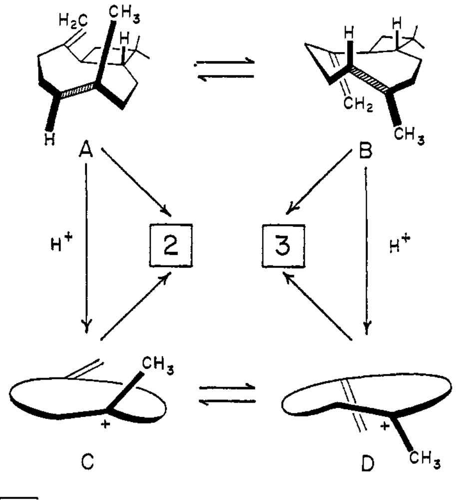
to the *endo* double bond and the resulting cation could adopt the "methyl up" and "methyl down" forms by conformational flipping (C $\rightleftarrows$ D). The C-12 to C-8 bond can be created only from the inside face[10] of the *endo* link, but the H$^+$ could attack from either the inside face or the outside face of the *endo* double bond. Therefore, net *cis* or *trans* addition is possible, and six stereochemically distinct paths are recognizable. For D$^+$ initiation, these paths are summarized in Table I along with the predicted D configurations.

Table I

		Deuterium configuration	
Path	Description	Caryo-lanol	Clo-vene
1	*trans* addition to A and to B with no intervening flipping	β	α
2	*cis* addition to A and to B with no intervening flipping	α	β
3	D$^+$ attack from "outside" on A only followed by interconversion of C and D	β	β
4	D$^+$ attack from "inside" on A only followed by interconversion of C and D	α	α
5	D$^+$ attack from "outside" on B only followed by interconversion of D and C	α	α
6	D$^+$ attack from "inside" on B only followed by interconversion of D and C	β	β

Cyclization of caryophyllene with D$_2$SO$_4$ in anhydrous ether at 0° for 12 min, followed by alkaline hydrolytic work-up, gave caryolan-1-ol (17% d_0, 81% d_1, 1.5% d_2, 0.5% d_3) and clov-2-ene, which was oxidized to clovenic anhydride (15.5% d_0, 82.5% d_1, 2% d_2). Recovered caryophyllene had 97% d_0, 3% d_1. The deuterium configurations in the tricyclic products were determined by infrared spectral comparisons with authentic samples of caryolan-1-ol-9α-*d* and -9β-*d* and the corresponding clovenic-α-*d* and -β-*d* anhydrides, which were synthesized by stereospecific routes.[11] Infrared examination of artificial mixtures established that as little as 3% of the caryolanol-α-*d* could be detected in the β-*d* epimer, and as little as 4% of clovenic-β-*d* anhydride could be detected in the α-*d* epimer. The natural abundance compounds do not show bands in the relevant fingerprint regions and so do not interfere in the spectroscopic assays. Examination of the products from cyclization showed that the deuterium had the β configuration in caryolanol (>97%) and the α configuration in clovenic anhydride (>96%). These results are compatible only with path 1.[12] Importantly, if D$^+$ attack and ring closure are synchronous (they need not be!), antiplanar addition requires the six-membered ring to develop *via* a boatlike transition state rather than *via* the (presumably) more stable chairlike form.[13]



A. C. Cope and B. A. Pauson, *J. Amer. Chem. Soc.*, **87**, 3644 (1965); G. Binsch and J. D.Roberts, *ibid.*, **87**, 5157 (1965).

(10) The plane of the *endo* link in a nine-membered ring is probably roughly perpendicular to the rest of the ring, hence the arbitrary terms "inside" and "outside" to represent the two faces of the olefinic plane.

(11) Described in the Ph.D. dissertation of F. Y. Edamura, Johns Hopkins University 1965. The synthetic schemes were made available to the editor and to the referees and will be described elsewhere.

(12) Any combination of two or more competing paths is also excluded.

(13) The chemical and spectroscopic (ir and nmr) properties of several substituted caryolane and clovane derivatives (including X-ray studies of 1-halocaryolanes) are consistent with chairlike geometry for the six-membered ring containing carbons 9, 10, and 11.[5,11]

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The Stereochemistry of the Silicon–Cobalt Bond and Some Implications for Homogeneous Transition Metal Catalysis[1]

Sir:

Recent discovery of methods for the preparation of compounds containing the transition metal–silicon bond,[2,3] together with the novel properties of these substances,[4] has stimulated lively interest in this area of chemistry during the past 3 years. The elegant studies of Chalk and Harrod[2b] concerning the silylcobalt carbonyls has appreciably increased the understanding of the mechanisms of homogeneous transition metal catalysis in organosilicon chemistry. Studies carried out in our laboratories[5–8] showed that transition metal catalyzed reactions of the silicon–hydrogen bond were highly stereospecific and suggested the possible involvement of intermediates possessing transition metal–silicon bonds. These observations led us to the conclusion that stereochemical studies could make a significant contribution toward elucidating

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[1] Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

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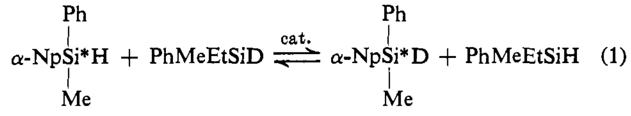
mechanisms of reactions involving the silicon–transition metal bond.

