The assignment of the constitution of the intermediates **16b–d** was supported by the following data.

5-(2-Aminoethyl)-1-methoxy-1-methyl-2,8-bis(trimethylsilyl)-2,5,8-triaza-1-silacyclooctane (16b): ^{29}Si NMR ($CDCl_3$) δ 4.1 (*Si*Me_3), −19.5 (*Si*Me); GC/MS (CI, NH_3) 363 (100%, MH^+) 331 (63%, MH^+ − MeOH); ^{1}H NMR ($CDCl_3$) 3.27 (OCH_3), 0.14 ($SiCH_3$), 0.10 ($Si(CH_3)_3$).

5-(2-Aminoethyl)-1-methoxy-1-methyl-2-(trimethylsilyl)-2,5,8-triaza-1-silacyclooctane (16c). The presence and constitution of **16c** were further substantiated by spectroscopic characterization of an enriched sample obtained under optimized reaction conditions. Thus, undried methanol (64 mg, 2.0 mmol) was added via syringe to a solution of 314 mg (0.950 mmoles) of **13b** in 3 mL of $CHCl_3$. The solution was refluxed for 15 min. After the solution was cooled to room temperature, volatiles were removed in vacuo. The residue was distilled in a Kugelrohr distillation apparatus, yielding 217 mg of a yellow oil (bp 85–90 °C/0.1 Torr), which was identified by its NMR and GC/MS data as a mixture of **16c** (ca. 88%), **4** (ca. 4%), and tren (**6**, ca. 8%). No further purification of the product was attempted: ^{29}Si NMR ($CDCl_3$) δ 2.90 (*Si*Me_3), −21.70 (*Si*Me); ^{13}C NMR ($CDCl_3$) δ 61.21, 58.51, 56.66, 48.13, 42.17, 39.04 (NCH_2), 49.43 (OCH_3), 0.97 ($Si(CH_3)_3$), −2.62 ($SiCH_3$); ^{1}H NMR ($CDCl_3$) δ 3.28 (s, 3 H, OCH_3), 2.99 (m), 2.88 (m), 2.77 (m), 2.74 (m), 2.73 (m), 2.68 (m), 2.59 (m), 2.55 (m), 2.45 (m), 2.36 (m), 2.28 (m), 2.27 (m, NCH_2), 1.09 (br, N*H*), 0.79 (br t, N*H*), 0.01 (s, 3 H, $SiCH_3$), −0.02 (s, 9 H, $Si(CH_3)_3$); GC/MS (CI, isobutane) *m/e* (relative intensity) 291 (100, MH^+), 275 (12), 260 (33), 259 (44, MH^+ − MeOH), 231 (18); HRMS (EI, 70 eV) *m/e* calcd for $C_{10}H_{27}N_4OSi_2$ ($M^+ - CH_3$) 275.172 34, found 275.172 07.

***N,N*-Bis(2-aminoethyl)-*N'*-(trimethylsilyl)-*N'*-((dimethoxymethyl)silyl)ethylenediamine (16d)**: ^{29}Si NMR ($CDCl_3$) δ 2.84 (*Si*Me_3), −26.2 (*Si*Me); GC/MS (CI, NH_3) *m/e* (relative intensity) 323 (100, MH^+); ^{13}C NMR ($CDCl_3$) δ 57.57, 57.48, 41.49, 39.55 (NCH_2), 49.20 (OCH_3), 0.90 ($Si(CH_3)_3$), −5.35 ($SiCH_3$); ^{1}H NMR ($CDCl_3$) δ 3.16 (OCH_3), −0.19 ($Si(CH_3)_3$), −0.23 ($SiCH_3$)$_3$).

Methanolysis of 17. MeOH (48 mg, 1.5 mmol) was added via syringe to a solution of 145 mg (0.500 mmol) of **17** in 2.5 mL of $CDCl_3$. Formation of **7a** and a second product was established by ^{1}H and ^{29}Si NMR spectroscopy. The constitution of the second product was determined to be **18a** by its NMR (^{1}H, ^{11}B, ^{13}C, ^{29}Si) and MS data. In a separate experiment, the mixture of **7a** and **18a** obtained by the procedure described was treated with excess CD_3OD. The products formed in this reaction were assigned as $(CH_3O)_nSi(OCD_3)_{4-n}$ (n = 3, 4)[14] and $N[CH_2CH_2NHD\text{-}B(OCD_3)(CH_3)_2]_3$ (**18b**) via NMR spectroscopy.

