The dihalides of indium are mixed oxidation state complexes,[5,6] and their ready formation in aromatic solvents seems worth further comment. Chao and Rieke[4] have prepared activated indium metal which forms InI quantitatively on reaction with iodine in refluxing xylene. We have observed that the amount of InI formed in the reduction of indium(III) iodide with commercial indium shot in xylene is insignificant until the formation of indium diiodide is well advanced, and the same is true even with molten indium in refluxing mesitylene. This inhibition may be due solely to deactivation of the surface of the indium metal by adhering InI, but it appears probable that complex formation with the aromatic solvent is important in stabilizing InX_2 in solution. Benzene solvates of gallium compounds have been reported,[7] and the formation of π complexes in solution has been proposed[8] in the case of gallium(I). It is reasonable to expect similar solvation of indium(I); the ion $[(\eta^6\text{-arene})In]^+$ would be isoelectronic with the well-known cyclopentadienylindium(I),[9] which involves a η^5 ligand.[10] The existence of such arene-indium complexes is currently under study, as are the reactions of these materials with a variety of unsaturated organic molecules.

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Registry No. InI_3, 13510-35-5; InI_2, 13779-78-7; InI, 13966-94-4; $InBr_2$, 14226-34-7; $InCl_2$, 13465-11-7; GaI_3, 13450-91-4; In, 7440-74-6; I_2, 7553-56-2; $InBr_3$, 13465-09-3; $InCl_3$, 10025-82-8; Ga, 7440-55-3.

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Contribution from the Departments of Chemistry, State
University of New York, Stony Brook, New York 11794,
and Brookhaven National Laboratory, Upton, New York 11973

Temperature-Jump Study of the Reaction between Hexacyanoferrate(II) and -(III) and Tris(phenanthroline)cobalt(II) and -(III)

Albert Haim*[1a] and Norman Sutin*[1b]

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Most studies of outer-sphere redox reactions of metal ions and their complexes have been carried out with ions of the same charge type.[2a] Under these circumstances, the rate measurements yield second-order rate coefficients which are products of the equilibrium constant for the formation of the precursor complex (eq 1) and the rate constant for the

$$\text{Ox} + \text{Red} \rightleftharpoons \text{Ox}\|\text{Red} \qquad Q_p \qquad (1)$$

electron-transfer step (eq 2). By using highly charged

$$\text{Ox}\|\text{Red} \rightarrow \text{Ox}^- + \text{Red}^+ \quad k_{et} \qquad (2)$$

reactants of opposite charge, it has been proved possible to resolve an observed rate coefficient into its elementary components.[2b]

Table I. Equilibrium Quotient for Reaction 3[a]

$10^3[Fe(CN)_6^{4-}]_0$, M	$10^4[Fe(CN)_6^{3-}]_0$, M	$10^4[Co(phen)_3^{3+}]_{eq}$,[b] M	Q
0.86	5.30	3.96	5.8
1.01	5.04	3.54	4.7
2.01	5.04	3.05	4.9
2.14	5.30	4.28	5.0[c]
4.73	5.09	2.22	4.7
4.79	5.08	2.20	4.7
9.46	5.09	1.64	5.3
9.58	5.08	1.69	5.7
15.2	5.01	1.20	5.3
20.3	5.01	0.80	4.0
2.01	4.81	3.92	16.5[d]

[a] At 25°, [phen] = 0.010 M, $[KNO_3]$ = 0.10 M, and $[Co(phen)_3^{2+}]_0 = 1.03 \times 10^{-3}$ M. [b] From eq 4. [c] $[Co(phen)_3^{2+}] = 2.59 \times 10^{-3}$ M. [d] At 15°.

The present study was initiated with the expectation of obtaining Q_p and k_{et} for the $Co(phen)_3^{3+}$–$Fe(CN)_6^{4-}$ reaction. This expectation was not realized, but the results still show the importance of electrostatic factors in determining rates of outer-sphere reactions as well as the need to consider carefully the nature of the coordination sheres of metal ions in the estimation of ion-pair formation constants.

Experimental Section

Materials. Triply distilled water was used in the preparation of all of the solutions. All chemicals used were of the highest quality available and were used as received.[3] The ion $Co(phen)_3^{2+}$ was prepared in situ by the reaction of $Co(NO_3)_2$ with excess phenanthroline.