We wish to report: (a) that dicobalt octacarbonyl and bis(triphenylphosphine)carbonylchloroiridium(I) are catalysts for Si*H–Si*D exchange in homogeneous solution (eq 1); (b) *that these exchanges are stereospecific and occur with complete retention of configuration at the asymmetric silicon center;* and (c) that the mechanism of $Co_2(CO)_8$ catalyzed exchange most probably involves an optically active intermediate containing a silicon–cobalt bond. In this connection we have: (d) prepared *the first optically active compound containing a Si*–Co bond;* (e) shown that it is an active catalyst for stereospecific Si*H–Si*D exchange; and (f) studied the stereochemistry of several of its reactions.



$$\alpha\text{-Np}\overset{\text{Ph}}{\underset{\text{Me}}{\text{Si*H}}} + \text{PhMeEtSiD} \xrightleftharpoons{\text{cat.}} \alpha\text{-Np}\overset{\text{Ph}}{\underset{\text{Me}}{\text{Si*D}}} + \text{PhMeEtSiH} \quad (1)$$

$$[\alpha]\text{D} -35^\circ \qquad\qquad [\alpha]\text{D} -35^\circ$$

cat. = $Ir[P(C_6H_5)_3]_2COCl$; $Co_2(CO)_8$

Optically active α-naphthylphenylmethylsilylcobalt tetracarbonyl, $R_3Si^*Co(CO)_4$ (I), may be readily prepared (eq 2) from (−)-R_3Si^*H, $[\alpha]D$ −35°, and dicobalt octacarbonyl in hydrocarbon solvent according to the method of Chalk and Harrod.[2b] It is a white, crystalline compound, mp 102–104.5°, which may be purified by fractional crystallization from pentane and heptane. *Anal.* Calcd for $C_{21}H_{15}O_4CoSi$: C, 60.29; H, 3.61. Found: C, 60.39; H, 3.51. The infrared spectrum exhibits all the bands related to the α-NpPhMeSi* moiety as well as the following absorptions which are characteristic of silylcobalt carbonyls: 2095 (s), 2040 (s), 2010 (vs), 1995 (vs, sh), 1960 (w) cm^{-1}.

$$\underset{[\alpha]\text{D} -35^\circ}{2\alpha\text{-NpPhMeSi*H}} + \text{Co}_2(\text{CO})_8 \longrightarrow \underset{[\alpha]\text{D} -2^\circ}{2\alpha\text{-NpPhMeSi*Co(CO)}_4} + \text{H}_2 \quad (2)$$

The sign of the plain dispersion curve of I is opposite that of the starting silane. Specific rotations in heptane at a number of wavelengths are as follows: −2° (589), +5° (510), +10° (490), +50° (420), +100° (388), +200° (360). At 360 mμ the molecular rotation of I is approximately double that of optically pure (−)-R_3Si^*H and of opposite sign.

The original optically active silane, (−)-R_3Si^*H, may be regenerated from I by silyl–ligand exchange[2b] with excess triethylsilane (eq 3), showing that $R_3Si^*Co(CO)_4$ had a minimum optical purity of 85%. Thus, the over-all result of (2) and (3) is *retention* of configuration at the silicon center.

$$\underset{[\alpha]\text{D} -2^\circ}{\alpha\text{-NpPhMeSi*Co(CO)}_4} + (\text{C}_2\text{H}_5)_3\text{SiH} \rightleftharpoons \underset{[\alpha]\text{D} -31^\circ}{\alpha\text{-NpPhMeSi*H}} + (\text{C}_2\text{H}_5)_3\text{SiCo(CO)}_4 \quad (3)$$

Treatment of I with methanol, on the other hand, leads to (+)-$R_3Si^*OCH_3$ having the opposite configuration from that of (−)-R_3Si^*H[9] (eq 4). Since $HCo(CO)_4$ is an acid of approximately the same strength as HCl,[10] the $Co(CO)_4$ group would be expected to be a good leaving group from silicon.[11] Hence, reaction 4 can be assigned inversion stereochemistry. This leads to the assignment of retention for reactions 2 and 3, as expected.

