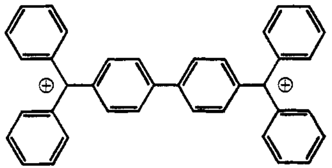

$2SbCl_6^{\ominus}$

I

The dark red crystals of $C_{38}H_{28}Sb_2Cl_{12}$ (mol wt 1153.2) belong to the monoclinic system, with a = 16.67 ± 0.03, b = 12.81 ± 0.02, c = 21.52 ± 0.02 A; β = 105°. The space group is $P2_1/c$ with four $C_{38}H_{28}Sb_2Cl_{12}$ entities in the unit cell. Intensity data were obtained by visual estimates of equiinclination Weissenberg photographs (Cu Kα). A total of 3118 independent structure amplitudes was obtained. The structure was determined by the heavy atom method and, at the present stage of refinement, the crystallographic R factor is 0.11 on all observed reflections. Further refinement is in progress, but the essential structural details are now evident and are summarized below. The estimated standard deviations in C–C bonds is 0.04 A and in C–C–C angles is 2.0°.

A drawing of the structure showing the atom numbering is given in Figure 1. The angles around atoms C(7) and C(26) range from 119 to 122°, with the sum of the angles around these atoms being 360.0° in each case. C(7) and C(26) each lie within 0.015 A from the plane defined by the three atoms to which they are bonded; these groups of four atoms must be considered planar within the accuracy of the analysis. A difference map shows no significant residual electron density at positions corresponding to bonding sites near C(7) and C(26). The foregoing evidence seems conclusively in favor of the existence of the dicarbonium ion species in the crystal.

The average C–C length involving either C(7) or C(26) is 1.44 A, shorter than the accepted C(sp^2)–C(sp^2) single bond distance of approximately 1.48 A.[9,10] Similar shortenings have been observed in the triphenylmethyl[11] and *sym*-triphenylcyclopropenium[12] cations. The angles of twist of the best planes of the phenyl rings A, B, and C (Figure 1) from the best plane through atoms C(1), C(7), C(8), and C(14) are 37, 27, and 30°, respectively, while the planes through the rings D, E, and F make angles of 36, 32, and 33° with the best plane through C(23), C(26), C(27), and C(33). These values compare with 31.8° reported for the triphenylmethyl cation[11] and 28.2° found in the tetra-*p*-anisylethylene dication,[8] but are considerably greater than the 7–21° range found in the *sym*-triphenylcyclopropenium system.[12]

The angle of twist between rings C and D is 40°, which is much greater than the value found in crystalline biphenyl (where the molecule is planar)[13] or the values (~20°) generally assumed[6,7,14] to prevail in solution, and may indicate that the dication in I behaves more as two separate triphenylmethyl cations than was hitherto anticipated.[6,7] It is interesting to note that a similarly large angle (41°) has been found between the two planes containing a central carbon atom and its bonded neighbors in the tetra-*p*-anisylethylene dicarbonium ion.[8]

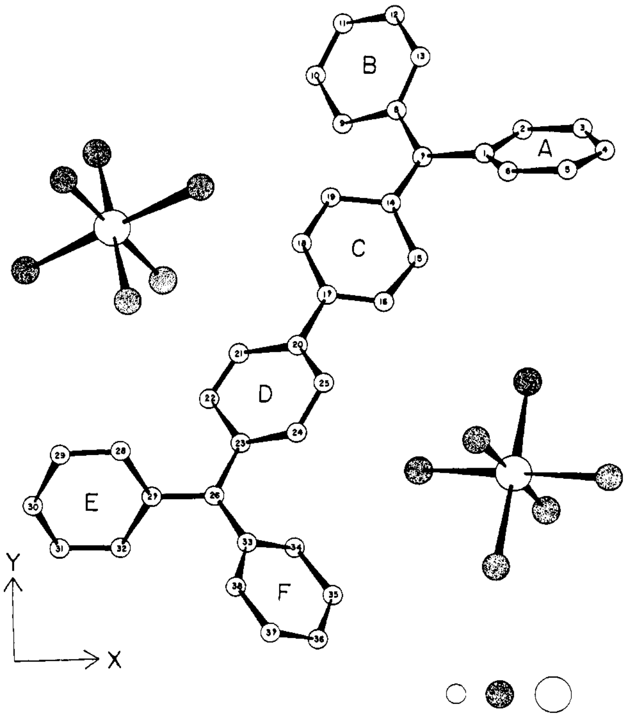

Figure 1. A view of the structure looking along the c direction.

The hexachloroantimonate anions are octahedral with a mean Sb–Cl distance of 2.355 A. The shortest contact between either C(7) or C(26) and a chlorine atom is 3.50 A involving C(7).