Equilibrium Measurements. The equilibrium quotient for reaction

$$Fe(CN)_6^{3-} + Co(phen)_3^{2+} \rightleftharpoons Fe(CN)_6^{4-} + Co(phen)_3^{3+} \quad Q \qquad (3)$$

3 was determined by a spectrophotometric technique. Following chemical and temperature equilibrium, the absorbance A of solutions containing the desired concentrations of $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, and $Co(phen)_3^{2+}$ was measured at 420 nm, the wavelength for maximum absorption by $Fe(CN)_6^{3-}$. The concentration of $Co(phen)_3^{3+}$ at equilibrium was calculated from the expression

$$[Co(phen)_3^{3+}]_{eq} = \frac{A - (A_1 + A_2 + A_3)}{\epsilon_1 - \epsilon_2 - \epsilon_3 + \epsilon_4} \qquad (4)$$

where A_1, A_2, and A_3 (measured for each experiment) are the absorbances of solutions of $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, and $Co(phen)_3^{2+}$ at concentrations equal to the initial concentrations (i.e., before equilibration), and ϵ_1, ϵ_2, ϵ_3, and ϵ_4 are the molar absorptivities at 420 nm of $Fe(CN)_6^{4-}$ (2), $Fe(CN)_6^{3-}$ (1026), $Co(phen)_3^{2+}$ (126), and $Co(phen)_3^{3+}$ (139), respectively. The equilibrium quotient for reaction 3 was then calculated from the known initial concentrations of $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, and $Co(phen)_3^{2+}$ and the calculated equilibrium concentration of $Co(phen)_3^{3+}$.

Kinetic Measurements. The temperature-jump apparatus described previously[4] was used. The cell (equipped with gold electrodes) was filled with the solution containing the desired concentrations of $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, and $Co(phen)_3^{2+}$, as well as 0.10 M potassium nitrate as supporting electrolyte, and then placed in a constant-temperature bath. The condenser was discharged through the solution, bringing the temperature to 25°, and the chemical relaxation was followed spectrophotometrically at 420 nm. Transmittance vs. time oscillograms were photographed, and relaxation times were calculated from the log T vs. t linear plots.

Results and Discussion

The values of the equilibrium quotient for reaction 3 are presented in column 4 of Table I. The average value 5.0 ± 0.4 at 25° and $[KNO_3]$ = 0.10 M is in satisfactory agreement with the value 1.0 calculated from the reduction potentials for the $Fe(CN)_6^{3-,4-}$ and $Co(phen)_3^{3+,2+}$ couples.[5,6] From the average value Q = 5.0 at 25° and the single measurement at 15° (16.5), we calculate $\Delta H° = -20 \pm 3$ kcal mol^{-1} and $\Delta S° = -65 \pm 10$ eu. The negative values for $\Delta H°$ and $\Delta S°$ appear

Table II. Kinetics of Equilibration of Reaction 3[a]

$10^3[Fe(CN)_6^{4-}]_0$, M	$10^4[Fe(CN)_6^{3-}]_0$, M	$10^3([Co(II)]_{eq} + [Fe(III)]_{eq})$,[b] M	$10^3([Co(III)]_{eq} + [Fe(II)]_{eq})$,[b] M	$10^6\tau$,[c] sec	$10^{-6}Q_sk_r^{et}$,[d] M^{-1} sec^{-1}
0.86	5.30	0.79	1.62	162	1.1
1.01	5.04	0.82	1.73	144	1.2
1.84	6.00	1.74[e]	2.77[e]	81[e]	1.1
2.01	5.04	0.92	2.62	132	1.1
2.63	4.82	2.31[f]	3.39[f]	71[f]	1.0
4.73	5.09	1.08	5.19	74	1.3
9.46	5.09	1.22	9.78	52	1.2
15.2	5.01	1.30	15.4	36	1.2

[a] At 25°, [phen] = 0.010 M, $[KNO_3]$ = 0.10 M, $[Co(phen)_3^{2+}]_0 = 1.03 \times 10^{-3}$ M. [b] Calculated from $[Fe(CN)_6^{4-}]_0$, $[Fe(CN)_6^{3-}]_0$, $[Co(phen)_3^{2+}]_0$, and Q. [c] Average of three or four replicate experiments; reproducibility ±10%. [d] Calculated from eq 9. [e] $[Co(phen)_3^{2+}]_0 = 2.07 \times 10^{-3}$ M. [f] $[Co(phen)_3^{2+}]_0 = 2.59 \times 10^{-3} M$.