$$\underset{[\alpha]\text{D} -2^\circ}{\text{R}_3\text{Si*Co(CO)}_4} + \text{CH}_3\text{OH} \longrightarrow \underset{[\alpha]\text{D} +8^\circ}{\text{R}_3\text{Si*OCH}_3} \quad (4)$$

(+)-Neopentylphenylmethylsilane behaves in a similar manner; the over-all exchange process (5) occurs with retention. The silylcobalt carbonyl was not isolated in this case; however ir and ORD data for hydrocarbon solutions were comparable with those of I.

$$\underset{[\alpha]\text{D} +6^\circ\ (c\ 4,\ \text{toluene})}{(+)\text{-neo-C}_5\text{H}_{11}\text{PhMeSi*H}} + \text{Co}_2(\text{CO})_8 \xrightarrow[25^\circ]{\text{toluene}} \left[\underset{[\alpha]\text{D} -43^\circ}{(-)\text{-neo-C}_5\text{H}_{11}\text{PhMeSi*Co(CO)}_4}\right]$$

$$\xrightarrow{\text{Ph}_3\text{SiH, excess}} \underset{[\alpha]\text{D} +6^\circ}{(+)\text{-neo-C}_5\text{H}_{11}\text{PhMeSi*H}} + \text{Ph}_3\text{SiCo(CO)}_4 \quad (5)$$

We have advanced the possibility of the stereospecific formation of a transition metal–silicon bond as an explanation for the group VIII metal catalyzed Si*H–Si*D exchange reactions (eq 1).[5] Whereas our previous work[5] was largely concerned with heterogeneous metal catalysts, we have recently extended this investigation to encompass homogeneous catalytic systems.

When 2 mmol of optically active R_3Si^*D and 2 mmol of racemic phenylmethylethylsilane are stirred in the presence of 2×10^{-5} mol of $Co_2(CO)_8$ in refluxing hexane (68°) for 24 hr, stereospecific Si*H–Si*D exchange (eq 1) is complete.[12] The relevence of eq 2, 3, and 5 to the mechanism of this exchange is obvious. Furthermore, if a combination of (2) and (3) represents the *mechanism of Si*H–Si*D exchange, then I should* be an effective catalyst for this process. *α-Naphthylphenylmethylsilylcobalt tetracarbonyl (I) was indeed found to be an active catalyst for stereospecific Si*H–Si*D exchange* under conditions similar to those used for the $Co_2(CO)_8$ catalyzed reaction (eq 1).

The catalytic activity of bis(triphenylphosphine)carbonylchloroiridium(I) in Si*H–Si*D exchange was also studied. When a benzene solution of 2 mmol of optically active R_3Si^*H, 2 mmol of racemic phenylmethylethyldeuteriosilane, and 10^{-5} mol of the Ir(I) complex was stirred at room temperature under nitrogen for 17 hr, complete scrambling of the hydrogen and deuterium between the available silanes was observed.[12] The exchange occurred with complete *retention* of configuration at the asymmetric silicon center (eq 1). It is possible that exchange proceeds *via* the initial formation of an unstable[13] addition compound containing the silicon–iridium bond such as in (6). The stereochemical data require that such a compound, if formed, be optically active and further that its formation

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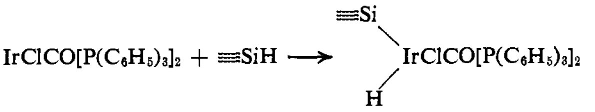
[12] Infrared spectroscopy was used to determine the extent of exchange by comparing the relative intensities of the Si–H band, ~4.75 μ, and the Si–D band, ~6.25 μ, in each of the products.

[13] Chalk and Harrod[2a] report that stable Ir(I) complexes are formed only by silanes possessing highly electronegative groups, *i.e.*, Cl_3SiH, $(RO)_3SiH$. Stable adducts are not formed from trialkyl- and triarylsilanes.

as well as subsequent exchange processes must occur with complete *retention* at the silicon center.



$$\mathrm{IrClCO[P(C_6H_5)_3]_2} + \equiv\mathrm{SiH} \longrightarrow \mathrm{IrClCO[P(C_6H_5)_3]_2}\begin{matrix}\diagup\equiv\mathrm{Si}\\ \diagdown\mathrm{H}\end{matrix} \qquad (6)$$

Research is continuing on the stereochemistry of reactions involving compounds containing silicon–transition metal bonds. A series of novel leaving groups including platinum as well as cobalt species are currently under investigation.

