administered by Iowa State University. We thank Professor James H. Espenson for directing us to E. L. King's kinetic treatment and for the loan of a thermostatable cell holder and a constant temperature bath, Dr. Dave Scott for assistance with the NMR experiments, and J. Alan Hays for help with computer software used in data manipulation.

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# $\sigma$-Bond Metathesis Reactions of Si–H and M–Si Bonds. New Routes to $d^0$ Metal Silyl Complexes

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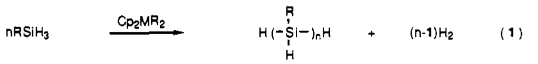
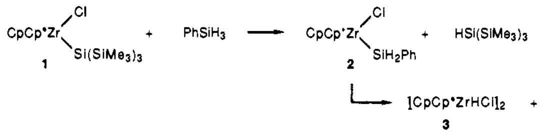
The recent development of early transition-metal silyl chemistry has resulted in observation of a number of unusual chemical transformations.[1] For example, the catalytic dehydrogenative polymerization of silanes to polysilanes by Ti and Zr metallocene derivatives[2] (eq 1) has generated much interest, since routes to



$$n\mathrm{RSiH_3} \xrightarrow{\mathrm{Cp_2MR_2}} \mathrm{H(-\overset{R}{\underset{H}{Si}}-)_nH} + (n-1)\mathrm{H_2} \qquad (1)$$

these polymers are presently quite limited.[3] More versatile synthetic methods are expected to promote development of a number of applications for polysilanes, for example as photoresists,[4a,b] photoconductors,[4c] dopable semiconductors,[4d] preceramics,[4e–g] and nonlinear optical materials.[4h] The newly discovered coordination polymerization (eq 1) undoubtedly involves metal–silicon bonded intermediates with Si–H bonds, but the mechanism is still very much in question.[2b–d] Here we report stoichiometric $\sigma$-bond metathesis reactions that are possibly related to the initiation process of the polymerization. The reactions described also provide a new, general route to $d^0$ metal silyl complexes with $\alpha$ Si–H bonds. Such species are typically not available via the silyl anion route, because of the limited availability of appropriate silyl anion reagents.[5] This synthetic method is therefore expected to greatly enhance further studies of early transition-metal silyl chemistry.

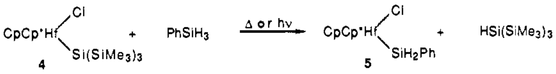
In the dark, benzene-$d_6$ solutions of zirconium silyl $\mathrm{CpCp^*Zr[Si(SiMe_3)_3]Cl}$[6] (**1**, Cp = $\eta^5$-$\mathrm{C_5H_5}$; Cp* = $\eta^5$-$\mathrm{C_5Me_5}$) react with $\mathrm{PhSiH_3}$ over 6 h to give four products identified by $^1$H NMR spectroscopy (eq 2). Early in the reaction, the major



(2)

products are zirconium silyl **2**[7] and $\mathrm{HSi(SiMe_3)_3}$. As the reaction proceeds to completion, **2** decomposes to hydride **3** and a mixture of polysilanes. Broad $^1$H and $^{29}$Si NMR resonances for the polysilanes were assigned based on comparisons to spectra reported by Aitken et al.[2a] and to isolated $(-\mathrm{SiHPh}-)_n$ polymer.[2] We have not isolated enough of this polymeric material to carry out molecular weight measurements, but it is evident from $^1$H NMR spectra that $\mathrm{PhH_2SiSiH_2Ph}$ and $\mathrm{PhH_2SiSiHPhSiH_2Ph}$ are not present. In the presence of fluorescent room light, the reaction between **1** and $\mathrm{PhSiH_3}$ is complete within 5 min and gives **2** and $\mathrm{HSi(SiMe_3)_3}$ cleanly. Compound **2** then slowly decomposes to **3** and $(-\mathrm{SiHPh}-)_n$.