Acknowledgment. Our thanks are due to Dr. Heinrich Volz of the Technische Hochschule, Karlsruhe, Germany, who kindly supplied the crystalline sample used in this study. Mr. Patrick Ng carried out the visual estimations of the X-ray intensities.

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[9] L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 18, The Chemical Society, London, 1965, p 15s.

[10] O. Kennard, "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 276.

[11] A. H. Gomes de Mesquita, C. H. MacGillavry, and K. Eriks, *Acta Cryst.*, **18**, 437 (1965).

[12] M. Sundaralingam and L. H. Jensen, *J. Am. Chem. Soc.*, **85**, 3302 (1963); **88**, 198 (1966).

[13] G. B. Robertson, *Nature*, **191**, 593 (1961); **192**, 1026 (1961); J. Trotter, *Acta Cryst.*, **14**, 1135 (1961); A. Hargreaves and S. Hasan Rizvi, *ibid.*, **15**, 365 (1962).

[14] H. Suzuki, *Bull. Chem. Soc. Japan*, **32**, 1340 (1959), and references cited therein.

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Stereospecific Exchange Reactions of Optically Active $R_3Si^*H(D)$ Catalyzed by Group VIII Metals[1]

Sir:

Recent studies of the silicon–hydrogen bond have shown that group VIII metal catalysts give two types of reactions that are highly stereospecific.[2,3] The hydro-

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[1] Current support of this work by the National Science Foundation, Grant GP-5662, is gratefully acknowledged. Preliminary studies were carried out at The Pennsylvania State University with support from Dow-Corning Corp.

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

[3] L. H. Sommer and J. E. Lyons, *ibid.*, **89**, 1521 (1967).

Table I. Transition Metal Catalyzed Exchange Reactions of (+)-R_3Si^*H and PhMeEtSiD

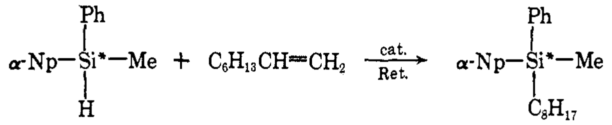
			Products				
Catalyst	Solvent	Contact time, min	$[\alpha]^{25}D$ of R_3Si^*H,D, deg	$[R_3Si^*H]/[R_3Si^*D]$	[PhMeEtSiH]/[PhMeEtSiD]	% exchange	Stereospecificity
10% Pd-C[a]	CH_2Cl_2	1020	+31.0	1.0	1.1	100	95% retn
10% Pd-C[a]	CH_2Cl_2	10	+33.2	1.0		100	98% retn
Ra Ni[b]	CH_2Cl_2	10	+34.5	1.1		>90	100% 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] $((C_2H_4)PtCl_2)_2$.

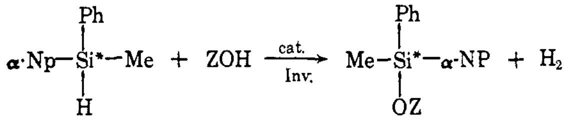
Table II. Transition Metal Catalyzed Reactions of (+)-R_3Si^*D with H_2

Catalyst	$[\alpha]^{25}D$ of starting material, deg	Contact time, min	H_2 pressure, atm	$[\alpha]^{25}D$ of product, deg	% reaction	Stereospecificity
10% Pd-C	+33.2	60	1.8	+33.2	100	100% retn
Ra Ni	+33.2	60	1.8	+32.3	100	98% retn
5% Pt-C	+33.3	60	1.8	+33.3	14	100% retn

silation of olefins (1) occurs with nearly complete retention of configuration[2] in the presence of platinum and platinum complexes, whereas palladium and nickel catalyze substitution reactions of optically active silicon hydrides (2) with inversion.[3]



$$\alpha\text{-Np}-\overset{\text{Ph}}{\underset{\text{H}}{\text{Si}^*}}-\text{Me} + C_6H_{13}CH{=}CH_2 \xrightarrow[\text{Ret.}]{\text{cat.}} \alpha\text{-Np}-\overset{\text{Ph}}{\underset{C_8H_{17}}{\text{Si}^*}}-\text{Me} \qquad (1)$$



$$\alpha\text{-Np}-\overset{\text{Ph}}{\underset{\text{H}}{\text{Si}^*}}-\text{Me} + \text{ZOH} \xrightarrow[\text{Inv.}]{\text{cat.}} \text{Me}-\overset{\text{Ph}}{\underset{\text{OZ}}{\text{Si}^*}}-\alpha\text{-NP} + H_2 \qquad (2)$$

