maleic anhydride, and acrylonitrile, whereas it does react with electron-rich olefins. That is, *o*-benzoquinone methide preferentially behaves as an *electron-deficient* diene. Therefore the reaction of *o*-benzoquinone methide with an olefin can be regarded as an example of an inverse-electron-demand Diels–Alder reaction[8] involving a neutral diene.[9]

(8) Bradsher, C. K.; Carlson, G. L. B.; Porter, N. A.; Westerman, I. J.; Wallis, T. G. *J. Org. Chem.* **1978**, *43*, 822. Kwart, H.; King, K. *Chem. Rev.* **1968**, *68*, 415. Desimoni, G.; Tacconi, G. *Chem. Rev.* **1975**, *75*, 651.

(9) An example of the inverse-electron-demand Diels–Alder reaction involving a cationic diene is described in the following: Gupta, R. B.; Franck, R. W. *J. Am. Chem. Soc.* **1987**, *109*, 5393.

Catalysis by a Lewis Acid Silane for Reductions by an Analogous 10-Si-5 Hydridosiliconate[1]

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The 10-Si-5 lithium hydridosiliconate **2**, originally prepared[2] by reaction of $HSiCl_3$ with the dilithio derivative of hexafluorocumyl alcohol, is better synthesized[3] by reaction of 8-Si-4 silane **1** with $LiAlH_4$. It was found[4a,b] to be unstable when synthesized by the earlier method, probably because of the presence of destabilizing impurities. Sakurai et al.[4a] made a more stable, but not isolated, bis(phosphoranyl)iminium salt for use as a reducing agent. We also used purified tetrabutylammonium salt **4**, prepared from stable **2** as in Scheme I, and found both **2** and **4**, as well as the deuterium analogues **3** and **5**, to reduce ketones, aldehydes, etc. slowly. All were found to be much more efficient, and more selective, in the presence of silane **1** as a catalyst.

The catalyzed reduction of *p*-(dimethylamino)benzaldehyde (DMAB, **6**) in CH_2Cl_2 is kinetically third order, as shown in Scheme II. The hydridosiliconate reduction is clearly catalyzed by silane **1**. The two bidentate ligands of **1** were designed earlier,[2] with an electronegative oxygen and an electropositive carbon on each ligand, to stabilize 10-X-5 trigonal-bipyramidal hypervalent species. Silane **1** is a Lewis acid found[5] to coordinate strongly to the carbonyl oxygen of **6**. The carbonyl group becomes more electron deficient, accelerating the transfer of a hydride anion from **2** or **4** to the cationic carbon of **7** to form **8**.

Silane **1** catalyzes reductions of aldehydes,[6] ketones, and ketals, as well as α,β-unsaturated esters, aldehydes, ketones, and nitriles, providing 1,4-addition of the hydrides, with less 1,2-addition to the carbonyl group. For example, cyclohex-2-en-1-one (**9**) reacts with deuterated **3**, in the presence of **1**, to give only β-deuterated cyclohexanone **10**. The reduction of **9** by bis(1,2-benzenediolato)hydridosiliconate, with no silane present as a catalyst, was reported by Sakurai[7] to give only cyclohex-2-en-1-ol.

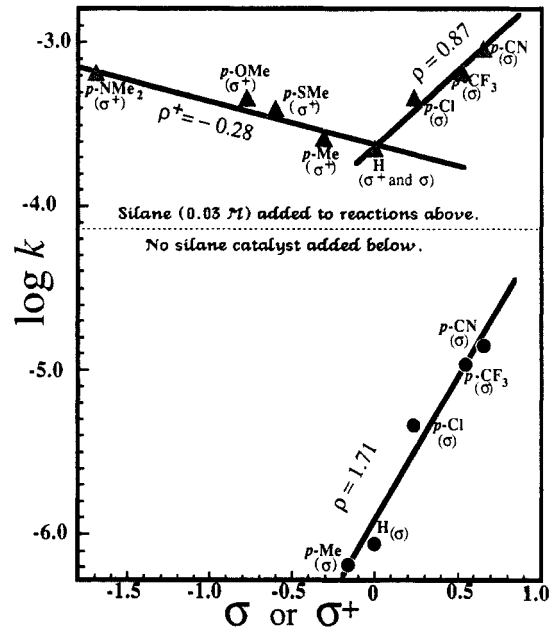
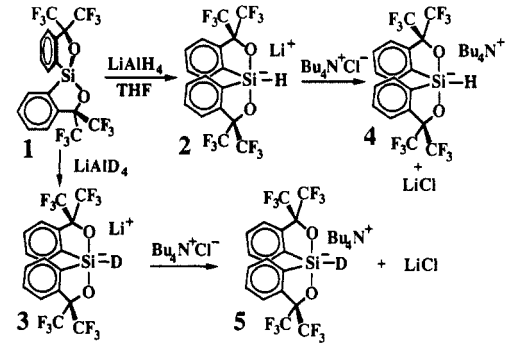
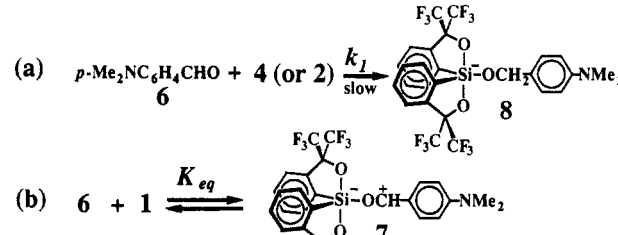