reasonable for the reaction under consideration, since the charges of the products are higher than those of the reactants. Under these circumstances the products are more hydrated than the reactants, and the reaction is exothermic and endoentropic. The magnitudes of $\Delta H°$ and $\Delta S°$ also appear to be reasonable. Since the difference between the partial molal entropies of $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ is −48 eu,[7] the difference between the partial molal entropies of $Co(phen)_3^{2+}$ and $Co(phen)_3^{3+}$ is calculated to be −17 ± 10 eu. Within the rather large uncertainty, this compares satisfactorily with the value −5 ± 2 eu reported[7] for the analogous $Fe(phen)_3^{2+,3+}$ couple.

The results of the kinetic measurements are presented in Table II. Assuming the mechanism given by eq 5, where the

$$Fe(CN)_6^{3-} + Co(phen)_3^{2+} \underset{}{\overset{Q_p}{\rightleftharpoons}} Fe(CN)_6^{3-}\|Co(phen)_3^{2+} \underset{k_r^{et}}{\overset{k_f^{et}}{\rightleftharpoons}}$$
$$Fe(CN)_6^{4-}\|Co(phen)_3^{3+} \overset{1/Q_s}{\rightleftharpoons} Fe(CN)_6^{4-} + Co(phen)_3^{3+} \tag{5}$$

precursor and successor ion pairs form and dissociate very rapidly and the electron transfer is rate determining, the relaxation time is given by eq 6. If the equilibrium constants

$$\frac{1}{\tau} = k_f^{et}\frac{[Fe(CN)_6^{3-}]_{eq} + [Co(phen)_3^{2+}]_{eq}}{1/Q_p + [Fe(CN)_6^{3-}]_{eq} + [Co(phen)_3^{2+}]_{eq}} +$$
$$k_r^{et}\frac{[Fe(CN)_6^{4-}]_{eq} + [Co(phen)_3^{3+}]_{eq}}{1/Q_s + [Fe(CN)_6^{4-}]_{eq} + [Co(phen)_3^{3+}]_{eq}} \tag{6}$$

for the formation of precursor and successor ion pairs are both small,[8] then eq 6 reduces to eq 7 where $Q = Q_pk_f^{et}/Q_sk_r^{et}$. The

$$\frac{1}{\tau} = Q_sk_r^{et}\{Q([Fe(CN)_6^{3-}]_{eq} + [Co(phen)_3^{2+}]_{eq}) +$$
$$[Fe(CN)_6^{4-}]_{eq} + [Co(phen)_3^{3+}]_{eq}\} \tag{7}$$

relaxation times conform to eq 7 rather precisely, as will be seen by the constancy of $Q_sk_r^{et}$ (last column of Table II). The average value of $Q_sk_r^{et}$ is (1.2 ± 0.1) × 10^6 M^{-1} sec^{-1}. From this value and Q = 5.0 ± 0.4, we calculate $Q_pk_f^{et}$ = (6 ± 0.6) × 10^6 M^{-1} sec^{-1}. Assuming that deviations from eq 7 would have been observed if the concentration terms in the denominators of eq 6 contributed approximately 20%, we estimate $Q_p \leq 100$ M^{-1} and $Q_s \leq 20$ M^{-1}. Therefore, $k_f^{et} \geq 6 \times 10^4$ sec^{-1} and $k_r^{et} \geq 6 \times 10^4$ sec^{-1}.