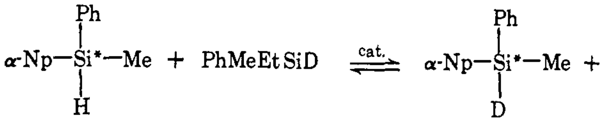
It has previously been demonstrated with optically inactive compounds that the silicon–hydrogen bond is extremely labile in the presence of platinum[4] and chloroplatinic acid,[5] resulting in SiH–SiD exchange at room temperature (3). The observation that reactions 1 and

$$R_3SiD + R_3'SiH \overset{\text{cat.}}{\rightleftharpoons} R_3SiH + R_3'SiD \qquad (3)$$

2 are highly stereospecific implies that, if Si*H–Si*H exchange processes are rapid and concurrent in eq 1 and 2, they must proceed with an exceedingly high degree of retention of configuration.

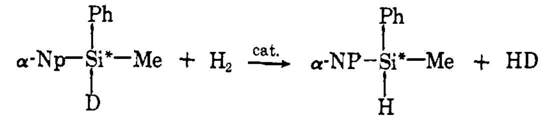
We wish to report that (a) a wide variety of hydrosilation and substitution catalysts promote Si*H–Si*D exchanges that are much faster than either hydrosilation or substitution; and (b) *such exchanges proceed with nearly complete retention of configuration at the asymmetric center* (4).

In addition, we have found that optically active α-naphthylphenylmethyldeuteriosilane reacts rapidly with



$$\alpha\text{-Np}-\overset{\text{Ph}}{\underset{\text{H}}{\text{Si}^*}}-\text{Me} + \text{PhMeEtSiD} \overset{\text{cat.}}{\rightleftharpoons} \alpha\text{-Np}-\overset{\text{Ph}}{\underset{\text{D}}{\text{Si}^*}}-\text{Me} + \text{PhMeEtSiH} \qquad (4)$$

hydrogen gas in the presence of palladium and nickel catalysts (5), the configuration of the starting silane being nearly completely retained. The results of these experiments are reported in Tables I and II.



$$\alpha\text{-Np}-\overset{\text{Ph}}{\underset{\text{D}}{\text{Si}^*}}-\text{Me} + H_2 \xrightarrow{\text{cat.}} \alpha\text{-NP}-\overset{\text{Ph}}{\underset{\text{H}}{\text{Si}^*}}-\text{Me} + \text{HD} \qquad (5)$$

Chalk and Harrod[6] have pointed out the close relationship between the metal-catalyzed hydrosilation of olefins and the hydrogenation of olefins. Reactions 4 and 5 show that a marked similarity exists between the exchange reactions of R_3Si^*H and those of H_2 in the presence of transition metals (6). The formation of a

$$H_2 + D_2 \xrightarrow{\text{cat.}} 2HD \qquad (6)$$

metal–hydrogen bond (7) is believed to be responsible

$$H_2 + 2M \longrightarrow 2MH \qquad (7)$$

for the exchange reaction between hydrogen and deuterium in the presence of these catalysts.[7] *If the silicon–hydrogen bond is cleaved in a similar manner, the formation of the silicon–metal bond as well as its subsequent cleavage must be highly stereospecific.*[8] This result

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

(5) J. W. Ryan and J. L. Speier, *J. Am. Chem. Soc.*, **86**, 895 (1964).

(6) A. J. Chalk and J. F. Harrod, *ibid.*, **87**, 16 (1965).

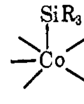
(7) D. Hayward and B. Trapnell, "Chemisorption," Butterworth & Co. (Publishers) Ltd., London, 1964, pp 236–237.

(8) Ponomarenko, *et al.*,[4] have postulated that radical species such as $R_3Si\cdot$ are involved in the exchange reaction at silicon centers. In view of the exceedingly high degree of stereospecificity of reaction 4 it appears highly unlikely that free silyl radicals are involved in the mechanism of this reaction.

is in striking contrast to the racemization of R_3C^*H on the surface of group VIII metals.[9]

It has been shown that a wide variety of compounds containing a transition metal–silicon bond may be prepared by the action of R_3SiH on transition metal complexes.[6,10,11] An interesting study by Chalk and Harrod[11] has shown further that compounds containing a silicon–cobalt bond undergo exchange with organosilicon hydrides (8). A cobalt complex formed by expansion of its coordination sphere to accommodate two silicon centers (I) has been postulated as a probable mechanism.[11] Speier has proposed a similar scheme for chloroplatinic acid catalyzed SiH–SiD exchange in solution whereby a single metal center coordinates two silicons (II).[5] Our present finding of retention of configuration for Si*H–Si*D exchange catalyzed by chloroplatinic acid or platinum–ethylene complex $((C_2H_4)PtCl_2)_2$ is consistent with intermediates such as I or II. Our studies on the dynamic stereochemistry and mechanisms of organosilicon reactions catalyzed by group VIII metals are continuing.