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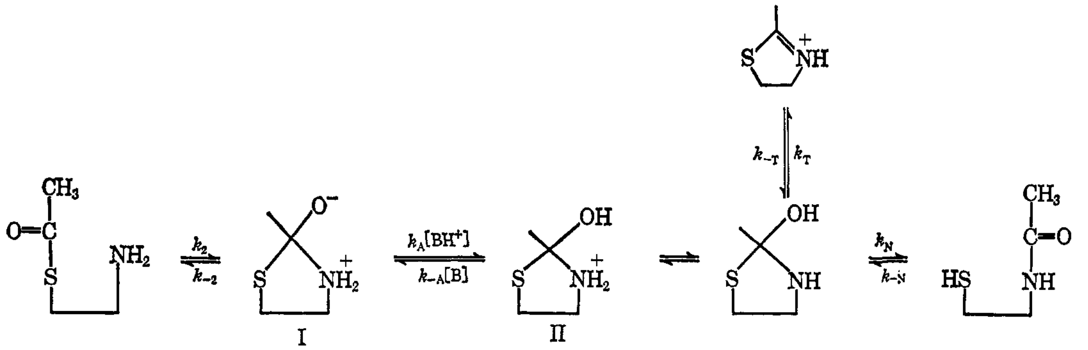
Rate-Limiting Diffusion-Controlled Proton Transfer in an Acetyl Transfer Reaction[1]

Sir:

We wish to suggest that the rate-determining step of the intramolecular S to N acetyl transfer reaction of S-acetylmercaptoethylamine above pH 2.3 is a diffusion-controlled proton transfer and propose a mechanism for the reaction which appears to resolve the "thiazoline dilemma." [2] The evidence for this proposal is (a) a change in rate-determining step in this reaction at pH 2.3 can be accounted for by the proposed mechanism, but cannot be accounted for by steps which involve only bond formation or breaking with carbon, and (b) general acid catalysis of the reaction by carboxylic acids and phosphate occurs with an α value indistinguishable from zero, as expected for a diffusion-controlled reaction.



(2)

It is known that this intramolecular thiol ester aminolysis proceeds through a neutral transition state in acid solution and undergoes a change to a rate-determining step with a cationic transition state at pH 2–3; this step also proceeds through a neutral transition state above pH 4. Above pH 3 the reaction is subject to general acid catalysis. Martin and Hedrick first suggested that a slow proton-transfer step could account for these kinetic results and for the pH dependence of product yields from the hydrolysis of 2-methyl-Δ^2-thiazoline;[3] however, it was later pointed out that the proposed scheme does not account for all of the experimental data.[2]

Thiol ester disappearance or formation at 50° was followed spectrophotometrically at 230 mμ and thiazoline disappearance at 260 mμ. Above pH 2.3 the reaction of the cationic substrate is subject to general base catalysis with a Brønsted slope, β, of 0.97 for catalysis by carboxylate anions and phosphate dianion (Figure 1). This corresponds to a Brønsted slope, α, of 0.03 when the reaction is described by the kinetically equivalent k' for general acid catalysis of the reaction of the free amine (eq 1). This α value is equal, within experimental error, to the α value of zero expected for

$$v = k_B[SH^+][A^-] = k'[S][HA] \qquad (1)$$

a diffusion-controlled proton-transfer reaction,[4] and we suggest that the rate-determining step of the over-all reaction under conditions in which this catalysis is observed is, in fact, a diffusion-controlled proton transfer.

We have confirmed the earlier observation[5] that the ratio of thiol ester to amide product (1.0 at 50°) in thiazoline hydrolysis is independent of pH below pH 2 and have shown, by measuring initial rates of thiazoline disappearance and thiol ester formation, that the decrease in yield of thiol ester at higher pH values is not caused by secondary S to N acetyl transfer. The dependence on pH of the change in product ratio ("pK" = 2.37) corresponds to the change in rate-determining step in the intramolecular aminolysis reaction ("pK" = 2.30). The kinetic argument may be stated as follows. Below pH 2 the tetrahedral intermediate formed in thiazoline hydrolysis (eq 2) breaks down equally easily to thiol ester and to amide through transition states of zero charge. The decrease (a) in the rate of thiol ester aminolysis and (b) in the yield of thiol ester from thiazoline hydrolysis with increasing pH demands that *another step with a cationic transition state become rate determining* on the thiol ester limb of eq 2. This must be a simple proton-transfer step, and we suggest that it is step k_A of eq 2. The alternative assignment to k_3' of eq 3 would require a value of k_{-2}' of $\approx 10^{16}\ M^{-1}\ \mathrm{sec}^{-1}$ if the pK of the cationic intermediate is assumed to be 6.

Assuming that k_A for the solvated proton is $6.5 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$ at 50°,[4,6] the values for most of the rate

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(6) This assumes $E^{\ddagger} = 2$ kcal/mol and that ionic strength has little effect on diffusion coefficients.