Theoretical values[2a] of Q_p and Q_s can be estimated from eq 8 where $U(a)$ is the Debye–Hückel interaction potential

$$K_0 = \frac{4\pi Na^3}{3000}\exp\left(-\frac{U(a)}{kT}\right) \tag{8}$$

and a the distance between the centers of the reactants. Using $a = 11.5 \times 10^{-8}$ cm (based on radii of 7.0×10^{-8} and 4.5×10^{-8} cm for $Co(phen)_3^{2+,3+}$ and $Fe(CN)_6^{4-,3-}$, respectively), the calculated values of Q_p and Q_s are 21 and 114 M^{-1}, respectively. Therefore, it is not surprising that the precursor ion pair could not be detected kinetically. However, if the value of Q_s were as high as 100, some deviations in the values of $Q_sk_r^{et}$ would have been observed at the highest $Fe(CN)_6^{4-}$ concentrations. The kinetic data indicate that Q_s is less than the calculated value. By contrast, the data[2b] for the $Fe(CN)_6^{4-}$–$Co(NH_3)_5OH_2^{3+}$ reaction show that Q_s = 1500 M^{-1}. The value calculated from eq 8 with $a = 8 \times 10^{-8}$ cm is 440 M^{-1}. The discrepancies between calculated and experimental values for ion-pair formation between $Fe(CN)_6^{4-}$ and $Co(NH_3)_5OH_2^{3+}$ or $Co(phen)_3^{3+}$ show the importance of specific ion effects, rather than general electrostatic effects, in determining the magnitude of ion-pair interactions.[9]

Although ion-pair interaction between reactants and/or products could not be detected kinetically, the importance of electrostatic effects can be seen by comparing the measured rate constant for eq 3 with the value calculated using Marcus' equation $k_{12} = (k_{11}k_{22}K_{12})^{1/2}$. The rate constants for the exchange reactions between $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ and between $Co(phen)_3^{2+}$ and $Co(phen)_3^{3+}$ are 1.9 × 10^4 and 4.4 × 10 M^{-1} sec^{-1}, respectively.[10,11] Therefore, $Q_pk_f^{et} = (1.9 \times 10^4 \times 4.4 \times 10 \times 5)^{1/2} = 2.1 \times 10^3$ M^{-1} sec^{-1}, in very poor agreement with the measured value 6.0 × 10^6 M^{-1} sec^{-1}. However, it must be noted that the work terms in the exchange reactions involve bringing together ions of the same charge, whereas in the cross reaction ions of opposite charge are brought together. Therefore, before comparing exchange and cross reactions, a correction for electrostatic effects must be done by means of[2a]

$$\Delta G_{12}{}^* = \Delta G_{12}{}^{**} + w_{12} \tag{9}$$

where

$$\Delta G_{12}{}^{**} = \frac{\Delta G_{11}{}^{**} + \Delta G_{22}{}^{**}}{2} + \frac{\Delta G_r{}°}{2}$$

$$\Delta G_{11}{}^{**} = \Delta G_{11}{}^* - w_{11}$$

$$\Delta G_{22}{}^{**} = \Delta G_{22}{}^* - w_{22}$$

$$\Delta G_r{}° = \Delta G_{12}{}° + w_{21} - w_{12}$$

The work terms are calculated using eq 10.[12] Single and

$$w = \frac{z_1z_2e^2}{Da}\exp(-\kappa a) \tag{10}$$

double asterisks are used for measured and corrected free energies of activation, respectively, while subscripts 1 and 2 pertain to the iron and cobalt couples, respectively. We calculate (all values in kcal mol^{-1}) w_{12} = −0.66, w_{11} = 2.20, w_{22} = 0.42, w_{21} = −1.33, $\Delta G_r°$ = −1.65, $\Delta G_{11}{}^{**}$ = 9.47, $\Delta G_{22}{}^{**}$ = 14.87, and $\Delta G_{12}{}^{**}$ = 11.34. Therefore, from eq 9, $\Delta G_{12}{}^*$ = 10.68 kcal mol^{-1}, and k_{12} = 1.0 × 10^5 M^{-1} sec^{-1}, to be compared with the experimental value 6.0 × 10^6 M^{-1} sec^{-1}. However, it is known[13] that eq 10 overcorrects for ionic strength effects outside the region of the Debye–Hückel limiting law. Using the limit of zero ionic strength, the calculated values (kcal mol^{-1}) are w_{12} = −2.20, w_{11} = 5.63, w_{22} = 1.81, w_{21} = −4.40, $\Delta G_r°$ = −3.18, $\Delta G_{11}{}^{**}$ = 6.04, $\Delta G_{22}{}^{**}$ = 13.48, and $\Delta G_{12}{}^{**}$ = 8.17. Therefore, from eq 9, $\Delta G_{12}{}^*$ =

5.97 kcal mol^{-1}, and $k_{12} = 2.8 \times 10^8\ M^{-1}\ \text{sec}^{-1}$. This calculation undercorrects for ionic strength effects. Using the average of the work terms calculated for the prevailing ionic strength and the $\mu = 0$ limit, we obtain a value of $k_{12} = 5.3 \times 10^6\ M^{-1}\ \text{sec}^{-1}$, in remarkable agreement with the observed value $6.0 \times 10^6\ M^{-1}\ \text{sec}^{-1}$.