Tris[2-((dimethylboryl)amino)ethyl]amine (18a): ^{11}B NMR ($CDCl_3$) δ 45.7; ^{13}C NMR ($CDCl_3$) δ 56.8, 40.7 (NCH_2), 6.6 (br), 2.4 (br, BCH_3); ^{1}H NMR ($CDCl_3$) δ 4.2 (br, 3 H, N*H*), 2.98 (m, 6 H, NCH_2), 2.42 (t, 6 H, NCH_2), 0.20 (br, 9 H, BCH_3), 0.16 (br, 9 H, BCH_3); MS (CI, NH_3) *m/e* (relative intensity) 323 (100, MH^+).

Tris[(methoxy-d_3)dimethylborane-(2-(deuterioamino)ethyl]amine (18b): ^{11}B NMR ($CDCl_3$) δ 26.6; ^{13}C NMR ($CDCl_3$) δ 54.2, 37.9 (NCH_2), 5.0 (br, BCH_3); ^{1}H NMR ($CDCl_3$) δ 3.5 (br, 3 H, N*H*), 2.63 (m, 6 H, NCH_2), 2.42 (m, 6 H, NCH_2), −0.12 (s, 18 H, BCH_3), 3.47 (s, wk, $BOCH_3$ due to OCH_3/OCD_3 scrambling).

Synthesis of Mixtures of Partially Silylated Azasilatranes 8a–c and 12a–c. Typically, 1 mmol of the azasilatranes **3–5** was dissolved in 5 mL of benzene, to which was then added 2.5 mL of triethylamine followed by 1.5–2 mmol of chlorotriorganosilane via syringe. The mixture was then stirred for 1 h, after which the precipitate that formed was removed by filtration. After the volatiles were removed in vacuo, the residue was dissolved in $CDCl_3$, and the products were characterized by ^{1}H and ^{29}Si NMR spectroscopy (see Table I).

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Addition of Carbenium Ions to Allylsilanes: Interpretation of Kinetic Data via the Quantitative Analysis of Ligand Effects

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Summary: The transference of the stereoelectronic parameters of PR_3 to SiR_3 substituents allows the quantitative separation of the electronic and steric factors influencing the addition of the (*p*-anisylphenyl)carbenium ion to allylsilanes.

The stereoelectronic factors controlling the reactivity and regiochemistry of allylsilanes as well as the facial selectivity of chiral allylsilanes is of experimental and theoretical interest.[1] Despite this activity, the quantitative evaluation of kinetic and stereochemical data has not been possible because of the lack of a method for handling the combined stereoelectronic effects of the silyl groups. In this report, we disclose that the concepts of the quantitative analysis of ligand effects (QALE) appear to allow a quantitative assessment of these stereoelectronic effects.[2]

As originally conceived, QALE is the analysis of changes in the reactivity and stability of transition-metal complexes that result from variations in the stereoelectronic properties of ligating or incipient trialkylphosphine (PR_3) groups.[2] QALE divides the free energy of activation (log k) into electronic (log k_{el}), steric (log k_{st}), and intrinsic (independent of the stereoelectronic properties of the ligand) factors. The electronic and steric components are linearly related respectively to χ (a measure of Lewis

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Table I. Kinetic Data (log *k*) for Reaction 2 and the Stereoelectronic Parameters for the SiR_3 Substituents

entry no.	SiR_3	log k_a	χ^b	θ^c	entry no.	SiR_3	log k	χ^b	θ^c
1	$SiMe_3$	2.29	8.55	118	6	$SiHx_3$[d]	2.73	5.0	136
2	$SiClMe_2$	−0.56	21.7	120	7	$SiBuMe_2$	2.31	5.7	139
3	$SiPhMe_2$	1.59	10.6	122	8	$SiPh_3$	0.51	13.25	145
4	$SiEt_3$	2.50	6.3	132	9	$Si(^iPr)_3$	2.64	3.75	160
5	$SiBu_3$	2.71	5.25	136					