Figure 1. Log rate constants, at 24 °C, for the reduction of para-substituted benzaldehydes (0.3 M) in CH_2Cl_2 with hydridosiliconate (0.044 M), at the bottom of the graph, and in the presence of the silane (0.03 M), at the top, plotted against σ or σ^+ substituent constants.

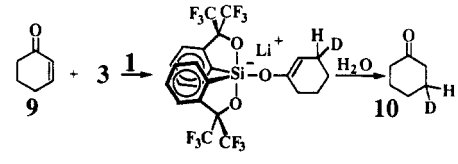
Scheme I



Scheme II[a]



[a] Rate = k_1[6][4] + k_2K_{eq}[1][6][4].



(1) The *N*-X-*L* classification scheme characterizes species in terms of the number (*N*) of formal valence shell electrons about an atom X and the number of ligands (*L*) bonded to X. Perkins, C. W.; Martin, J. C.; Arduengo, A. J., III; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753.

(2) Perozzi, E. F.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 1591.

(3) Silane **1** (2.44 g, 4.76 mmol) and $LiAlH_4$ (0.182 g, 4.79 mmol) in 40 mL of tetrahydrofuran were mixed at −78 °C under N_2 and warmed to room temperature over 1 h. Removal of THF followed by addition of 20 mL of ether and filtration of the AlH_3 provided **2**, which was recrystallized from ether/pentane to give 2.25 g (3.8 mmol, 80%) of **2**: mp 96–97 °C; ^{29}Si NMR δ −79.5 (d, $^1J_{Si-H}$ = 250 Hz); mass spectrum FAB *m/e* 513 (M^-). Anal. ($C_{22}H_{17}F_{12}O_3SiLi$) C, H. Solutions of **2** and Bu_4NCl in CH_2Cl_2 were mixed at −40 °C and slowly brought to room temperature. Filtration of solid LiCl was followed by recrystallization of **5**: mp 167–168 °C; ^{1}H NMR (CD_2Cl_2) δ 8.09 (dd, 2, SiCC*H*), 7.56 (d, 2, SiCCRC*H*), 7.37 (m, 4, SiCCCC*H* and SiCCHC*H*), 5.37 (s, 1, Si–*H*, with small d, $^1J_{H-Si}$ = 248 Hz), 2.99 (m, 8 NCH_2), 1.47 (m, 8, NCCH_2), 1.34 (m, 8, NCCCH_2), 0.94 (t, 12, CH_3); ^{19}F NMR (CD_2Cl_2) δ −75.33, −75.59 (2 q, 12, *J* = 8.9 Hz). Anal. ($C_{34}H_{45}F_{12}O_2SiN$) C, H, N.

(4) (a) Kira, M.; Sato, K.; Sakurai, H. *Chem. Lett.* **1987**, *46*, 2243. (b) Also determined earlier in our research.

(5) Stevenson, W. H., III; Martin, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6352.

(6) Benzaldehyde (43 mg, 0.405 mmol), hydridosiliconate **4** (303 mg, 0.416 mmol), and silane catalyst **1** (147 mg, 0.29 mmol) were dissolved in CH_2Cl_2 (1.0 mL) for 2 h at 25 °C. Solvent was removed in vacuum, and the silane was removed by washing with hexane to form solid tetrabutylammonium (benzyloxy)siliconate. Recrystallization (THF/hexane) gave 330 mg (0.383 mmol, 95%): mp 165–166.5 °C. Anal. ($C_{41}H_{51}NO_3F_{12}Si$) C, H, N. Addition of H_2O provides hydrolysis to form benzyl alcohol (completely, by ^{1}H NMR). The ^{19}F NMR spectrum of 0.7 M **4**, 0.5 M **1**, and 0.7 M in ether showed 95% formation of the (benzyloxy)siliconate within 10 min.

