponomarenko, *et al.*, *Dokl. Akad. Nauk SSSR*, **131**, 321 (1960).

(8) A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 16 (1965).

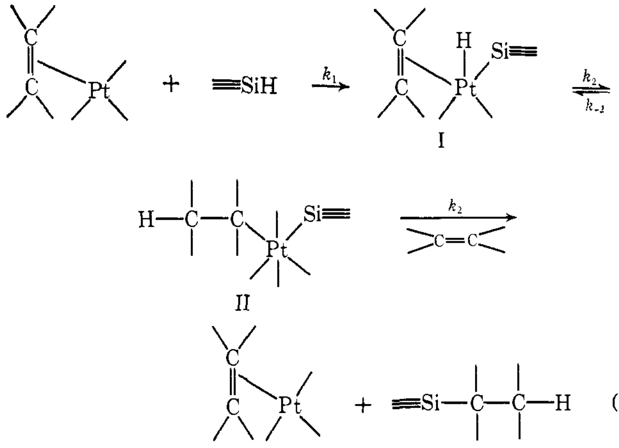
Table I. Hydrosilation of 1-Octene with $(+)R_3Si^*H$[a]

Run no.[b]	Catalyst	Reaction temp, °C	Reaction time	[α]D of product, deg	Yield, %	Predominant stereochemistry,[d,e] % retention
1[c]	Pt-C	130–140	24 hr	−1.8	85	100
2	$H_2PtCl_6 \cdot 6H_2O$	130–140	24 hr	−1.8	75	100
3	$H_2PtCl_6 \cdot 6H_2O$	∼25	2 weeks	−1.7	61	97
4	Pt(II)–olefin	130–140	65 hr	−1.5	56	92
5	Pt(II)–olefin	∼25	2 weeks	−1.4	27	89

[a] The α-naphthylphenylmethylsilane reactant had [α]D +34.6°. [b] Runs 1, 2, and 4 used a 1:2 molar ratio of silane to olefin, 5 g of R_3Si^*H, and 10 mg of catalyst for each run. Runs 3 and 5 used a 1:4 molar ratio of silane to olefin, 3 g of R_3Si^*H, 10 mg of catalyst for run 3, and 20 mg of catalyst for run 5. [c] The room temperature Pt–C reaction is very slow relative to runs 3 and 5. [d] A predominant stereochemistry of, say, 90% retention means that the product was 80% optically pure and that the reaction formally gave a reaction path comprising 90% retention and 10% inversion. [e] $R_3Si^*\text{-}n\text{-}C_8H_{17}$ having [α]D 1.8° is assumed to be optically pure, based on previous studies which have shown that R_3Si^*Cl and RLi give products of high optical purity.[11]

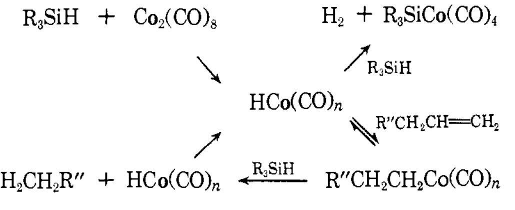
silicon hydrides, retaining both the hydride and silicon fragments in the iridium coordination sphere.

On the basis of the above results, both research groups[6c,8] have concluded that hydrosilation catalyzed by chloroplatinic acid or Pt(II)–olefin involves an intermediate in which silicon and alkyl are both bonded to a platinum center, and that such intermediates may form adducts or revert to olefin which may be isomerized. The detailed mechanism advanced for catalysis by Pt(II)-olefin is as follows.[8]



(5)

The behavior of silanes in the presence of dicobalt octacarbonyl, on the other hand, is quite different.[9] Although a compound having a silicon–cobalt bond is formed, it is not believed to be an intermediate in the hydrosilation reaction. Exchange processes such as (4) are believed to involve the initial formation of the silicon–cobalt bond. The cobalt-catalyzed reactions occurring during hydrosilation and exchange are summarized below.[9]



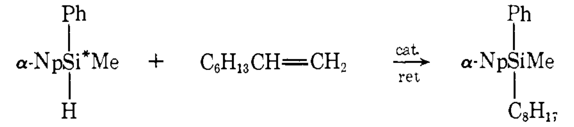
(6)

$$R'_3SiH + R_3SiCo(CO)_4 \rightleftharpoons R_3SiH + R'_3SiCo(CO)_4 \quad (7)$$

A wide variety of reactive transition metal centers, which may be either soluble metal complexes or part of a heterogeneous metal surface, catalyze both hydrosilation and SiH–SiD exchange. Indeed, mechanistic analogies may exist between the homogeneous and heterogeneous catalytic processes which could involve a series of interesting species possessing a silicon–metal band. The availability of optically active α-naphthylphenylmethylsilane, R_3Si^*H, has enabled us to study the dynamic stereochemistry of the interaction of the silicon–hydrogen bond with reactive transition metal centers in relation to both heterogeneous and homogeneous catalysis.

Results and Discussion

Hydrosilation. We have shown that addition to 1-octene of an optically active silane, α-naphthylphenylmethylsilane, R_3Si^*H, proceeds with a high degree of stereospecificity with three catalyst systems: 5% Pt-C, chloroplatinic acid, and $((C_2H_4)PtCl_2)_2$. Furthermore, as indicated in Table I, *all three catalysts give retention of configuration at the asymmetric silicon center.*[10]



$$\alpha\text{-NpSi}^*(\text{Ph})(\text{Me})\text{H} + C_6H_{13}CH{=}CH_2 \xrightarrow[\text{ret}]{\text{cat.}} \alpha\text{-NpSi}(\text{Ph})(\text{Me})C_8H_{17} \quad (8)$$

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,[11] the stereochemical sequence given below shows the $(+)R_3Si^*H$ and $(-)R_3Si^*\text{-}n\text{-}C_8H_{17}$ have the same configuration.

$$\underset{[\alpha]D\ +34.6°}{(+)R_3Si^*H} \xrightarrow[\text{ret}]{Cl_2} \underset{[\alpha]D\ -6.3°}{(-)R_3Si^*Cl} \xrightarrow[\text{inv}]{n\text{-}C_8H_{17}Li} \underset{[\alpha]D\ +1.8°}{(+)R_3Si^*\text{-}n\text{-}C_8H_{17}} \quad (9)$$

The finding of a highly stereospecific retention stereochemistry for asymmetric silicon in hydrosilation has some interesting mechanistic implications. For example, the cleavage of the Si–H bond by the metal center must proceed with virtually pure retention of configuration. Furthermore, the transfer of asymmetric silicon from the metal center 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

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(9) A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, 89, 1640 (1967).

(10) L. H. Sommer, K. W. Michael, and H. Fujimoto, *J. Am. Chem. Soc.*, **89**, 1519 (1967).

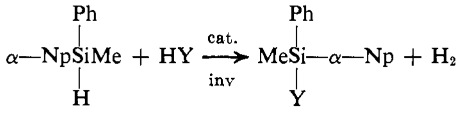
(11) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965; L. H. Sommer, W. D. Korte, and P. G. Rodewald, *J. Am. Chem. Soc.*, **89**, 862 (1967).

elegant studies, Benkeser and coworkers 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.[12] 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.[13] More recently, it has been found[4e] 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 5 if the following stereochemical processes are involved: (a) insertion of the platinum center 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.[14] Process c may be regarded as proceeding by a quasi-cyclic (SNi–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.

The important and interesting question concerning whether Pt–C in the present work is really functioning as a heterogeneous catalyst for hydrosilation, or whether traces of Pt(II) or Pt(IV) on its surface comprise the real catalyst and are extracted by the reaction medium, is not answered by the demonstration of highly stereospecific retention of configuration for R_3Si^*H addition to 1-octene. Stereospecific replacement reactions of R_3Si^*H using group VIII metal catalysts such as supported palladium, rhodium, ruthenium, and Raney nickel in *heterogeneous* reactions have been found to proceed with *inversion* of configuration.[15,16] Thus, high stereospecificity at asymmetric silicon does not prove homogeneous catalysis, and the finding of a *retention* stereochemistry for R_3Si^*H in hydrosilation is not a trivial one.



$$\alpha\text{—Np}\underset{\text{H}}{\overset{\text{Ph}}{\text{Si}}}\text{Me} + \text{HY} \xrightarrow[\text{inv}]{\text{cat.}} \text{Me}\underset{\text{Y}}{\overset{\text{Ph}}{\text{Si}}}\text{—}\alpha\text{—Np} + \text{H}_2 \qquad (10)$$

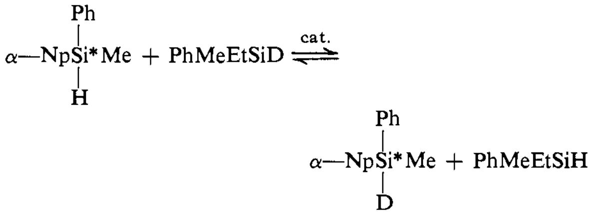
Y = —OH, —OR, —OCOR, —OAr, —NR_2, —NHR

Although dicobalt octacarbonyl has been reported to be an effective catalyst for the hydrosilation of olefins,[9] reaction of 1-octene with R_3Si^*H proceeded very slowly at 60°. Low yields of (−)-α-naphthylphenylmethyl-*n*-octylsilane, $[\alpha]_D$ −0.62°, were obtained and the product was obviously impure. Dicobalt octacarbonyl, however, does catalyze Si*H–Si*D exchange at a reasonable rate.