$$R_3SiCo(CO)_4 + R'_3SiH \rightleftharpoons R_3SiH + R'_3SiCo(CO)_4 \quad (8)$$



I

Si_2PtH_2

II

The SiH–SiD exchange reactions (4) were carried out by mixing the desired catalyst with a solution of 0.248 g (1 mmole) of optically active α-naphthylphenylmethylsilane and 0.151 g (1 mmole) of racemic phenylmethylethyldeuteriosilane 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 (4) was complete in 10 min at room temperature over palladium or nickel but took considerably longer when 5% platinum on carbon was used. Infrared spectroscopy was used to determine the extent of exchange by comparing the relative intensities of the SiH band, ~4.75 μ, and the SiD band, ~6.25 μ, 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 (5). Reaction was slower with platinum on carbon than when nickel or palladium catalysts were used. Retention stereochemistry was observed in all cases.

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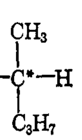
[9] R. L. Burwell, *et al.*, *J. Am. Chem. Soc.*, **79**, 5142 (1957). Isotopic exchange between (+)-3-methylhexane and deuterium on palladium and nickel catalysts have shown that nearly every exchange of the hydrogen atom at position 3 leads to racemization under the conditions of this study. In contrast to this, nearly every exchange between R_3Si^*H and deuterium (5) in the presence of palladium and nickel occurs with retention of configuration.



$$C_2H_5-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle C_3H_7}{|}}{C^*}}-H$$

[10] W. Jetz and W. Graham, *ibid.*, **89**, 2773 (1967).

[11] A. J. Chalk and J. F. Harrod, *ibid.*, **89**, 1646 (1967).

Nonequivalence of the Nuclear Magnetic Resonance Spectra of Enantiomers in Optically Active Solvents. IV. Assignment of Absolute Configuration

Sir:

We wish to report an expeditious method for assigning the absolute configuration of alkylarylcarbinols (**1**). The nmr chemical shifts of enantiomeric nuclei in type **1** carbinols differ sufficiently in optically active α-(1-naphthyl)ethylamine (**2**) solvent to allow direct comparison of the relative intensities of the resonances of these nuclei.[1] Figure 1 demonstrates that, in dex-

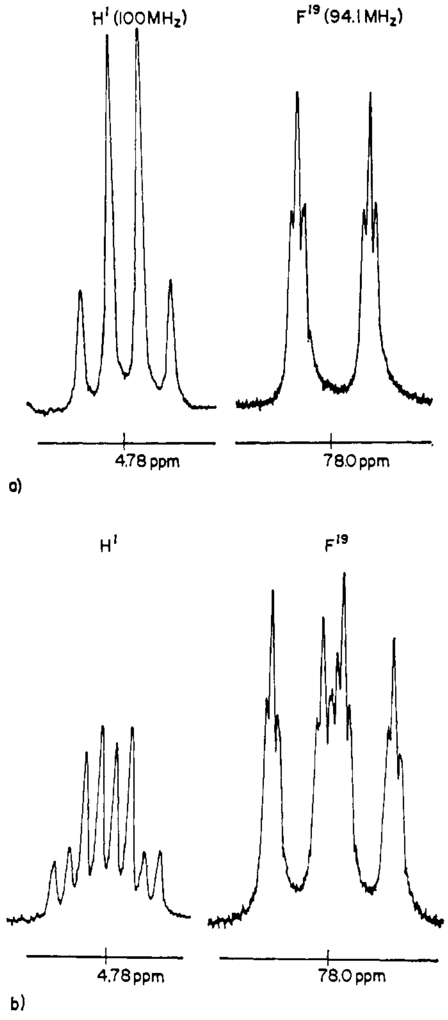


Figure 1. Portions of the nmr spectra of partially resolved 2,2,2-trifluorophenylethanol ($[\alpha]^{22}D$ 2.19° (neat)) in (a) racemic and (b) optically active α-(1-naphthyl)ethylamine ($[\alpha]^{25}D$ +80° (neat)). The carbinyl proton resonances are downfield from tetramethylsilane while those of fluorine are upfield from fluorotrichloromethane. The carbinyl proton–fluorine spin–spin coupling is 6.9 Hz. The spectra were obtained by N. Bhacca of Varian Associates.

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[1] (a) W. H. Pirkle, *J. Am. Chem. Soc.*, **88**, 1837 (1966); (b) T. G. Burlingame and W. H. Pirkle, *ibid.*, **88**, 4294 (1966); (c) W. H. Pirkle and T. G. Burlingame, *Tetrahedron Letters*, in press.