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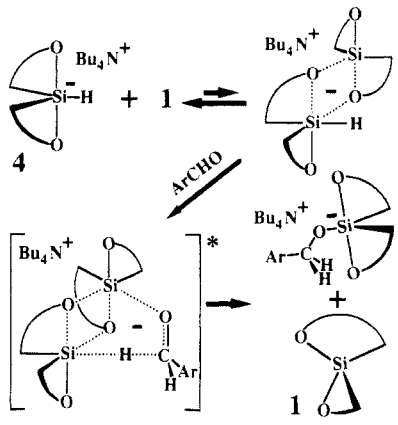
Scheme III



Reductions of carbonyl groups by hydrogen-substituted silanes were earlier found[8] to be catalyzed by nucleophiles coordinating to the silane to form a hydridosiliconate, or a 12-Si-6 species. Lewis acids[9] and protonic acids[10] were also found to catalyze reductions by hydrogen-substituted silanes, although they could not be used with hydridosiliconates. Catalysis by silane **1** as a Lewis acid, however, allows the continuing use of the hydridosiliconate (**2** or **4**) in the presence of this catalyst.

Observed pseudo-first-order kinetics for the reduction of excess aldehyde **6** (0.27 M) in CH_2Cl_2 by the measured low concentrations of hydridosiliconate **4** (initially 0.04 M) was increased linearly by added concentrations of silane **1** (0.0–0.064 M). The reduction rates are clearly third order: first order for the catalytic silane **1**, for DMAB (**6**), and for hydridosiliconate **4**. Even at 0.03 M, a low concentration, the silane provides faster rates of reductions by **4** (Figure 1), by factors of more than 250 for electron-rich aldehydes (from *p*-NMe_2 to H, $\rho^+ = -0.28$). It is clear that these aldehydes are in equilibrium, as Lewis bases, for coordination of the silane to the carbonyl oxygens (Scheme IIb) increasing the rate of hydride transfer from **4**. Although the ρ value for electron-attractive substituents (H to *p*-CN in Figure 1) is positive ($\rho = 0.87$), showing that the reaction is faster when a more electron attractive substituent makes the carbonyl carbon more electrophilic for attraction of the hydride, silane **1** still provides catalysis, although not by initial coordination to the aldehyde. We suggest another possible mechanism (Scheme III) with **1** providing catalysis by rapidly reversible coordination of **1** to the apical oxygen of hydridosiliconate **4**, and possibly coordination of one of the silane oxygens to the silicon of **4** to form a 12-Si-6 species that could provide faster hydride transfer to the carbonyl carbon. The transition state could provide simultaneous transfer of the silane catalyst to the carbonyl oxygen, as pictured in Scheme III. Small changes in the ^{19}F and ^1H NMR of **4**, upon addition of **1**, are compatible with Scheme III. The kinetics for reductions in the absence of **1** are much slower, but with $\rho = 1.71$, compatible with the mechanism of Scheme IIa. The mechanism of Scheme III provides a lower positive ρ value than that of Scheme IIb.

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Uroporphyrinogen III Methylase Catalyzes the Enzymatic Synthesis of Sirohydrochlorins II and IV by a Clockwise Mechanism

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Sirohydrochlorin (**3**), the iron-free prosthetic group of nitrite and sulfite reductases,[1-3] is normally obtained by oxidation of the vitamin B_{12} intermediate dipyrrocorphin (**2**), which is biosynthesized by C-methylation of uroporphyrinogen III (**1**) at positions 2 and 7.[4,5] Recently sirohydrochlorin I (**6**), the C-methylated isobacteriochlorin derived from uroporphyrinogen I (**4**) and a possible intermediate in the biosynthesis of the newly discovered zinc corphinate S factors,[6,7] has been synthesized enzymatically.[8] The enzyme responsible for the addition of the *S*-adenosylmethionine (SAM) derived methyl groups to the uroporphyrinogen framework, uroporphyrinogen methyl transferase (M-1), has been overexpressed as a result of the cloning of the cysG gene in *Escherichia coli*.[9] M-1 not only methylates uroporphyrinogen isomers I and III at positions 2 and 7 to yield the corresponding dipyrrocorphins (**2** = precorrin-2[10] and **5**) but also carries out a further, unexpected methylation at position 12 to yield trimethyl pyrrocorphins (Scheme I).[10] In an effort to obtain a better understanding of the regiospecificity of this enzyme, the nonphysiological uroporphyrinogen isomers, IV (**7**) and II (**10**), were

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