Because analogous $\sigma$-bond metathesis reactions with $\mathrm{CpCp^*Hf[Si(SiMe_3)_3]Cl}$[6] (**4**) give more stable metal silyl derivatives, these reactions were examined in more detail. As expected, the thermal (dark) reaction of **4** with 1 equiv of $\mathrm{PhSiH_3}$ is much slower than observed for **1** (complete reaction after 2 days at room temperature). With illumination by fluorescent room lighting, this reaction is complete within 1 h in pentane or benzene solution, giving quantitative conversion to the $\sigma$-bond metathesis products $\mathrm{CpCp^*Hf(SiH_2Ph)Cl}$ (**5**) and $\mathrm{HSi(SiMe_3)_3}$ (eq 3). In



(3)

contrast to **2**, yellow crystalline **5** is stable indefinitely as a solid at room temperature under an inert atmosphere. When heated to 75 °C in benzene-$d_6$, **5** decomposes by a second-order process ($k$(75 °C) = $1.1(1) \times 10^{-4}\ \mathrm{M^{-1}\ s^{-1}}$; $\Delta H^\ddagger$ = 19.5 (2) kcal mol$^{-1}$; $\Delta S^\ddagger$ = −21.2 (6) eu) to cleanly produce $\mathrm{[CpCp^*HfHCl]_2}$ and $(-\mathrm{SiHPh}-)_n$. Compound **5** was completely characterized by analytical and spectroscopic data.[7] NMR chemical shifts for the diastereotopic hydrogens on silicon ($\delta$ 4.68, 5.14) and the $^1J_{\mathrm{SiH}}$ coupling constant (150 Hz) are consistent with bonding of the silyl group to a chiral, $d^0$ metal center.[5] Further study of the latter reaction should provide mechanistic information relevant to the catalytic dehydrogenative polymerization of silanes to polysilanes.

A number of new hafnium silyl derivatives have been obtained by reaction of **4** with 1 equiv of a primary or secondary silane ($\mathrm{RSiH_3}$, R = Ph, $p$-$\mathrm{MeC_6H_4}$, 2,4,6-$\mathrm{Me_3C_6H_2}$, $\mathrm{CH_2Ph}$, and $c$-$\mathrm{C_6H_{11}}$; $\mathrm{Ph_2SiH_2}$; $\mathrm{PhMeSiH_2}$). These reactions are quantitative by $^1$H NMR spectroscopy, and isolated yields range from 65–75%. For $\mathrm{CpCp^*Hf(SiHPhMe)Cl}$, a 7:5 mixture of diastereomers are observed. Generally, the rates of these photochemical reactions are quite sensitive to steric effects. Secondary silanes and sterically hindered primary silanes such as $(2,4,6\text{-}\mathrm{Me_3C_6H_2})\mathrm{SiH_3}$ react sluggishly (over 1–2 days for 1:1 reactions) in the presence of room light. Tertiary silanes such as $\mathrm{Me_3SiH}$ and $\mathrm{Et_3SiH}$ react very slowly under analogous conditions, and as yet we have observed only small quantities of the $\mathrm{HSi(SiMe_3)_3}$ product after several days. Generally, hafnium silyls $\mathrm{CpCp^*Hf(SiRR'R'')Cl}$ undergo clean $\sigma$-bond metathesis reactions with primary or secondary silanes that introduce a smaller silyl ligand.

The thermal reactions of **1** and **4** with silanes may occur via four-center transition states, similar to those recently described

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[7] Characterization data for all new compounds are listed in the Supplementary Material. Selected data for **2**: $^1$H NMR (benzene-$d_6$, 22 °C, 300 MHz) $\delta$ 1.73 (s, 15 H, $\mathrm{C_5Me_5}$), 4.27 (d, $^2J_{\mathrm{HH}}$ = 1.2 Hz, 1 H, SiH), 4.70 (d, $^2J_{\mathrm{HH}}$ = 1.2 Hz, 1 H, SiH), 5.66 (s, 5 H, $\mathrm{C_5H_5}$); $^{29}$Si NMR (benzene-$d_6$, 22 °C, 59.6 MHz) $\delta$ −14.33 (t, $J_{\mathrm{SiH}}$ = 144 Hz). For **3**, prepared independently from **1** and $\mathrm{H_2}$: IR 1595 m (Zr–H); $^1$H NMR (benzene-$d_6$, 22 °C, 300 MHz) $\delta$ 1.84 (s, 15 H, $\mathrm{C_5Me_5}$), 5.85 (s, 5 H, $\mathrm{C_5H_5}$), 6.59 (s, 1 H, ZrH). For **5**: IR 2050 s (Si–H); $^1$H NMR (benzene-$d_6$, 22 °C, 300 MHz) $\delta$ 1.81 (s, 15 H, $\mathrm{C_5Me_5}$), 4.68 (d, $^2J_{\mathrm{HH}}$ = 1.2 Hz, 1 H, SiH), 5.14 (d, $^2J_{\mathrm{HH}}$ = 1.2 Hz, 1 H, SiH), 5.63 (s, 5 H, $\mathrm{C_5H_5}$); $^{29}$Si NMR (benzene-$d_6$, 22 °C, 59.6 MHz) $\delta$ 1.49 (t, $J_{\mathrm{SiH}}$ = 150 Hz).