It has become apparent that the initial step in both hydrosilation (8) and substitution (10) reactions is the interaction of the silane with the reactive transition metal center. In order to gain insight into the nature of group VIII metal catalyzed reactions of the silicon–hydrogen bond it is necessary to understand those interactions which are occurring between the silane and the catalyst itself. The next section furnishes some instructive data.

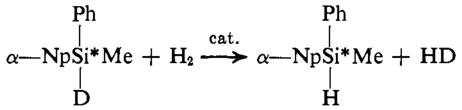
Exchange Processes. The observation that reactions 8 and 10 are highly stereospecific implies that if Si*H–Si*H exchange processes are rapid and concurrent in reactions 8 and 10, they must proceed with an exceedingly high degree of retention of configuration.

Our results[17] show 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 center* (11).



$$\alpha\text{—Np}\underset{\text{H}}{\overset{\text{Ph}}{\text{Si}}}{}^*\text{Me} + \text{PhMeEtSiD} \overset{\text{cat.}}{\rightleftharpoons} \alpha\text{—Np}\underset{\text{D}}{\overset{\text{Ph}}{\text{Si}}}{}^*\text{Me} + \text{PhMeEtSiH} \qquad (11)$$

In addition we have found that optically active α-naphthylphenylmethylsilane reacts rapidly with hydrogen gas in the presence of palladium and nickel catalysts (12), the configuration of the starting silane being nearly completely retained.[17a] The results of these experiments are listed in Tables II–V.



$$\alpha\text{—Np}\underset{\text{D}}{\overset{\text{Ph}}{\text{Si}}}{}^*\text{Me} + \text{H}_2 \xrightarrow{\text{cat.}} \alpha\text{—Np}\underset{\text{H}}{\overset{\text{Ph}}{\text{Si}}}{}^*\text{Me} + \text{HD} \qquad (12)$$

Although retention stereochemistry is observed for all the exchange processes which we have investigated, it is obvious that the mechanistic pathways are not the same for all catalyst systems. In some instances catalytic activity may best be explained by the intermediacy of a species having a transition metal–silicon bond. In other cases SiH–MH exchanges may be occurring which need not involve a silicon–metal bond at any stage in the reaction. Some of the reactions catalyzed by metal complexes clearly occur in solution while reactions over supported metal catalysts are most probably examples of heterogeneous catalysis. While similarities may exist between homogeneous and heterogeneous catalytic processes, it is convenient to separate the two for the purpose of discussion.

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[12] R. A. Benkeser and R. A. Hickner, *J. Am. Chem. Soc.*, **80**, 5298 (1958); R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Swisher, *ibid.*, **83**, 4385 (1961).

[13] T. G. Selin and R. West, *ibid.*, **84**, 1863 (1962).

[14] J. Halpern, J. F. Harrod, and B. R. James, *ibid.*, **88**, 5150 (1966). We are indebted to a referee for calling our attention to this reference and to the possibility of operation of process b.

[15] L. H. Sommer and J. E. Lyons, *J. Am. Chem. Soc.*, **89**, 1521 (1967).

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

[17] (a) L. H. Sommer, J. E. Lyons, K. W. Michael, and H. Fujimoto, *ibid.*, **89**, 5483 (1967); (b) L. H. Sommer and J. E. Lyons, *ibid.*, **90**, 4197 (1968).

Table II. Exchange Reactions Catalyzed by Transition Metal Complexes

			Products				Predominant
Catalyst	Solvent	Contact time, min	$[\alpha]D^{25}$ of R_3Si^*H,D, deg	$[R_3Si^*H]/[R_3Si^*D]$	[PhMeEtSiH]/[PhMeEtSiD]	% exchange	stereochemistry,[d] % retention
$IrClCO(PPh_3)_2$	C_6H_6	1020	+35[b]	1.0	1.0	100	100
$Co_2(CO)_8$	$n\text{-}C_6H_{14}$[a]	1440	+35[b]	1.0	1.1	100	100
$R_3Si^*Co(CO)_4$	$n\text{-}C_6H_{14}$[a]	1440	+35[b]	1.0	1.1	100	100
$H_2PtCl_6\cdot 6H_2O$	CH_2Cl_2	180	+34.5[c]	1.1		100	100
$[(C_2H_4)PtCl_2]_2$	C_6H_6	280	+34.3[c]	1.0	1.0	100	100

[a] Reaction carried out in refluxing hexane (68°). [b] [α]D of starting silane is +35°. [c] [α]D of starting silane is +34.5°. [d] Defined as in Table I.

Table III. Transition Metal Catalyzed Exchange Reactions between (+)-α-NpPhMeSi*D and Racemic PhMeEtSiH[a]

			Products				
Catalyst	Solvent	Contact time, min	$[\alpha]^{25}D$ of R_3Si^*H,D, deg	[α-NpPhMeSi*H][e]/[α-NpPhMeSi*D]	[PhMeEtSiH][e]/[PhMeEtSiD]	% exchange[f]	Predominant stereochemistry,[g] % retention
10% Pd-C[b]	CH_2Cl_2	1020	+31.0	1.0	1.1	100	95
10% Pd-C[b]	CH_2Cl_2	10	+33.2	1.0		100	98
Raney Ni[c]	CH_2Cl_2	10	+34.5	1.1		>90	100
5% Pt-C[d]	CH_2Cl_2	420	+34.5	1.2	1.4	100	100
5% Pt-C[d]	CH_2Cl_2	15	+34.6	1.8		71	100
10% Pd-C[b]	$n\text{-}C_5H_{12}$	60	+34.2	1.0	1.0	100	99
10% Pd-C[b]	$n\text{-}C_5H_{12}$	10	+34.0	1.0	1.0	100	99
Raney Ni[c]	$n\text{-}C_5H_{12}$	180	+33.3	1.2	1.4	100	98
Raney Ni[c]	$n\text{-}C_5H_{12}$	10	+33.6	1.0	1.0	100	98
5% Pt-C[d]	$n\text{-}C_5H_{12}$	30	+33.4	2.2	0.515	67	98

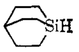
[a] Reactions carried out at room temperature (24 ± 1°) using 1 mmol of each silane, 30–40 mg of catalyst, and 5 ml of the designated solvent. [b] 10% Pd–C, dried over P_2O_5 *in vacuo*. [c] No. 28 Raney active nickel in water, Raney catalyst Division, W. R. Grace and Co., Silver Springs, Md. (water removed at reduced pressure and stored under pentane). [d] 5% Pt–C, untreated. [e] Ratios calculated according to eq i (Experimental Section). [f] Extent of exchange calculated according to eq ii (Experimental Section). [g] Defined in Table I.

Table IV. Transition Metal Catalyzed Reactions[a] of (+)-α-NpPhMeSi*D with H_2 (26)

Catalyst	$[\alpha]^{25}D$ of starting material, deg	Contact time, min	H_2 pressure, atm	$[\alpha]^{25}D$ of product, deg	% reaction	Predominant stereochemistry,[b] % retention
10% Pd-C[c]	+33.2	60	1.8	+33.2	100	100
Raney Ni[d]	+33.2	60	1.8	+32.3	100	100
5% Pt-C[e]	+33.3	60	1.8	+33.3	14	100
$IrClCO(PPh_3)_2$	+35.0[f]	1200	1.9		<5	

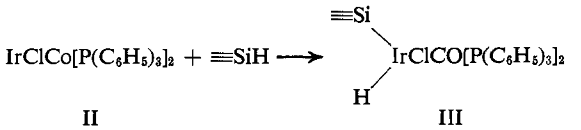
[a] Reactions were carried out at room temperature (24 ± 1°) in *n*-pentane, unless otherwise noted. [b] Defined in Table I. [c] Dried over P_2O_5 *in vacuo*. [d] Dried No. 28 active Raney nickel. [e] Untreated catalyst. [f] Reaction carried out in benzene.

Table V. Palladium[a] Catalyzed Exchange Reactions[b] of (+)-α-NpPhMeSi*D[c] and $R_3'SiH$

		Product			
$R_3'SiH$	Contact time, min	$[\alpha]^{25}D$ of R_3Si^*H, D, deg	[α-NpPhMeSi*H][d]/[α-NpPhMeSi*D]	% exchange[e]	Predominant stereochemistry,[f] % retention
$(C_2H_5)_3SiH$	15	+34.5	0.72	80	99
	15	+35.0	0.12	22	100
	15	+35.0	0.10	15	100

[a] 10% Pd- C dried over P_2O_5 *in vacuo*. [b] Reactions were carried out at room temperature (24 ± 1°) in *n*-pentane solutions which were 25 *M* in each silane and contained 10 mg of catalyst per milliliter of solution. [c] The starting silane was optically pure [α]D +35°. [d] Calculated according to eq i. [e] Calculated according to eq ii. [f] Defined in Table I.

