

Figure 2. The 100-MHz pmr spectra of the α -phenethylamine derivatives in chloroform- d_1 . The solutions have been treated with D_2O to reduce the intensity of the amino protons and simplify the spectra. At -60° the spectrum of the complexes prepared from the (*R*)- α -phenethylamine is identical with that of the complexes prepared from the racemic amine.

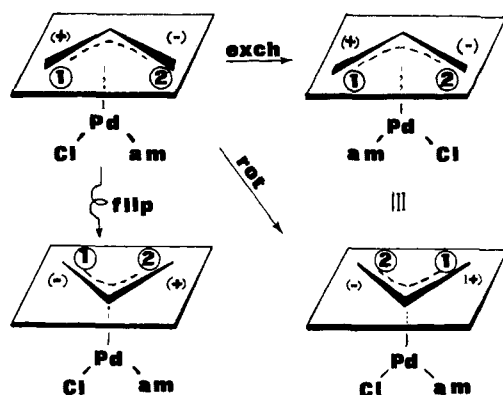


Figure 3. The mechanisms consistent with the averaging process giving rise to the 35° pmr spectrum with the (*R*)- α -phenethylamine complex. The arbitrary symbols (+) and (-) refer to the absolute configurations at the terminal allyl carbon atoms.

free amine occurs and that intermolecular amine exchange dominates proton environment interconversion throughout the accessible temperature range (up to the decomposition point $\sim 50^\circ$).

Having unambiguously demonstrated the existence of intermolecular ligand exchange, the possibility of additional epimerization occurring *via* a flip mechanism

remains to be considered. Since the flip mechanism averages different pairs of resonances from the exchange mechanism, the simultaneous occurrence of both mechanisms would coalesce the two AA'BB'X spectra in the (*R*)- α -phenethylamine complex, which is not consistent with the observed spectra.

The study of the pmr of these amine complexes up to 35° allows observation of the effects of a rapid epimerization mechanism ($k > 100 \text{ sec}^{-1}$ at 35°); conceivably other mechanisms with slower rates ($k < 0.5 \text{ sec}^{-1}$ at 35°) could contribute to epimerization, but would not alter the pmr spectrum. Our results lead us to conclude that racemization and epimerization in π -allyl(amine)palladium complexes are primarily a consequence of dissociation of the compound into free amine and dimer, rather than conversion to a σ -bonded intermediate. This is rather surprising in view of the part played by the σ -bonded intermediate in phosphine and arsine derivatives. Consequently, the absence of an effect from a σ -bonded intermediate or a flip mechanism requires that the face of the π -allyl moiety bonded to the palladium atom is invariant during epimerization or racemization caused by amine exchange.¹⁹

Studies are being pursued to determine the implications of these results in rearrangements of substituted π -allylpalladium derivatives, as well as molybdenum π -allyls.^{21,23}

(19) The configurations at the terminal carbon atoms of the π -allyl group [*i.e.*, the chirality of the Pd-($H_2C^*==C$) centers] are preserved during the epimerization of the unsubstituted complexes by amine exchange. Inversion of configuration at the terminal carbon atoms *via* a σ -bonded intermediate has been proposed as the most likely mechanism of epimerization in substituted π -allyl derivatives.²⁰ For the unsubstituted compounds reversible broadening of the *syn* and *anti* resonances (as well as decomposition) is observed in benzene solution above 50° , and this does indeed support an additional epimerization pathway *via* a σ -bonded intermediate. Nevertheless, this mechanism, which allows a different face of the allyl group to become bonded, does not contradict the previous conclusions, since it proceeds at a much slower rate ($k < 0.5 \text{ sec}^{-1}$ at 35°).

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(21) The absence of a flip mechanism gives further support to a planar rotation mechanism in molybdenum π -allyl rearrangements. Presumably the ability to undergo facile 3:4 = 3:3:1 = 3:4 stereochemically nonrigid rearrangements²² in this "seven-coordinate" complex might allow the effective planar rotation of the π -allyl, which has not yet been observed in the palladium complexes due to the prior occurrence of exchange.

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Stereochemical Course of the Reaction of an Optically Active Hydrosilane with Carbon Tetrachloride by a Free-Radical Mechanism. Retention of Configuration¹

Sir:

When free radicals are generated from compounds containing an asymmetric carbon atom, which bears the

(1) Silyl Radicals. II.