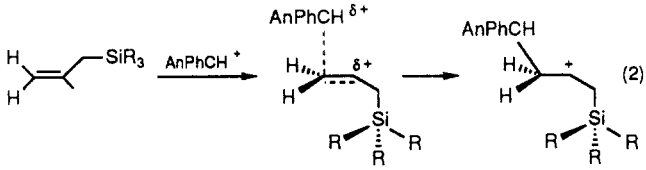
[a] Kinetic data were taken from ref 5. [b] χ values for this group of σ-donor ligands are a measure of their σ-donicity.[2d] χ values for $SiClMe_2$ and $SiBuMe_2$ were calculated from data provided in ref 3. [c] Cone angles were taken or calculated from data provided in ref 4. [d] Hx = 1-hexyl.

basicity or "σ-donicity")[3] and the cone angle θ (a measure of steric size).[4] In transition-metal chemistry, relatively sharp thresholds often usher in steric effects. The relationship between log k and the stereoelectronic parameters is shown in eq 1 for a reaction involving spectator ligands[2d] and exhibiting steric effects in the transition state only.

$$\log k = a\chi + b(\theta - \theta_{st})\lambda + c \qquad (1)$$

The coefficients a and b and the constants θ_{st} and c provide information about the stereoelectronic nature of the transition and the ground states.[2] a is related to the changes in M–P bonding, whereas b reflects the flexibility of the transition state. θ_{st} is the steric threshold for the reaction and is related to the congestion in the transition state. λ is a switching function that turns on the steric effect when the size of the ligand or the substituent exceeds the steric threshold; i.e., λ equals 0 when θ is less than θ_{st} and λ equals 1 when θ exceeds θ_{st}.[2e] The constant c contains information about the "intrinsic" reactivity of the system.

Recently, an extensive set of kinetic data was reported for the addition of the (*p*-anisylphenyl)carbenium ion to allylsilanes (eq 2) where the pendent groups on the silicon were varied both electronically and sterically (Table I).[5]



It was noted that the rate of addition was decreased by electronegative groups on the silicon and accelerated by bulky alkyl groups. The obvious similarities between SiR_3 substituents and PR_3 ligands (isostructural groups containing adjacent third-row central atoms) suggested that the stereoelectronic parameters of PR_3 can be transferred directly to SiR_3. In fact, the linear relationship between the A_1 ν_{CO} value of $(CO)_4CoSiR_3$[6] and the A_1 ν_{CO} values of $(CO)_3NiPR_3$ supports the notion. Accordingly, we performed the analysis of the kinetic data as a function of the silyl group, using as their stereoelectronic parameters χ and θ of the isostructural phosphorus(III) compound. The relationship between log k, χ, and θ is given by eq 3, which was obtained by linear regression analysis of the kinetic data for eq 2.

$$\log k = [-0.221\ (\pm 0.011)]\chi - [0.0192\ (\pm 0.004)]\theta + 6.407\ (\pm 0.707)$$

$$\sigma = 0.117 \qquad r = 0.994 \qquad (3)$$

We believe that transference of the stereoelectronic parameters from PR_3 to SiR_3 is valid on the basis of the facts that there is an excellent statistical fit of the data to eq 1 and that the results are intuitively reasonable. The coefficients of eq 3 are consonant with our current view of electrophilic addition to allylsilanes.[1a] A comparison of the range of χ values and θ for the silyl groups used in eq 3 shows that the dominant effect is electronic in nature with a somewhat smaller steric contribution. Coefficient a is negative, indicating that the reaction is retarded by more electronegative silyl groups (more positive χ). Since steric effects are operative for all ligands, the transition state for reaction 2 must be congested with a steric threshold less than 118°, the cone angle of the smallest silyl group ($SiMe_3$) used. Coefficient b is negative, indicating that the reaction is retarded by increasing size of the silyl group. The original observation[5] that reaction 2 is accelerated by substitution of larger alkyl groups on the silyl group is readily explained, since the silyl groups with the larger alkyl substituents are better electron donors. The accelerating effect of their enhanced electron donor ability more than compensates for their small steric inhibition of the reaction. The overall effect caused by the variations of the stereoelectronic properties of the silyl groups is quite small when compared to the constant term of eq 3. This large constant term indicates that the rate of reaction is also dependent upon factors that may be independent of the substituents on the silicon atom.

From these observations we conclude that it may be possible to separate the steric and electronic effects that silyl groups have on the kinetics of organic reactions. However, at the present time this method of analysis must be viewed cautiously until supported by the results of additional systematic studies. Certainly, such a quantitative separation might help to shed light on the manner in which the electronic effect of the silyl group is transmitted to the reaction center. A continued exploration and application of this method to addition reactions of chiral allylic metals where π facial selectivity becomes a relevant issue is currently underway.

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