Homogeneous Catalysis by Group VIII Metal Complexes. There are two general ways in which a metal complex may interact with an organosilicon hydride to form a metal–silicon bond:[9,10,18] coordinative addition of the silane to the metal complex (13); replacement of H by the metal (14, 15).



$$IrClCo[P(C_6H_5)_3]_2 + \equiv SiH \longrightarrow (\equiv Si)(H)IrClCO[P(C_6H_5)_3]_2 \quad (13)$$

II III

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(18) (a) W. Jetz and W. Graham, *J. Org. Chem.*, 89, 2773 (1967); (b) B. J. Aylett and J. M. Campbell, *Chem. Commun.*, 159 (1967); (c) A. P. Hagen and A. G. MacDiarmid, *Inorg. Chem.*, 6, 686 (1966).

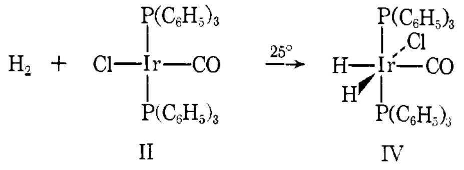
$$Co_2(CO)_8 + {\equiv}SiH \longrightarrow {\equiv}SiCo(CO)_4 + HCo(CO)_4 \quad (14)$$

$$HCo(CO)_4 + {\equiv}SiH \longrightarrow {\equiv}SiCo(CO)_4 + H_2 \quad (15)$$

Dicobalt octacarbonyl I has been found to catalyze both the hydrogenation and the hydrosilation of olefins.[9] Bis(triphenylphosphine)carbonylchloroiridium (I), compound II, is an effective catalyst for homogeneous hydrogenation of olefins as well as for H_2–D_2 exchange processes (16).[19] It was of considerable interest, therefore, to examine the stereochemistry of catalytic processes involving organosilanes in the presence of these two substances. Both compounds catalyze the Si*H–Si*D exchange reaction (11) with *complete retention* of configuration at the asymmetric center (Table II). When II is present in catalytic amounts, the exchange goes to completion in several hours at room temperature.[20] It is probable that exchange proceeds through an unstable, optically active Ir(I)–Si*H addition complex III such as in eq 13.[21]

$$H_2 + D_2 \overset{Ir(I)}{\rightleftharpoons} 2HD \quad (16)$$

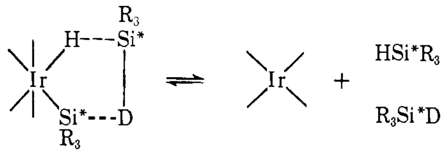
Vaska[22] has shown that hydrogen adds readily to bis(triphenylphosphine)carbonylchloroiridium (I) to form a *cis*-Ir(I) compound IV (17). The hydrogen addition compound has been proposed as an intermediate in the homogeneous Ir(I)-catalyzed hydrogen–deuterium exchange process (16).[19] Heterogeneous palladium, platinum, and nickel catalysts which promote hydrogen–deuterium exchange (16) also catalyze stereospecific H_2–Si*D exchange (12).[17a] The latter exchange does not occur in the presence of the Ir(I) complex, II, however. Instead II was converted to the relatively stable hydrogen adduct, IV, which was not catalytically active.



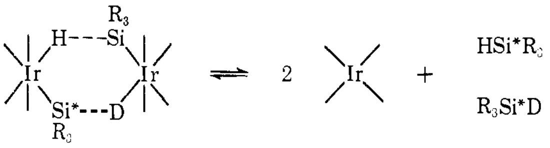
(17)

II IV

There are two alternative schemes (18, 19) which may be proposed to account for the Si*H–Si*D exchange process, assuming the stereospecific formation of an Ir(I)–Si*H adduct, III, in the first step. Several mechanistic pathways, some of which may involve seven- or eight-coordinate iridium,[23] are also possible, however.



(18)



(19)

Dicobalt octacarbonyl, I, is a less effective catalyst for Si*H–Si*D exchange than is the Ir(I) complex, II, however at slightly elevated temperatures (68°) exchange is complete within 24 hr. The reason for the low catalytic activity of I may be that trialkyl- and triarylsilanes react with dicobalt octacarbonyl to form relatively stable compounds (14, 15)[9] of the type $R_3SiCo(CO)_4$.

Chalk and Harrod have shown that compounds containing a silicon–cobalt bond undergo exchange (20) with organosilicon hydrides.[9] It seems probable, therefore, that such a process is the pathway through which Si*H–Si*D exchange occurs in the presence of catalytic amounts of I. Our observation *that Si*H–Si*D exchange is catalyzed by small amounts of $R_3Si^*Co(CO)_4$ supports this conclusion.*

$$R_3SiCo(CO)_4 + R_3'SiH \rightleftharpoons R_3'SiCo(CO)_4 + R_3SiH \quad (20)$$

We have shown that optically active α-naphthylphenylmethylsilylcobalt tetracarbonyl, V, can be prepared (21) by the reaction of $(-)R_3Si^*H$ with I. Furthermore, V undergoes stereospecific exchange with triethylsilane (22). The over-all result of reactions 21 and 22 is retention of configuration at the asymmetric silicon center.

$$\underset{[\alpha]_D\ -35°}{2(-)R_3Si^*H} + \underset{I}{Co_2CO_8} \longrightarrow \underset{[\alpha]_D\ -2°,\ V}{2(-)R_3Si^*Co(CO)_4} + H_2 \quad (21)$$

$$\underset{[\alpha]_D\ -2°,\ V}{(-)R_3Si^*Co(CO)_4} + (C_2H_5)_3SiH \rightleftharpoons \underset{[\alpha]_D\ -31°}{(-)R_3Si^*H} + (C_2H_5)_3SiCo(CO)_4 \quad (22)$$

Treatment of V with methanol, on the other hand, leads to $(+)R_3Si^*OCH_3$ having the opposite configuration from $(-)R_3Si^*H$ (23).[24] Since $HCo(CO)_4$ is an acid of approximately the same strength as HCl,[25] the $-Co(CO)_4$ group would be expected to be a good leaving group from silicon.[26] Hence, reaction 23 can be tentatively assigned inversion stereochemistry. This requires the assignment of retention for reactions 21 and 25.

$$\underset{[\alpha]_D\ -2°}{(-)R_3Si^*Co(CO)_4} + CH_3OH \longrightarrow \underset{[\alpha]_D\ +8°}{(+)R_3Si^*OCH_3} \quad (23)$$

(+)Neopentylphenylmethylsilane behaves in a similar manner; the over-all exchange process occurs with retention. The silylcobalt carbonyl was not isolated in

$$\underset{[\alpha]_D\ +6°\ (c\ 4\ \text{in toluene})}{(+)\text{-neo-}C_5H_{11}PhMeSi^*H} + Co_2(CO)_8 \xrightarrow[25°]{\text{toluene}} \left[\underset{[\alpha]_D\ -43°}{(-)\text{-neo-}C_5H_{11}PhMeSi^*Co(CO)_4}\right]$$

$$\xrightarrow{Ph_3SiH,\ \text{excess}} \underset{[\alpha]_D\ +6°}{(+)\text{-neo-}C_5H_{11}PhMeSi^*H} + Ph_3SiCo(CO)_4$$

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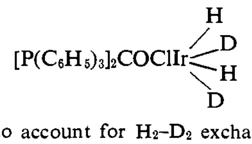
[19] C. G. Eberhardt and L. Vaska, *J. Catal.*, **8**, 183 (1967).

[20] Infrared spectroscopy was used to determine the extent of exchange by comparing the relative intensities of the Si–H band, ~4.75 μ, and the Si–D band, ~6.25 μ, in each of the products.

[21] Chalk and Harrold[9] report that only silanes possessing highly electronegative groups form complexes, with $IrCl(CO)(PPh_3)_2$. Stable adducts are not formed from trialkyl- and triarylsilanes.

[22] L. Vaska and R. E. Rhodes, *J. Am. Chem. Soc.*, **87**, 4970 (1965).

[23] The eight-coordinate iridium species



has been proposed[19] to account for H_2–D_2 exchange in homogeneous solution when 11 is used as the catalyst.

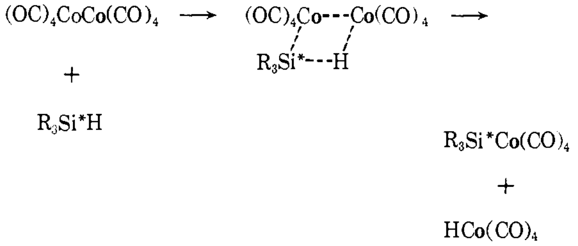
[24] L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Am. Chem. Soc.*, **86**, 327 (1964).

[25] I. Wender, *et al.*, U. S. Bureau of Mines Bulletin No. 600, 1962, p 29.

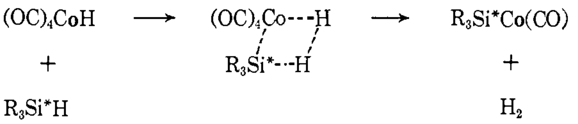
[26] L. H. Sommer, G. A. Parker, N. C. Lloyd, C. L. Frye, and K. W. Michael, *J. Am. Chem. Soc.*, **89**, 857 (1967).

this case, however ir and ORD data for hydrocarbon solutions were comparable with I.

