mode in reactions of V^{3+}.[11,12] It is interesting to note that $\Delta S^{\ddagger}$ is -11 ± 4 eu at 100° for $Fe(DMSO)_6^{3+}$ exchange and -16 eu for $Ni(DMSO)_6^{2+}$ DMSO exchange.[5] $V(DMSO)_6^{3+}$ should be especially interesting.

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Dihalocarbene Insertions into Optically Active R_3Si^*H with Retention of Configuration[1]

Sir:

Recently there has been much interest in carbene (or carbenoid) insertions into Si–X bonds in which X = H,[2] C (ring strained),[3] and Cl.[4] We wish to report the first stereochemical studies on such insertions, using optically active α-naphthylphenylmethylsilane, R_3Si^*H.[5] Specifically, the present work involved insertion of CCl_2 and CBr_2 using the appropriate organomercury compounds, trichloromethyl- and tribromomethylphenylmercury, $PhHgCX_3$.[6] The general procedure comprised refluxing a 200-ml benzene solution of the silane (40 mmol) and organomercury compound (40 mmol). Reaction times were 24 hr for $PhHgCCl_3$ and 4 hr for $PhHgCBr_3$. The phenylmercuric halide which formed was filtered, the solvent removed by distillation, and the crude product taken up in CCl_4 solvent. Unreacted R_3Si^*H in the crude product was converted to R_3Si^*OH by treatment with Cl_2 followed by hydrolysis of the Si–Cl bond, and the product was then passed through a column of silica gel for removal of the R_3Si^*OH. This procedure gave $R_3Si^*CHX_2$ of good purity as determined by infrared and nmr spectra and analysis for C, H, and X. Using dextrorotatory R_3Si^*H the insertions proceeded as follows.

$$\begin{array}{lcl} (+)\text{-}R_3Si^*H + PhHgCX_3 & \longrightarrow & (+)\text{-}R_3Si^*CHX_2 \\ [\alpha]_D\ +35.0^\circ & & X = Cl;\ [\alpha]_D\ +21.0^\circ \\ & & X = Br;\ [\alpha]_D\ +14.3^\circ \end{array}$$

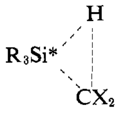
The problem of correlation of configuration between R_3Si^*H and $R_3Si^*CHX_2$ was overcome by preparation of the insertion products *via* independent syntheses involving reactions of known stereochemistry. The latter used organolithium reagents in coupling reactions with R_3Si^*Cl, a class of reactions known to proceed with inversion of configuration.[7] The dichloromethyllithium reagent was prepared in THF solvent by the general low-temperature method previously reported for α-chloroalkyllithium compounds.[8]

$$\begin{array}{lcl} (-)\text{-}R_3Si^*H + Cl_2 \xrightarrow{\text{retention}} (+)\text{-}R_3Si^*Cl & \xrightarrow[\substack{LiCHX_2 \\ -90^\circ}]{\text{inversion}} & (+)\text{-}R_3Si^*CHX_2 \\ [\alpha]_D\ -35.2^\circ \qquad\qquad\qquad [\alpha]_D\ +6.3^\circ & & X = Cl;\ [\alpha]_D\ +22.6^\circ \\ & & X = Br;\ [\alpha]_D\ +13.8^\circ \end{array}$$

Dibromomethyllithium was prepared by the reaction of dichloromethyllithium with dibromomethane[9] in THF solvent. Thus based on assignment of an inversion stereochemistry to the coupling reactions of $LiCHX_2$ with R_3Si^*Cl, (+)-$R_3SiCHCl_2$ and (+)-$R_3Si^*CHBr_2$ have the same configuration as (+)-R_3Si^*H and *the insertion of CCl_2 and CBr_2 into the silicon–hydrogen bond proceeds with retention of configuration.* The solid $R_3Si^*CHCl_2$ from the coupling reactions was recrystallized up to constant rotation, $[\alpha]_D$ +24.4°, indicating optical purity. From this it appears that the insertion proceeded with a high degree of stereospecificity, ~93%.

The insertion products of R_3Si^*H and those obtained by coupling reactions of $LiCHX_2$ with R_3Si^*Cl had identical infrared and nmr spectra.

The present finding of a retention stereochemistry for the insertion reactions of CCl_2 and CBr_2 with R_3Si^*H is certainly consistent with a three-center mechanism involving direct electrophilic attack of CX_2 on the silicon–hydrogen bond (I). It is interesting to note that a very similar mechanism (II) has been advanced previously[10] for the reactions of R_3Si^*H with X_2 (X = Cl or Br) which also proceed with retention of configuration. These reactions were postulated to involve electrophilic attack on R_3Si^*H by X^+. Transition states I and II both involve attack of electrophilic species on the silicon–hydrogen bond,[11] and both proceed with retention of configuration.



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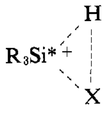

II

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[1] Current support of this work by the National Science Foundation is gratefully acknowledged. Initial studies were carried out at The Pennsylvania State University with support from Dow Corning Corp.
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[6] It has been emphasized previously by Seyferth and coworkers that the use of $PhHgCX_3$ for CX_2 insertion into SiH comprises an especially useful method which avoids strong bases that can give nucleophilic substitution with Si–H bonds.
[7] For recent numerous examples, see: L. H. Sommer, W. D. Korte, and P. G. Rodewald, *J. Am. Chem. Soc.*, **89**, 862 (1967).
[8] D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *ibid.*, **87**, 4147 (1965). Our procedure employed −90° instead of −100° as reported.
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[11] In many respects dihalocarbenes behave as electrophilic species. For a summary see: W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, pp 163–164. Also recent evidence indicates that $PhHgCX_3$ functions as a source of free CX_2 carbene: D. Seyferth, J. Yick-Pui Mui, and J. M. Burlitch, *J. Am. Chem. Soc.*, **89**, 4953 (1967).

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A Distinctly Bent Metal–Nitrosyl Bond. The Preparation and Structure of Chlorocarbonylnitrosylbis(triphenylphosphine)iridium Tetrafluoroborate, $[IrCl(CO)(NO)(P(C_6H_5)_3)_2][BF_4]$

Sir:

We wish to report the first accurately documented example of a distinctly bent M–N–O linkage in a metal nitrosyl complex and to present an explanation for this unusual mode of bonding.