In order to test the generality of this treatment of electrostatic factors, we carried out similar calculations for two other reactions between ions of opposite charge. The value of k_{12} for eq 11 (where DMP stands for 4,7-dimethyl-1,10-phenanthroline) is $1.1 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ at 25° and $\mu = 0.10\ M$.[13] The values of k_{11} and k_{22}, the rate constants for the Fe(DMP)_3^{2+}–Fe(DMP)_3^{3+} and IrCl_6^{3-}–IrCl_6^{2-} exchange reactions, are 3×10^8 and $2.3 \times 10^5\ M^{-1}\ \text{sec}^{-1}$, respectively.[14,15] The value of k_{12} calculated using eq 9 and 10[16] (with the average work term approximation indicated above) is $1.6 \times 10^9\ M^{-1}\ \text{sec}^{-1}$. The value of k_{12} for eq 12 is $2.0 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ at 10° and $\mu = 0.50\ M$.[4] The rate constant calculated as indicated above is $1.3 \times 10^9\ M^{-1}\ \text{sec}^{-1}$.[17,18]

$$\text{IrCl}_6^{2-} + \text{Fe(DMP)}_3^{2+} \underset{}{\overset{k_{12}}{\rightleftharpoons}} \text{IrCl}_6^{3-} + \text{Fe(DMP)}_3^{3+} \qquad (11)$$

$$\text{Mo(CN)}_8^{3-} + \text{Os(bpy)}_3^{2+} \overset{k_{12}}{\rightleftharpoons} \text{Mo(CN)}_8^{4-} + \text{Os(bpy)}_3^{3+} \qquad (12)$$

It must be pointed out, in view of the arbitrary averaging procedure used above, that the unusually good agreement between measured and calculated rate constants is probably largely fortuitous.[19] Nevertheless, since the comparisons involve complexes of different coordination numbers, coordination spheres, and self-exchange rates, the above calculations do illustrate the importance of electrostatic effects in determining reaction rates between metal complexes of different charge type. Neglect of the work terms for the systems under consideration results in discrepancies of more than 10^3 between observed and calculated rates. Although the importance of correcting for differences in the work terms is most readily seen for cross reactions involving ions of opposite charge, the work term differences are not necessarily negligible for reactions between ions of the same charge type since these terms also include nonelectrostatic contributions. Thus, it has been proposed[20] that contributions of the latter type could be responsible for the poor agreement between observed and calculated rates found for reactions of certain similarly charged ions. Evidently, the work terms must be considered carefully when comparing reaction rates in different systems.

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Registry No. Fe(CN)_6^{3-}, 13408-62-3; Co(phen)_3^{2+}, 16788-34-4; Fe(CN)_6^{4-}, 13408-63-4; Co(phen)_3^{3+}, 18581-79-8.

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(19) Less satisfactory agreement was obtained using the Debye–Hückel corrected expression $w = z_1 z_2 e^2/[Da(1 + \kappa a)]$. This expression yields rate constants of 5.1×10^5, 3.2×10^8, and $4.9 \times 10^7\ M^{-1}\ \text{sec}^{-1}$ for the Fe(CN)_6^{3-}–Co(phen)_3^{2+}, IrCl_6^{2-}–Fe(DMP)_3^{2+}, and Mo(CN)_8^{4-}–Os(bpy)_3^{2+} reactions, respectively.
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Contribution from the Department of Chemistry,
University of Colorado, Boulder, Colorado 80302

Preparation and Properties of 6-Ethoxy-, 6-Phenyl-, and 6-Trimethylsiloxydecaborane(14)[1]

Robert E. Loffredo, Linda F. Drullinger, Jane A. Slater,
Charles A. Turner, and Arlan D. Norman*