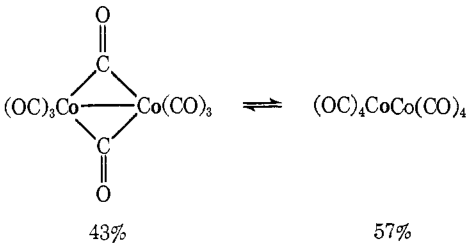
It has been shown[9] that the formation of V (24) may take place in two separate steps (14, 15). The retention stereochemistry observed for these reactions makes four-center mechanisms (24, 25) appear quite attractive.[27] It is probable that the majority of reaction 21



(24)



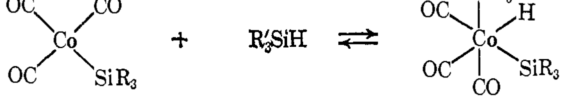
(25)



takes place according to eq 24 since it has been shown that cobalt hydrocarbonyl reacts rapidly to form dicobalt octacarbonyl in hydrocarbon solution.[9,25]

$$2HCo(CO)_4 \longrightarrow Co_2(CO)_8 + H_2 \qquad (26)$$

Chalk and Harrod[9] have suggested a mechanism (27)

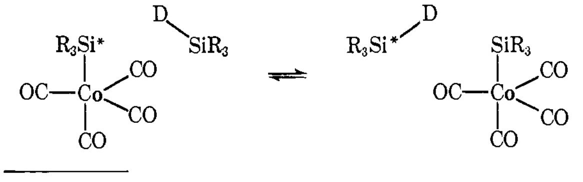


(27)

VI

VII

for SiH–SiCo exchange involving a hypothetical silylcobalt tricarbonyl species, VI, which may be converted to a six-coordinate species, VII, having two silyl groups bonded to the central cobalt. If reaction 27 were reversible, it could result in exchange as in eq 22. Such a mechanism would be consistant with retention stereochemistry; however, other mechanisms are possible. One alternative that cannot be ruled out is a concerted mechanism (28) in which the formation of a cobalt-hydrogen bond need not occur.



(28)

Thus, the mechanism of Si*H–Si*D exchange catalyzed by metal complexes (Table II) in homogeneous solution may be best rationalized by the initial formation of a metal–silicon bond followed by a reversible exchange process. Both processes occur with retention of configuration at the asymmetric silicon center making concerted mechanisms involving quasi-cyclic transition states quite attractive.

Platinum complexes such as chloroplatinic acid, VIII, and the platinum(II)-ethylene complex, $[(C_2H_4)PtCl_2]_2$, IX, have been found to catalyze Si*H–Si*D exchange with retention. It is not certain, however, that these are instances of homogeneous catalysis. In the absence of olefinic substrates trialkylsilanes are capable of reducing VIII to the metal. We have observed that hydrocarbon solutions of IX and R_3Si^*H,D after stirring for several hours at room temperature exhibit a Tyndall effect indicating the presence of colloidal particles. It is unclear at this time whether the Si*H–Si*D exchange processes occurring in the presence of catalytic amounts of platinum(II) complexes are examples of heterogeneous or homogeneous catalysis.

Heterogeneous Catalysis by Group VIII Metals. Supported metals such as palladium on carbon and platinum on carbon catalyze Si*H–Si*D exchange (11) at room temperature (Table III). A skeletal metal, Raney nickel, is also an effective catalyst for exchange. As in the case of the homogeneous systems, these exchange processes occur with *retention of* configuration at the asymmetric silicon center.

Palladium and nickel catalysts were found to be extremely efficient, complete exchange occurring within several minutes after mixing. The rate of exchange is thousands of times faster than the rate of racemization of R_3Si^*H over these metals. The exceedingly high degree of stereospecificity argues strongly against mechanisms which invoke free silyl radicals to account for Si*H–Si*D exchange.[28]

The rapid reaction of R_3Si^*D with hydrogen gas (12) also occurs with complete retention at silicon. This result is in striking contrast to the racemization of R_3C^*H on the surface of group VIII metals.[29] The exchange between (+)-3-methylhexane, R_3C^*H, and deuterium on palladium and nickel catalysts have shown that nearly every exchange of the hydrogen atom at position 3 leads to racemization under the conditions of this study. In contrast to this, nearly every exchange between R_3Si^*D and hydrogen (12) in the presence of palladium and nickel occurs with retention of configuration.

Schemes (29, 30) may be advanced to account for processes 11 and 12. Reaction 30 is closely related to classical chemisorption processes and involves formation of a stereospecifically absorbed intermediate. We have seen that the formation of the silicon–metal bond with group VIII metal complexes occurs with retention; thus the surface reaction 29 is not unreasonable. Reaction 30, involving a small amount of metal hydride which may be present in commercially available supported metal catalysts, is attractive due to its simplicity. It does not necessitate the formation of a silicon–metal bond and bears a formal similarity to the SNi–Si mecha-

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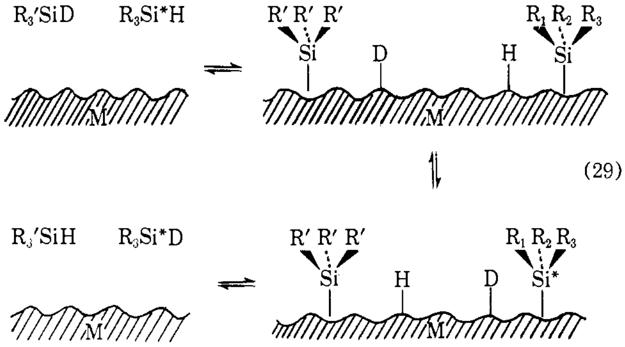
[27] (a) K. Noack, *Spectrochim. Acta*, **19**, 1925 (1963); (b) K. Noack, *Helv. Chim. Acta*, **47**, 1064 (1964). The authors conclude that pentane solutions of I contain only 43% of the bridged form at room temperature.

[28] Ponomarenko, *et al.*,[7] have postulated that radical species such as $R_3Si\cdot$ are involved in the SiH–SiD exchange reaction.

[29] R. L. Burwell, *et al.*, *J. Am. Chem. Soc.*, **79**, 5142 (1957).

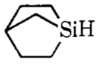


(29)

(30)

nism which is operative in the reaction of R_3Si^*D with lithium aluminum hydride.[30]

Since Si^*H–Si^*D exchange proceeds with over-all retention, it was of considerable interest to investigate the nature of this reaction when silicon is at the bridgehead of a bicyclic structure. It was found that both 1-silabicyclo[2.2.1]heptane, IX, and 1-silabicyclo[2.2.2]-octane, X, undergo exchange with R_3Si^*D more slowly than does triethylsilane, XI (Table V). When a pentane solution of XI and R_3Si^*D is stirred for 15 min in the presence of palladium on carbon, exchange is 80% complete. Under identical conditions, exchange between IX and R_3Si^*D is only 20% complete. In certain instances the relative rates of reactions of IX, X, and XI appear to reflect the nature of developing charge in the transition state.[31] It is doubtful that the exchange data can be interpreted on these grounds. It should be noted that in exchange reactions involving bridgehead silanes, the catalyst took on the sort of sintered appearance that occurs when certain types of catalyst poisons are added. The adsorption characteristics of the bridgehead silanes may be the controlling factor in the lower rates of reaction.



IX

X

In summary, a number of reactions involving optically active, α-naphthylphenylmethylsilane, R_3Si^*H, have been studied in the presence of reactive transition metal centers. The bulk of the evidence obtained indicates that *the initial process in these reactions may be a stereospecific interaction of the silicon–hydrogen bond with the reactive transition metal center. This reaction occurs with an exceedingly high degree of retention of configuration in all cases.* The result of this interaction may be the formation of a metal–silicon bond which then reacts with carbon or hydrogen centers with complete retention of configuration at the asymmetric silicon.

Experimental Section

A. Hydrosilation Reaction between (+)-α-Naphthylphenylmethylsilane and 1-Octene.[32] **1. Platinum on Charcoal as a Catalyst at Elevated Temperature.** A 50-ml one-necked flask with a thermometer well was equipped with a condenser and a mantel heater. A thin glass tube was inserted through the condenser and the whole system was flushed with nitrogen before the reaction. Nitrogen was slowly passed through the system during the reaction; $(+)R_3Si^*H$, $[\alpha]_D$ +34.6° (*c* 1.24, pentane) (5 g, 20.1 mmol), 1-octene (4.54 g, 40.3 mmol), and 11.0 mg of 5% platinum on charcoal (Matheson Coleman and Bell) were charged into the flask and the reaction mixture was heated for 24 hr at 130–144°. After having been cooled to room temperature, the solution was washed with water and dried over potassium carbonate. The product was distilled using a semimicro spinning band column. At 181–186°, 1.31 g, at 186–188°, 4.85 g were obtained under 0.45 mm. Both fractions had the same infrared spectrum, and the combined yield was 85%. The product has $[\alpha]_D$ −1.62° (*c* 26.5, pentane), n^{23}_D 1.5780. The infrared spectrum showed the absorption bands characteristic of the R_3Si– system plus the bands at 3.42 (vs), 3.50 (m), 3.52 (s), 6.83 μ (m), apparently related with the octyl moiety.