Table I. Reaction of (+)-R₃Si*H with Carbon Tetrachloride in the Presence of Dibenzoyl Peroxide at 80.0°

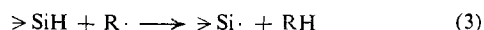
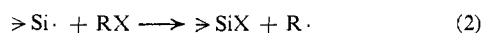
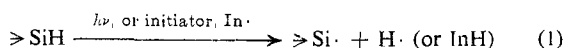
Run	Reactant used, mmoles			Reaction time, hr	R ₃ Si*Cl			R ₃ Si*H after redn	
	(+)-R ₃ Si*H	BPO	CCl ₄		Mole %	[α] _D , deg	Opt purity, %	[α] _D , deg	Opt purity, %
1	6.76	0.47	105.7	14	93.2	-5.34	85.5		
2	11.52	0.85	120.2	11	94.9	-5.20	83.2	-31.7	93.9
3	7.44	0.27	59.8	12	64.6	-3.57	57.1		
4	(0.981 g) ^a	0.14	Ca. 3 ml	12	92.1	-4.76	76.4	-29.4	87.8

^a Products of run 3 were used as a mixture.

unpaired electron, the optical activity of the parent compounds is lost and racemic products are formed, except in unusual situations.² The loss of optical activity in the products can be ascribed either to planar configurations or to the very rapid inversion of the radicals.³

In spite of current interest in silyl radicals, no investigation on the stereochemical course of reactions in which silyl radicals play an important role has been reported to date. The silyl radical derived from an optically active hydrosilane has been presumed to lose its optical activity.⁴ However, we now report that the silyl radical produced from an optically active hydrosilane undergoes chlorine-abstraction reaction mostly with *retention of configuration*.

The abstraction of chlorine atoms by silyl radicals was reported by several investigators; the silyl radicals may be produced by photolysis,^{5,6} peroxide-catalyzed reaction,⁷⁻⁹ and thermolysis¹⁰ of hydrosilanes. The free-radical nature of the reaction has been clearly established, and a chain reaction involving chlorine abstraction by silyl radicals was suggested. In addition, there



is other good evidence indicative of the formation of free silyl radicals from hydrosilanes in reactions catalyzed by peroxides.¹¹⁻¹³

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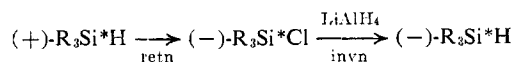
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When an optically active hydrosilane, (+)-α-naphthylphenylmethylsilane (**1**),¹⁴ [α]_D +33.7° (c 10.9, cyclohexane) [lit.¹⁴ [α]_D +34.3° (c 10.9, cyclohexane)], was heated with carbon tetrachloride without any catalyst in a sealed tube at 80.0°, no reaction took place even after 117 hr. However, the presence of a small amount of dibenzoyl peroxide resulted in the formation of the corresponding chlorosilane, (-)-α-naphthylphenylmethylchlorosilane (**2**) [lit.¹⁴ [α]_D -6.28° (c 10.5 cyclohexane)], in good yield. The product, obtained after evaporation of carbon tetrachloride followed by recrystallization from pentane, contained a small amount of **1** (glpc). Separation of **2** from the mixture was not feasible because of thermal racemization of **2**.¹⁵ Since unreacted **1** can be separated from the mixture by glpc with configuration retention (at least 95% optical purity),¹⁵ it is likely to assume that **1** in the mixture must have the same optical activity as it had originally. Therefore, optical activities of **2** in each run were determined on the basis of proportional allotment. Furthermore, **2** was converted to **1** again by the reduction with lithium aluminum hydride. The results are listed in Table I.

The stereochemical sequence established by Sommer and coworkers¹⁴ indicates clearly that free-radical chlorination of **1** proceeds with retention of configuration.



The most straightforward explanation of the results may be that the chlorine-abstraction step (reaction 2) is so fast that the optically active silyl radical can be trapped before racemization by inversion. However, several alternative explanations would be possible for such an unexpectedly highly stereospecific free-radical reaction. We will discuss details in a future publication.

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Stereospecific Photochemical Cyclodimerization of 2-Butene in Liquid Phase

Sir:

We wish to report stereospecific photochemical cyclodimerization of liquid 2-butene with retention of geometric configuration in both 2-butene fragments.