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Although many terminally substituted decaboranes(14) have been prepared, only two types of decaboranyl ethers, alkoxydecaboranes[2,3] and $6,6'\text{-B}_{10}\text{H}_{13}\text{OB}_{10}\text{H}_{13}$,[4] are known. Recently, during our studies of the syntheses of alkylsila-, alkylgerma-, and alkylstannaundecaboranes[5,6] and our attempts to extend these syntheses to arylstannaundecaboranes, we have found reactions which result in two new decaboranyl ethers, $6\text{-(CH}_3)_3\text{SiOB}_{10}\text{H}_{13}$ and $6\text{-C}_2\text{H}_5\text{OB}_{10}\text{H}_{13}$. The $6\text{-(CH}_3)_3\text{SiOB}_{10}\text{H}_{13}$ forms in reactions of $\text{NaB}_{10}\text{H}_{13}$ or $\text{Na}_2\text{B}_{10}\text{H}_{12}$ with $(\text{CH}_3)_3\text{SiX}$ (X = Cl, Br) in ethers. $6\text{-C}_2\text{H}_5\text{OB}_{10}\text{H}_{13}$ results from the reaction of $\text{NaB}_{10}\text{H}_{13}$ or $\text{Na}_2\text{B}_{10}\text{H}_{12}$ with SnCl_4 in diethyl ether. Also, pyrolysis of $(\text{C}_6\text{H}_5)_2\text{SnB}_{10}\text{H}_{12}$ results in $6\text{-C}_6\text{H}_5\text{B}_{10}\text{H}_{13}$, the latter of which although reported previously[7,8] had not been characterized completely.

Experimental Section

Infrared spectra were obtained with a Beckman IR-12 spectrometer. Proton NMR spectra at 60.0 and 100.0 MHz were recorded using Varian A-60 and JEOL-INM-PFT-100 spectrometers, respectively. Chemical shifts were measured relative to internal $(\text{CH}_3)_4\text{Si}$. Boron-11 NMR spectra were obtained with a Varian HA-100 equipped with standard 32.1-MHz probe and radiofrequency unit accessories. Chemical shifts were measured relative to external BBr_3 and are given relative to $\text{BF}_3\cdot\text{O(C}_2\text{H}_5)_2$. Mass spectra were obtained at 70 eV with Varian MAT CH-7 and CH-5 spectrometers.

Diphenyltin dichloride was prepared and purified as described by Gilman.[9] $\text{NaB}_{10}\text{H}_{13}$[10] and $\text{Na}_2\text{B}_{10}\text{H}_{12}$[11] salts were prepared from reactions of NaH with $\text{B}_{10}\text{H}_{14}$ in diethyl ether. Bulk $(\text{C}_2\text{H}_5)_2\text{O}$ was removed from the decaboronate salts before their use. The resulting compounds, presumed to be etherates $\text{Na}_2\text{B}_{10}\text{H}_{12}\cdot x(\text{C}_2\text{H}_5)_2\text{O}$ and $\text{NaB}_{10}\text{H}_{13}\cdot x(\text{C}_2\text{H}_5)_2\text{O}$, were used in all syntheses described below. Trimethylsilyl chloride, $(\text{CH}_3)_3\text{SiBr}$, and SnCl_4 (Alfa Inorganics) were distilled before use. Diethyl ether was distilled from LiAlH_4 prior to use.

$6\text{-(CH}_3)_3\text{SiOB}_{10}\text{H}_{13}$. $(\text{CH}_3)_3\text{SiCl}$ (20 mmol) was added under N_2 to 2.0 mmol of $\text{Na}_2\text{B}_{10}\text{H}_{12}$ or $\text{NaB}_{10}\text{H}_{13}$. After 6 h at 50°, reaction materials were sublimed (65°) through a U-trap at 0°. Pure $(\text{CH}_3)_3\text{SiOB}_{10}\text{H}_{13}$ was collected in the 0° trap after two sublimations; mp 36–37°. Yields from $\text{Na}_2\text{B}_{10}\text{H}_{12}$ and $\text{NaB}_{10}\text{H}_{13}$ reactions were ca. 20% and 5%, respectively. Anal.[12] Calcd for $\text{C}_3\text{H}_{22}\text{B}_{10}\text{SiO}$: C,