2. Platinum on Charcoal as a Catalyst at Room Temperature. $(+)R_3SiH$, $[\alpha]_D$ +34.6° (*c* 1.24, pentane) (1.33 g, 5.4 mmol), 1-octene (3 g, 26.7 mmol), and 54.6 g of 5% platinum on charcoal were put in a 25-ml suction flask. The flask was connected with a Gilman trap and flushed with nitrogen. Not all of the $(+)R_3SiH^*$ crystals were dissolved. The solution was left at room temperature for 25 days. Some crystals were still left unreacted. After having been worked up as above, the product showed considerable amount of $(+)R_3Si^*H$ left. The product was chlorinated in 20 ml of CCl_4, hydrolyzed in ether–water and chromatographed over a 10 in. × 0.5 in. silica gel column with elution by 100 ml of 80% pentane–20% benzene. An infrared spectrum of the recovered product was consistent with that of an authentic sample. The product (0.22 g) had $[\alpha]_D$ −1.89° (*c* 10.9, pentane), which was taken by a JASCO ORD/uv −5 spectropolarimeter.

3. Chloroplatinic Acid as a Catalyst at Elevated Temperature. The same apparatus as for 1 was used. To the mixture of (+)-R_3SiH, $[\alpha]_D$ +34.6° (*c* 1.24, pentane) (5 g, 20.1 mmol) and 1-octene (4.52 g, 40.2 mmol) was added 6 mg of chloroplatinic acid which partly dissolved in the solution and the solution was orange. The rest of the chloroplatinic acid was apparently reduced to platinum metal. The color of the solution became darker as the temperature was raised and finally was red brown. The solution was refluxed for 24 hr at 132–143°. The solution was dissolved in 75 ml of pentane, washed with water, and dried over anhydrous K_2CO_3. The product was distilled using a spinning band column. An infrared spectrum of the product (6.46 g) was consistent with that of an authentic R_3Si^*-*n*-C_8H_{17} except for a very small absorption band at 4.70 μ due to $(+)R_3Si^*H$ unreacted. A portion of the product with $[\alpha]_D$ −1.48° was chlorinated in CCl_4, hydrolyzed in ether–water, and chromatographed over a 12 in. × 0.5 in. silica gel column with elution by 100 ml of 80% pentane–20% benzene. $(-)R_3Si^*$-*n*-C_8H_{17}, $[\alpha]_D$ −1.78° (*c* 16.6, pentane), n^{23}_D 1.5771, was obtained.

4. Chloroplatinic Acid as a Catalyst at Room Temperature. To a mixture of $(+)R_3Si^*H$, $[\alpha]_D$ +34.6° (*c* 1.24, pentane) (3 g, 12.1 mmol) and 1-octene (5.44 g, 48.4 mmol) in a 25-ml suction flask was added 10 mg of $H_2PtCl_6 \cdot 6H_2O$ (1.9×10^{-2} mmol). Nothing seemed to happen for 3 hr and the solution was heated to 50–60°. Some of the chloroplatinic acid started to dissolve and the solution became dark reddish brown. The rest of the chloroplatinic acid was apparently reduced to platinum metal. The reaction mixture in a closed system under nitrogen atmosphere was left at room temperature for 2 weeks and the reaction was complete. The solution was worked up as mentioned in the preceding experiment. The product was distilled using a spinning band column and 2.70 g of $(-)R_3Si^*$-*n*-C_8H_{17} (71% yield), $[\alpha]_D$ −1.71° (*c* 19.3, pentane), n^{23}_D 1.5786, bp 186–188° (0.43 mm), was obtained.

5. $[PtCl_2(CH_2{=}CH_2)]_2$ as a Catalyst at Elevated Temperature. The same apparatus as for 1 was used. Platinum complex (10 mg) and 1-octene were put in a 50-ml flask. Platinum complex was dissolved with bubbling, presumably forming platinum-1-

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(30) L. H. Sommer, "Stereochemistry Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, pp 102–104.

(31) Base-catalyzed hydrolysis of bridgehead silanes proceeds far more rapidly than in acyclic systems whereas chlorination of bridgehead silanes occurs more slowly than with the acyclic analog. In base-catalyzed hydrolysis of R_3SiH, ρ^* is large and positive indicating the generation of negative charge in the transition state. In chlorination, ρ^* is large and negative reflecting the developing positive charge in the rate-controlling transition state; *cf.* L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw Hill Book Co., Inc., New York, N. Y., 1965.

(32) The first stereospecific hydrosilations with R_3Si^*H were unpublished results of L. H. Sommer and K. W. Michael.

octene complex.[45] The lemon yellow color of the solution became dark red brown upon addition of 5 g of (+)R_3Si^*H (20.1 mmol), $[\alpha]_D$ +34.6° (*c* 1.24, pentane). The reaction mixture was heated for 64 hr at 130–138°. A small amount of (+)R_3Si^*H was still left unreacted. The reaction mixture was taken up in 75 ml of pentane, washed with water, and dried over anhydrous sodium sulfate. After the solvent was stripped, distillation by a spinning band column afforded 3.91 g of the product, bp 187–189° (0.45 mm), considerable amount of naphthalene was observed to come out. An infrared spectrum of the product was consistent with that of an authentic sample except for a small peak at 4.70 μ due to (+)-R_3Si^*H. The product was chlorinated and freed from (+)R_3Si^*H as mentioned before. (+)R_3Si^*-*n*-C_8H_{17} (3.73 g, 52% yield), $[\alpha]_D$ −1.45° (*c* 22.7, pentane), $n^{23}D$ 1.5786, was obtained.

6. **$[PtCl_2(CH_2{=}CH_2)]_2$ as a Catalyst at Room Temperature.** 1-Octene (5.44 g, 48.4 mmol) and $[PtCl_2(CH_2{=}CH_2)]_2$ were mixed in a 25-ml suction flask. Platinum complex was dissolved with bubbling and the solution was lemon yellow. After flushing the flask with nitrogen 3 g of (+)B_3Si^*H (12.1 mmol), $[\alpha]_D$ +34.6° (*c* 1.24, pentane), was added. The color of the solution started to become dark soon. The flask was flushed with nitrogen and vented to the atmosphere through a Gilman trap. A (+)R_3SiH crystal slowly dissolved, which probably indicated that the reaction was going. All of the crystals were dissolved in 2 days. After 2 weeks, the solution was taken up in 60 ml of pentane. Small amounts of precipitate were filtered by a no. 42 filter, but most of the platinum complex (or colloidal platinum) remained in the solution. It was washed with water and platinum came out as a black material. Work-up following the same procedure as for 5 and distillation by a microdistillation apparatus afforded 1.51 g of crude product which included a considerable amount of (+)R_3Si^*H. The product was freed from (+)R_3Si^*H as mentioned before. (−)R_3Si^*-*n*-C_8H_{17} (1.2 g, 27% yield), $[\alpha]_D$ −1.44° (*c* 10.2, pentane), $n^{22}D$ 1.5794, was obtained.

7. **Cobalt Octacarbonyl $Co_2(CO)_8$ as a Catalyst.** (+)R_3Si^*H (2 g, 8.1 mmol), $[\alpha]_D$ +34.6° (*c* 1.24, pentane), and 1-octene (4.5 g, 40.3 mmol) were put in a 25-ml suction flask. The flask was heated and all of the R_3SiH crystals were dissolved. The flask was connected to a Gilman trap and flushed with nitrogen. $Co_2(CO)_8$ (39.1 mg, 0.11 mmol) was added to the solution. A part of the catalyst dissolved with bubbling and the solution was amber yellow. The flask was covered with an aluminum foil to prevent the decomposition of the catalyst. The solution was kept at room temperature and the reaction proceeded only partially. Then the temperature was raised to 60° using an oil bath. After 1 day, an aliquot was taken and showed that the reaction proceeded very little. About the same amount of dicobalt octacarbonyl as the initial one was added to the solution and the solution was heated for 5 days at 60°. An infrared spectrum of an aliquot showed that the reaction was *ca.* 20% complete. The solution was washed with water and dried over anhydrous sodium sulfate. The product was chromatographed over a 15 in. × 0.5 in. silica gel column with elution by 150 ml of 80% pentane–20% benzene solvent. The resulting product (1.71 g) was chlorinated in 25 ml of CCl_4, hydrolyzed in ether–water, and chromatographed. An infrared spectrum of the recovered material (0.24 g) showed it had aliphatic carbons besides octylsilane. The material had $[\alpha]_D$ −0.62° (*c* 19.3, pentane), taken by JASCO ORD/uv −5 spectropolarimeter.

