gratefully acknowledged. The author wishes to thank Dr. J. D. Baldeschwieler and Messrs. S. Buttrill, R. Dunbar, and J. Garcia for many helpful discussions.

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On the Mechanism of Complex Formation and Solvent-Exchange Reactions of Iron(3+) in Dimethyl Sulfoxide[1]

Sir:

Complex formation reactions of 3+ aquo metal ions such as Fe^{3+} and Al^{3+} have presented special problems to chemical dynamicists. Apparent rate sensitivity to entering ligands (basicity dependence) suggests an *associative* mode of activation[2] in an octahedral substitution, but there is a "proton ambiguity." No kinetic test distinguishes paths 1 and 2. Seewald and Sutin[3]

$$Fe(OH_2)_6{}^{3+} + X^- \longrightarrow Fe(OH_2)_5X^{2+} + H_2O \tag{1}$$

$$Fe(OH_2)_5OH^{2+} + HX \longrightarrow Fe(OH_2)_5X + H_2O \tag{2}$$

and Carlyle and Espenson[4] have produced ingenious indirect arguments supporting path 2 in some cases. If they are right, Fe^{3+} falls within the common *dissociative* pattern of octahedral substitution.

For the light they may shed on the "proton ambiguity," reactions of Fe^{3+} in dimethyl sulfoxide (DMSO) should be interesting. DMSO is an *aprotic* solvent in which metal ions have been shown to display kinetic behavior similar to their behavior in water.[5,6]

We have prepared $Fe(DMSO)_6(NO_3)_3$ by heating $Fe(NO_3)_3 \cdot 6H_2O$ in DMSO. Lemon yellow crystals form on cooling which may be recrystallized from DMSO. *Anal.* Calcd for $FeC_{12}H_{36}O_9S_6N_3$: C, 20.30; H, 5.11; N, 5.91. Found: C, 19.89; H, 5.09; N, 5.99. Reactions of $Fe(DMSO)_6{}^{3+}$ with SCN^- (ionic strength 0.024 maintained with $NaNO_3$) and sulfosalicylic acid (SSA) were examined at 25° in a Durrum stopped-flow spectrophotometer using wavelengths of 446 and 536 mμ, respectively. Since rates of approach to equilibrium were observed, the equilibrium constants for complex formation were estimated *via* the Newton and Arcand procedure[7] from more accurate spectrophotometric data obtained using a Gilford 240 manual spectrophotometer. All experiments were carried out using excess $Fe(DMSO)_6{}^{3+}$ to ensure pseudo-first-order kinetics and/or only monocomplex formation. Experimental concentration ranges were: Fe^{3+}, 1-4 × 10^{-3} *M;* ligand, 1-6 × 10^{-4} *M*.

We report over-all equilibrium constants for complex formation (precise to ∽5%) and second-order rate constants for complex formation as follows: SCN^-, 1180 M^{-1} and 670 ± 10 M^{-1} sec^{-1}; SSA, 420 M^{-1} and 23 ± 4 M^{-1} sec^{-1}.

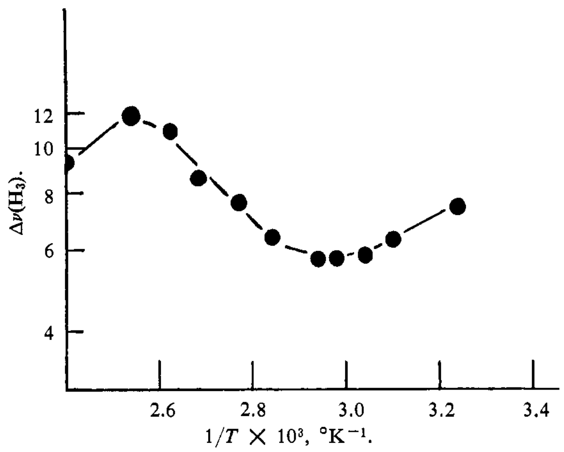

Figure 1. Paramagnetic broadening of DMSO proton resonance by Fe^{3+} as a function of temperature. Data are reported for 0.01 and 0.02 *M* solutions and presented normalized to 0.02 *M*.

Proton magnetic resonance spectra of DMSO and DMSO containing 0.01 and (at higher temperature) 0.02 *M* $Fe(DMSO)_6{}^{3+}(NO_3)_3$ were recorded as a function of temperature. Paramagnetic line broadening (line width corrected for ∽1.5 Hz pure solvent line width) as a function of $1/T$ is presented in Figure 1 normalized to 0.02 *M* Fe^{3+}. The observed broadenings are small for precise analysis since they are precise to ±0.2 Hz (solubility limitations prevent study of higher concentrations). An "Arrhenius region" is seen between about 80 and 100°. Following established procedures,[8] including correction for the low-temperature outer-sphere broadening, a solvent-exchange rate constant of 1400 ± 200 sec^{-1} is estimated for 100°. The activation energy, E_a, is 10 ± 2 kcal/mole; thus the solvent-exchange rate at 25° is estimated to be approximately 50 sec^{-1}. These values relate to the corresponding ones for H_2O exchange as might have been expected.[5,6]

According to Eigen's[9] mechanism, a complex formation reaction is written as

$$Fe(DMSO)_6{}^{3+} + L^{n-} \overset{K}{\rightleftharpoons} Fe(DMSO)_6{}^{3+},L^{n-} \xrightarrow{k_1} Fe(DMSO)_5L^{(3-n)+} + DMSO \tag{3}$$

Observed second-order rate constants, k_2, are interpreted as $k_2 = Kk_1$, where K is the equilibrium constant for outer-sphere association, and k_1 is the first-order rate constant for outer-sphere to inner-sphere conversion. For neutral ligands, K is expected to be of the order of unity. Using Fuoss' theory[10] and an ion size parameter of 5 Å, K for SCN^- is estimated to be 106 (at ionic strength 0.024). The k_1 values may then be *approximated* for the various ligands as: DMSO, 50 sec^{-1}; SCN^-, 6.3 sec^{-1}; SSA, 23 sec^{-1}. The clustering of these values suggests substitution insensitive to entering ligand and a normal *dissociative* mode of activation.

We are examining other ions. Negative $\Delta S^{\ddagger}$ values have recently been cited as evidence of the *associative*

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[1] We acknowledge with thanks the support of the National Research Council of Canada.

[2] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1966, Chapter 1.

[3] D. E. Seewald and N. Sutin, *Inorg. Chem.*, **2**, 643 (1963).

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[5] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

[6] S. Thomas and W. L. Reynolds, *ibid.*, **46**, 4164 (1967).

[7] T. W. Newton and G. M. Arcand, *J. Am. Chem. Soc.*, **75**, 2449 (1953).

[8] T. R. Stengle and C. H. Langford, *Coord. Chem. Rev.*, **2**, 349 (1967).

[9] M. Eigen and R. G. Wilkins, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 55.

[10] R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

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.

[11] W. Kruse and D. Thusius, *Inorg. Chem.*, 7, 464 (1968).

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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.

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

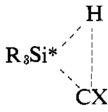
The problem of correlation of configuration between R_3Si^*H and $R_3Si^*CHX_2$ was overcome by preparation of the insertion products *via* independent syntheses involving reactions of known stereochemistry. The latter used organolithium reagents in coupling reactions with R_3Si^*Cl, a class of reactions 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]

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

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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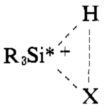

II

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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.

[9] G. Köbrich, *Angew. Chem. Intern. Ed. Engl.*, **6**, 41 (1967).

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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.