B. **Stereospecific Group VIII Metal Catalyzed Si*H–Si*D Exchange Reactions. 1. Preparation of (+)-α-Naphthylphenylmethyldeuteriosilane.** A suspension of 0.7132 g of lithium aluminum deuteride in 15 ml of anhydrous diethyl ether was stirred for 1 hr at reflux under nitrogen in a 50-ml, three-necked, round-bottomed flask equipped with a magnetic stirrer, thermometer, pressure regulated addition funnel, and reflux condenser vented to the atmosphere through a Gilman trap. Then a solution of 9.3 g of pure (−)-α-naphthylphenylmethyl-(−)-menthoxysilane, $[\alpha]_D$ −54.1° (*c* 10, cyclohexane), mp 82.5–83.5°, in 15 ml of anhydrous dibutyl ether was added quickly and the mixture stirred at reflux for 1 hr. A threeway stopcock which had been inserted between the Gilman trap and the flask and was connected to the nitrogen tank was opened to the atmosphere for 10 min to allow ether to escape while nitrogen was blown through the system. When the stopcock was closed, the temperature of the refluxing mixture in the reaction flask had risen to 80° where it was maintained for 19 hr. At this point more ether was removed and the reaction stirred at 85° for an additional 3 hr. After cooling to room temperature, 15 ml of acetone was added slowly to the mixture over a 1.5-hr period to destroy excess deuteride, taking care that the temperature never rose beyond 60°. After the reaction mixture had cooled to room temperature, it was poured over 20 ml of HCl in ice and worked up in the manner of Frye.[33]

Menthol was distilled from the crude reaction mixture in a microdistillation apparatus until the head temperature reached 150° (1 mm). On cooling, the clear, colorless, pot residue quickly solidified and was taken up in 50 ml of dry pentane. Small white crystals, 4.0 g of (+)-α-naphthylphenylmethyldeuteriosilane, $[\alpha]_D$ +35.4° (*c* 2, pentane), mp 63–64°,[33] were formed on standing at 20° overnight. Two further crops of crystals were obtained by concentration of the mother liquor bringing the total yield of deuteriosilane to 5.6 g (96% yield). The infrared spectrum of the deuteriosilane is identical with that of the authentic α-naphthylphenylmethylsilane except for the absence of the deep symmetrical band at 4.75 μ, due to Si–H and the presence of a strong absorption band at 6.45 μ, diagnostic of Si–D.[33]

2. **Preparation of Racemic Phenylmethylethyldeuteriosilane.** Racemic phenylethylmethylsilane, 10.7 g (bp 179–180°), prepared according to the procedure of Michael,[34] was dissolved in 70 ml of freshly distilled carbon tetrachloride in a 125-ml filter flask stoppered with a rubber serum cap and having a calcium chloride drying tube attached to the side arm. Chlorine gas was bubbled into this solution through a syringe needle until the greenish yellow end point was reached indicating completion of reaction. The solution was immediately connected to a vacuum pump and the carbon tetrachloride removed at reduced pressure. The clear liquid product, racemic phenylethylmethylchlorosilane,[34] was then dissolved in 80 ml of anhydrous ether and this solution added dropwise to 2.8 g of lithium aluminum deuteride in 60 ml of anhydrous ether. After stirring for 4 min, the mixture was cautiously poured onto 90 ml of concentrated HCl and 120 g of crushed ice and worked up in the manner of Michael.[34] The pure phenylethylmethyldeuteriosilane, 7.2 g (70% yield), was recovered by distillation on a small spinning band column, bp 178–180°. The infrared spectrum of the deuteriosilane is identical with that of the authentic phenylethylmethylsilane except for the absence of the deep symmetrical band at 4.7 μ due to Si–H[33] and the presence of a strong absorption band at 6.45 μ, diagnostic of Si–D.

3. **Treatment of the Exchange Data.** From a series of standard infrared spectra of synthetic mixtures having known concentrations of the silane and the deuteriosilane, in carbon tetrachloride, eq i and ii were derived

$$\frac{[R_3SiH]}{[R_3SiD]} = \frac{\alpha}{\alpha_s} \qquad \text{(i)}$$

$$\%\ \text{exchanged} = \frac{2\alpha}{\alpha + \alpha_s}100 \qquad \text{(ii)}$$

where $\alpha = (\log T_0/T_H)/(\log T_0'/T_D)$ and $\alpha_s = (\log T_{0s}/T_{HS})/(\log T_0'{}_s/T_{DS})$; and T_0 = transmittance, base line of blank; T_H = transmittance, 4.74-μ peak of silane; T_0' = transmittance, base line of blank; T_D = transmittance, 6.45 μ peak of deuteriosilane; and the subscript s refers to standard spectra where the ratio of $[R_3SiH]/[R_3SiD]$ is 1.0.

The infrared absorption bands corresponding to Si–H and Si–D were deep, symmetrical bands at 4.75 and 6.45 μ, respectively. The value of $1/\alpha_s$ for the α-naphthylphenylmethylsilyl compounds was determined to be 0.584 and for the phenylethylmethyl silyl compounds, 0.650. The value of α was calculated in each case from the pure SiH–SiD mixtures isolated from the exchange reactions.

4. **Palladium Catalyzed Exchange in Methylene Chloride. a. Reaction Time of 1020 Min.** An equimolar mixture of α-naphthylphenylmethylsilane, $[\alpha]_D$ +34.5°, 0.2483 g (1 mmol), and phenylethylmethyldeuteriosilane, 0.1512 g (1 mmol), was dissolved in 4 ml of pure, anhydrous methylene chloride in a dry 10-ml flask containing a magnetic stirring pea. The catalyst, 30 mg of rigorously dried (1 week at 0.02 mm over P_2O_5) 10% Pd–C, was added and the mixture magnetically stirred for 1020 min under dry nitrogen at room temperature. After this time the mixture was rapidly filtered through Whatman No. 42 filter paper using nitrogen pressure, and the solvent distilled from the reaction mixture. A pot-to-pot vacuum transfer yielded 0.131 g (86% yield) of the volatile isotopic mixture of pure phenylethylmethylsilanes which were trapped at −78°, and left behind 0.248 g (100% yield) of the crude isotopic

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(33) C. L. Frye, Ph.D. Thesis, The Pennsylvania State University, 1960.

(34) K. W. Michael, Ph.D. Thesis, The Pennsylvania State University, 1963.

mixture of (+)-α-naphthylphenylmethylsilanes which crystallized in the pot on the vacuum line. The crystalline silane was dissolved in 2 ml of refluxing pentane and allowed to crystallize first at room temperature for several hours and then at −78° for 20 hr. Recovered from this crystallization was 0.236 g (95% yield) of the isotopic mixture of pure (+)-α-naphthylphenylmethylsilanes, [α]D +31.0° (*c* 2, pentane).

From the infrared spectrum of recovered PhEtMeSiH,D in carbon tetrachloride (0.10 g/ml), the SiH/SiD ratio was calculated to be 1.1 with an estimated precision of ±10%. From the infrared spectrum of recovered (+)-α-NpPhMeSiH,D in carbon tetrachloride, 0.15 g/ml, the SiH/SiD ratio was calculated to be 1.0 with a similar precision. These data show that isotopic exchange at the asymmetric silicon center was complete.

b. Reaction Time of 10 Min. An equimolar mixture of (+)-α-naphthylphenylmethylsilane, [α]D +34.5°, 0.248 g (1 mmol), and phenylethylmethyldeuteriosilane, 0.151 g (1 mmol), was dissolved in 4 ml of pure, anhydrous methylene chloride. The catalyst, dry 10% Pd–C, was added and the mixture stirred for 10 min under dry nitrogen at room temperature. The mixture was rapidly filtered using nitrogen pressure and the solvent removed at reduced pressure. A pot-to-pot vacuum transfer yielded 0.127 g (84% yield) of the volatile isotopic mixture of pure phenylethylmethylsilanes, which were trapped at −78°, and left behind 0.244 g (98% yield) of crude (+)R_3Si*H,D which crystallized on standing. The solid silane was dissolved in 2 ml of refluxing pentane and allowed to crystallize first at room temperature and then at −78° for 24 hr. The white, crystalline isotopic mixture of pure (+)-α-naphthylphenylmethylsilanes, [α]D +33.2° (*c* 2, pentane), 0.258 g, was recovered in 97% yield. From the infrared spectrum of this material in carbon tetrachloride, 0.15 g/ml, the SiH/SiD ratio was calculated to be 1.0 ± 0.1 showing that exchange was complete in less than 10 min. These experiments are representative of the Si*H–Si*D exchange reactions over supported metals and Raney nickel (Table III).

C. Stereospecific Group VIII Metal Catalyzed Reactions of (+)-α-Naphthylphenylmethylsilane with Hydrogen. 1. Catalysis by Palladium. Optically active (+)-α-naphthylphenylmethyldeuteriosilane, [α]D +33.2°, isotopic purity of 50%, 0.254 g (1.02 mmol), was dissolved in 2.50 ml of freshly chromatographed pentane and syringed into a microhydrogenation tube containing 25 mg of dry 10% Pd–C. The tube was placed in a pressure bottle suitably padded with foam rubber to hold the tube firmly in place. The bottle was attached to a Parr hydrogenator, flushed several times with hydrogen gas, and shaken for 1 hr under 1.8 atm of hydrogen pressure. The reaction mixture was then filtered free of catalyst and the solvent evaporated at reduced pressure leaving 0.20 g (80% yield) of white, crystalline (+)-α-naphthylphenylmethylsilane, [α]D +33.2° (*c* 2, pentane). The infrared spectrum of this material showed the silane to be completely free of SiD.

2. Catalysis by Raney Nickel. Optically active (+)-α-naphthylphenylmethyldeuteriosilane, [α]D +33.2°, isotopic purity of 50%, 0.108 g, was dissolved in 1.0 ml of anhydrous pentane and syringed into a microhydrogenation tube containing 10 mg of dry Raney nickel catalyst. The tube was placed in a rubber padded hydrogenation bottle and shaken in a Parr hydrogenator under 1.8 atm of hydrogen pressure for 1 hr. The reaction mixture was filtered and solvent removed at reduced pressure leaving 0.10 g (92% yield) of (+)-α-naphthylphenylmethylsilane, [α]D +32.3° (*c* 2, pentane). The infrared spectrum of this material showed the silane to be completely free of SiD.

3. Catalysis by Platinum. Optically active (+)-α-naphthylphenylmethyldeuteriosilane, [α]D +33.3°, isotopic purity of 45%, 0.182 g, was dissolved in 2 ml of dry pentane and syringed into a microhydrogenation tube containing 19 mg of 5% Pt–C. The tube was placed in a rubber padded hydrogenation bottle and shaken in a Parr hydrogenator under 1.8 atm of hydrogen pressure for 1 hr. The reaction mixture was filtered and solvent removed at reduced pressure leaving 0.17 g (93% yield) of (+)-α-naphthylphenylmethylsilane, [α]D +33.4° (*c* 2, pentane). The infrared spectrum of this material showed that the SiH/SiD ratio was 1.52, and thus only 14% reaction has occurred.

D. Group VIII Metal Catalyzed Si*H–Si*D Exchange Reactions between (+)-α-Naphthylphenylmethyldeuteriosilane and Trialkylsilanes. 1. Exchange with Triethylsilane. Triethylsilane, 0.111 g (0.957 mmol), and (+)-α-naphthylphenylmethyldeuteriosilane, [α]D +35°, 0.249 g (1.01 mmol), were dissolved in 3.7 ml of anhydrous pentane. The catalyst, 37 mg of 10% Pd–C, was added and the reaction mixture stirred for 15 min under dry nitrogen. The mixture was filtered free of catalyst and the volatiles removed at reduced pressure leaving a residue of 0.240 g of white solid which was recrystallized at −78° to yield 0.23 g (93% yield) of (+)α-NpPhMeSiH,D, [α]D +34.5°. From an infrared spectrum of this material in CCl_4, 0.15 g/ml, an SiH/SiD ratio of 0.73 was calculated, requiring the extent of exchange to be slightly greater than 80%.

2. Exchange with 1-Silabicyclo[2.2.1]heptane. 1-Silabicyclo[2.2.1]heptane, 0.216 g (1.93 mmol), and (+)-α-naphthylphenylmethyldeuteriosilane, [α]D +35°, 0.491 g (1.98 mmol), were dissolved in 7.5 ml of anhydrous pentane and 75 mg of 10% Pd–C was added. The mixture was stirred at room temperature under nitrogen for 15 min during which time the catalyst took on an amorphous sintered appearance. The mixture was filtered and the volatiles removed at reduced pressure and collected in a −78° trap. The pot was heated to 60° at 0.05 mm in order to remove all of the bridgehead silane and the residue was crystallized from pentane at −78° giving 0.48 g (96% yield) of (+)-α-NpPhMeSiH,D, [α]D +35°. From the infrared spectrum of a CCl_4 solution, 0.15 g/ml, the SiH/SiD ratio in this material was calculated to be 0.12 and the extent of exchange was 22%.

The pure bridgehead silane, 0.108 g (50%), was recovered by sublimation of the residue from evaporation of the pentane from the trapped material above. An infrared spectrum of the 1-silabicyclo[2.2.1]heptane-d_1 showed approximately 20% incorporation (estimate) of deuterium.

3. Exchange with 1-Silabicyclo[2.2.2]octane. 1-Silabicyclo[2.2.2]octane, 0.164 g (1.30 mmol), and (+)-α-naphthylphenylmethyldeuteriosilane, [α]D +35°, 0.316 g (1.27 mmol), were dissolved in 5.2 ml of pentane. The catalyst, 54 mg of 10% Pd–C, was added and the mixture was stirred at room temperature under dry nitrogen for 20 min. It was noticed that the catalyst clumped together in amorphous lumps as if it were being badly poisoned. Very vigorous stirring was necessary to break up and disperse the catalyst. The reaction mixture was filtered and solvent reduced to 2 ml on a steam bath. The (+)-α-NpPhMeSiH,D, [α]D +35.0° (*c* 2, pentane), 0.304 g (96% yield), was recovered by crystallization at −78°. Traces of volatile materials were removed by gently warming the crystalline solid at reduced pressure (0.05 mm). An infrared spectrum of the pure, dry, crystalline compound in CCl_4, 0.15 g/ml, showed an SiH/SiD ratio of 0.10 and the extent of exchange was 15%.

The solution from the above crystallization was put on a steam bath and the pentane evaporated. Sublimation of the residue gave 0.080 g (49% yield) of the pure bridgehead silane. An infrared spectrum run in CCl_4 showed the incorporation of 10–20% (estimated) deuterium at the bridgehead silicon.

E. Homogeneous Catalysis by Group VIII Metal Complexes. 1. Iridium(I)-Catalyzed Si*H–Si*D Exchange. A mixture of 0.350 g (1.41 mmol) of (−)-α-naphthylphenylmethylsilane, [α]D −35°, and 0.210 g (1.40 mmol) of racemic phenylethylmethyldeuteriosilane was dissolved in 5.0 ml of anhydrous benzene containing 12 mg of bis(triphenylphosphine)carbonylchloroiridium(I). The yellow solution was stirred at room temperature under dry nitrogen for 17 hr during which time the color of the solution became somewhat less intense. The reaction mixture remained completely homogeneous throughout the entire reaction. The benzene was removed at reduced pressure and the silanes were redissolved in pentane leaving the pentane-insoluble iridium complex behind. The pale yellow solid, 8 mg, was recovered by filtration through a Hirsch funnel and a Nujol mull made up. The infrared spectrum was identical with that of the starting material except for the appearance of an absorption band of medium intensity at 1990 cm^{-1} which was not present in the spectrum of bis(triphenylphosphine)carbonylchloroiridium(I).

The pentane solution was concentrated and kept at −78° for 30 hr. The optically active silane, [α]D −34.8° (*c* 2, pentane), 0.34 g, was recovered in 97% yield. From an infrared spectrum of the (+)-α-NpPhMeSiH,D, in CCl_4, 0.15 g/ml, the SiH/SiD ratio was calculated to be 1.0. The pentane was evaporated from the filtrate of the above crystallization and the pure racemic PhEtMeSiH,D, 0.17 g (85% yield), recovered by a pot-to-pot vacuum transfer into a chilled (−78°) vessel. From the infrared spectrum of this material in CCl_4, 0.10 g/ml, the SiH/SiD ratio was calculated to be 1.0 and therefore Si*H–Si*D exchange was complete.

2. Attempted Iridium(I)-Catalyzed Reaction of (+)-α-Naphthylphenylmethyldeuteriosilane with Hydrogen. Optically active (+)-α-naphthylphenylmethyldeuteriosilane, [α]D +35.4° (*c* 2, pentane), 0.325 g, was weighed directly into a microhydrogenation tube and 4.0 ml of a benzene solution containing 8 mg of bis(triphenylphosphine)carbonylchloroiridium(I) was added through a syringe. The silane dissolved readily to give a yellow solution. The tube was placed in a rubber-cushioned microhydrogenation bottle and shaken on a Parr hydrogenator for 20 hr under a pressure of 1.9 atm of hydrogen. After this time the initially yellow solution had become completely clear. The benzene was removed at reduced pressure and the silane was taken up in pentane leaving the insoluble iridium compound behind. Filtration of the pentane solution yielded 5 mg of a cream colored powder whose infrared spectrum (Nujol) was identical with that reported for the bis(triphenylphosphine)carbonyliridium(III) dihydride.

Concentration of the pentane solution and crystallization as in previous experiments yielded 0.30 g (93% recovery) of (+)-α-naphthylphenylmethyldeuteriosilane, $[\alpha]_D$ +35.6° (*c* 2, pentane). From the infrared spectrum of this material in CCl_4, 0.15 g/ml, it was determined that less than 5% exchange had occurred and nearly all of the deuterium had remained on the silicon.

3. Dicobalt Octacarbonyl Catalyzed Si*H–Si*D Exchange. Racemic phenylethylmethylsilane, 0.3080 g (2 mmol), and optically active (+)-α-naphthylphenylmethyldeuteriosilane, $[\alpha]_D$ +35°, were weighed directly into a dry 25-ml round-bottomed flask and the vessel was flushed thoroughly with nitrogen. An 8-ml portion of a solution (1 mg/ml) of dicobalt octacarbonyl in *n*-hexane was syringed into the reaction flask. The solution was made up by chromatographing pure *n*-hexane through silica gel into a flask containing the dicobalt octacarbonyl. The entire chromatography was carried out under nitrogen so that the solvent was relatively free of oxygen when it came in contact with the cobalt compound. The hexane solution was magnetically stirred at gentle reflux for 24 hr under nitrogen by immersion of the reaction flask in a 74° oil bath. The solution was allowed to cool to room temperature and then syringed into a 25-ml filter flask and the volume of solution concentrated to 1.5 ml at reduced pressure. The concentrated solution was kept at −78° for 24 hr and 0.45 g (91% yield) of white, crystalline (+)-α-naphthylphenylmethylsilane-*d*, $[\alpha]_D$ +35°, crystallized out. From an infrared spectrum of this material in CCl_4, 0.15 mg/ml, the SiH/SiD ratio was calculated to be 1.0. An infrared spectrum of PhEtMeSiH,D, 0.22 g (73% yield), recovered in the usual manner, showed an SiH/SiD ratio of 1.1. Thus, it was concluded that stereospecific Si*H–Si*D exchange was complete.

F. Preparation and Reactions of Optically Active Silylcobalt Tetracarbonyls. 1. The Preparation of (−)-α-Naphthylphenylmethylsilylcobalt Tetracarbonyl. Pure, anhydrous pentane, 60 ml, was percolated through a 2-ft column of silica gel into a 125-ml filter flask containing 5.0 g of (−)-α-naphthylphenylmethylsilane, $[\alpha]_D$ −35°. The filter flask was equipped with a magnetic stirrer and the apparatus was assembled in such a way that the chromatography was carried out in an atmosphere of dry nitrogen. After all the silane had dissolved, the solution was syringed into a 100-ml round-bottomed, three-necked flask containing 6.0 g of dicobalt octacarbonyl under dry nitrogen. The flask had been thoroughly dried and was equipped with a condenser, magnetic stirrer, nitrogen inlet, and a rubber septum for additions and removal of liquid samples. It was vented to the atmosphere through a Gilman trap through which a constant slow stream of nitrogen was passed. The dicobalt octacarbonyl had been transferred from a fresh, unopened bottle which had been stored at 0° for 1 week. Addition of the pentane solution of the silane created a dark, red-brown solution from which a gas was slowly evolved. Aliquots of 0.2 ml were removed periodically by a syringe through the rubber septum and the infrared spectrum of the reaction mixture was checked *vs.* pentane as the reaction progressed. It was possible to follow the disappearance of both the Si–H band at 4.73 μ and the doublet centered at 1860 cm^{-1} due to the bridging carbonyls of $Co_2(CO)_8$. The carbonyl region between 2000 and 2100 cm^{-1} acquired the characteristics of silylcobalt tetracarbonyls and the silicon–phenyl absorption could be observed to shift to longer wavelengths. The Si–Ph absorption in the starting material was at 1113 cm^{-1} and in the silylcobalt tetracarbonyl it appears at 1100 cm^{-1}. The change in rotation of the reaction mixture was also followed throughout the reaction by scanning through the 600–450-mμ region of the plain dispersion curve at intervals of 5–10 hr. The rotation was observed to become gradually more positive and the sign of the plain dispersion curve switched from minus to plus.

After having stirred for 45 hr at room temperature under nitrogen, the stirring was stopped and a dark solid was allowed to settle out over a 3-hr period. The supernatant liquid, 40 ml, was syringed into a dry centrifuge tube under nitrogen and stoppered with a rubber serum cap. After centrifuging 2 hr, the supernate was transferred to a dry 100-ml round-bottomed flask under nitrogen and chilled at 0° for 1 hr.

A portion of this solution, 15 ml, was syringed into a dry 50-ml erlenmeyer flask and the volume reduced to 13 ml by bubbling dry nitrogen through the liquid. The flask was stoppered with a serum cap and kept at −20° for 2 days during which time a dark solid precipitated. The supernatant liquid was syringed away from the dark solid into a dry 25-ml erlenmeyer flask and the volume of pentane reduced to 11 ml by bubbling nitrogen through the solution. The flask was stoppered with a rubber serum cap and kept at −55° for 2 days. After this time 1.6 g of light tan crystals had separated, the surfaces, of which were coated with a dark brown solid. The dark solid was leached out of the crystalline material with a small amount of pentane leaving 1.4 g of a light pink crystalline solid. Recrystallization of this material from pure, dry deoxygenated *n*-hexane at −20° yielded 1.2 g (40% yield) of the white, crystalline (−)-α-naphthylphenylmethylsilylcobalt tetracarbonyl, $[\alpha]_D$ −2° (*c* 9, pentane), mp 102–104.5°.

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 of this material exhibits all the bands related to the α-NpPhMeSi* moiety as well as the following absorptions which are characteristics of silylcobalt carbonyls: 2095 (s), 2040 (s), 2010 (vs), 1995 (vs, sh), 1960 cm^{-1} (w). The sign of the plain dispersion curve of this compound is opposite that of the starting silane. Specific rotations in *n*-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 the silylcobalt tetracarbonyl is approximately double that of optically pure (−) R_3Si*H and of opposite sign.

2. The Exchange Reaction between (−)-α-Naphthylphenylmethylsilylcobalt Tetracarbonyl and Triethylsilane. A solution of 0.50 g of (−)-α-naphthylphenylmethylsilylcobalt tetracarbonyl, $[\alpha]_D$ −2° (*c* 9, pentane), in 5.0 ml of triethylsilane was stirred for 24 hr at room temperature. The clear, pale yellow solution was then placed in the Dry Ice chest at −60° for 50 hr yielding 0.26 g (96% yield) of white, crystalline (−)-α-naphthylphenylmethylsilane, $[\alpha]_D$ −31° (*c* 2, pentane).

3. Methanolysis of (−)-α-Naphthylphenylmethylsilylcobalt Tetracarbonyl. To a solution of 0.16 g of (−)-α-naphthylphenylmethylsilylcobalt tetracarbonyl, $[\alpha]_D$ −2° (*c* 9, pentane), in 6 ml of anhydrous pentane under nitrogen was added 0.016 ml of pure methanol. The mixture was stirred under nitrogen for 10 hr during which time a gas was given off and the solution darkened. Evaporation of the pentane left 0.16 g of greyish crystals which were dissolved in CCl_4 leaving behind a black insoluble material. An infrared spectrum of the CCl_4 solution was identical with that of α-naphthylphenylmethylmethoxysilane. The CCl_4 was removed at reduced pressure giving 0.14 g (78% yield) of the methoxysilane, $[\alpha]_D$ +8.0° (*c* 1.4, pentane).

4. (−)-α-Naphthylphenylmethylsilylcobalt Tetracarbonyl as a Catalyst for Si*H–Si*D Exchange. To a solution of 0.3871 g (1.53 mmol) of (+)-α-naphthylphenylmethyldeuteriosilane, $[\alpha]_D$ +35°, and 0.2326 g (1.54 mmol) of racemic phenylethylmethylsilane in 6.0 ml of pure anhydrous *n*-hexane was added 34 mg (8 × 10^{-5} mol) of (−)-α-naphthylphenylmethylsilylcobalt tetracarbonyl, $[\alpha]_D$ −2°. The solution was stirred at gentle reflux by immersion of the reaction vessel in a 75° oil bath for 24 hr. After this time a small amount of a brown solid had formed. The reaction mixture was allowed to cool to room temperature, filtered, and concentrated to 1.5 ml. Crystallization at −78° yielded 0.3777 g (97%) of white, crystalline (+)-α-naphthylphenylmethylsilane-*d*, $[\alpha]_D$ +35°, which was washed several times with pentane and dried *in vacuo* for 1 hr. From the infrared spectrum of (+)-α-NpPhMeSiH,D, which was contaminated with a trace of silylcobalt tetracarbonyl, an SiH/SiD ratio of 1.0 was calculated. The PhMeEtSiH,D, 0.20 g (86% yield), was recovered as in previous experiments. From the infrared spectrum of this material in CCl_4, 0.1 mg/ml, an SiH/SiD ratio of 1.1 was calculated. Thus, the silylcobalt tetracarbonyl is capable of catalyzing stereospecific Si*H–Si*D exchange.

5. Preparation of (−)-Phenylneopentylmethylsilylcobalt Tetracarbonyl. A solution of 2.4 g of dicobalt octacarbonyl and 1.0 g of (+)-phenylneopentylmethylsilane in 50 ml of pure toluene was made up according to the procedure described in experiment F1. The reaction mixture was allowed to stir under dry nitrogen for 50 hr during which time 0.2-ml aliquots were periodically removed and the infrared spectrum and optical rotations checked. After 50 hr the Si–H peak at 4.74 μ had completely disappeared and the infrared spectrum of the reaction mixture *vs.* toluene exhibited bands due to the neo-C_5H_{11}PhMeSi* moiety as well as absorptions characteristic of the silylcobalt tetracarbonyls: 2090 (s), 2050 (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 $[\alpha]_D$ −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 (−)-Phenylneopentylmethylsilylcobalt 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, $[\alpha]_D$ +1.6° (*c* 10, pentane), $[\alpha]_D$ +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 center. 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 noncatalytic 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

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

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

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

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-

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(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.

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