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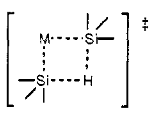
for reactions between $d^0$ M–R (R = H, alkyl, aryl) and C–H bonds.[8] The mechanism for the photochemical $\sigma$-bond metathesis



process is currently under investigation. Photochemical activation of CpCp*M(SiRR′R″)Cl (M = Zr, Hf) derivatives appears to result from excitation of low-intensity transitions in the visible region. In pentane the absorptions for **1** and **4** appear at 461 nm ($\epsilon$ = 500) and 405 nm ($\epsilon$ = 445), respectively, and are responsible for the observed photochemistry as determined by use of cutoff filters. It seems likely that these transitions involve silyl ligand to metal charge transfer, since they do not appear in UV-vis spectra of analogous alkyls, and there is a significant shift of the transition to higher energy on changing the metal from zirconium to hafnium. With a 365 (±5) nm band pass filter, the quantum yield for the reaction of **4** with $PhSiH_3$ in benzene-$d_6$ is 0.97. Given this relatively high quantum yield, it is difficult at this time to rule out a radical chain mechanism.

Previous studies have shown that photolysis of alkyl derivatives of the type $Cp_2MR_2$ (M = Ti, Zr) results in metal–carbon bond homolysis.[9] However, currently we have little chemical evidence for photochemical homolysis of the metal–silicon bonds in **1** and **4**. For example, no radical coupling products have been observed, and photolysis by visible light does not initiate polymerization of styrene or methyl methacrylate. Also, the photochemical reaction of **4** with $^t$BuBr, a good silyl radical trapping reagent,[10] is much slower than the corresponding reaction with $PhSiH_3$. The photochemical reaction of **4** with $PhSiD_3$ quantitatively gives $CpCp^*Hf(SiD_2Ph)Cl$ and $DSi(SiMe_3)_3$ (by $^1H$ and $^2H$ NMR). Reaction times for the photochemical reaction of **4** with silanes are strongly influenced by steric requirements of the incoming silane. Whereas the concentration of small primary silanes does not influence reaction times, bulkier silanes (e.g., 2,4,6-$Me_3C_6H_2SiH_3$ and secondary silanes) show a strong concentration dependence. Additionally, small Lewis bases (e.g., pyridine and $PMe_2Ph$) but not large ones (e.g., $PCy_3$) strongly inhibit these photochemical and thermal $\sigma$-bond metathesis reactions. It therefore appears that these processes may require an empty coordination site at the metal. Future studies will characterize further mechanistic details for these reactions.

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**Supplementary Material Available:** Characterization data ($^1H$ NMR, $^{13}C\{^1H\}$ NMR, $^{29}Si$ NMR, IR, UV–vis, and elemental analyses) for new compounds (4 pages). Ordering information is given on any current masthead page.

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# Specific Assemblies of the Naphthalene Unit in Monolayers and the Consequent Control of Energy Transfer[1]

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We describe in this paper controlled organization and the consequently modified fluorescence behavior (emission and sensitization of anthracene fluorescence) of the naphthalene unit in surface monolayers.

The fluorescence behavior of surface monolayers[2–6] is attracting much attention because it can provide fundamental data on the transfer processes of energy and electron. Chromophore orientation plays a decisive role in these processes, as attested by recent determination of the 3D structure of the bacterial photosynthetic reaction center.[7] Naphthalene and anthracene units are a representative chromophore pair in the organic energy-transfer process. Therefore, we chose amphiphiles **1** and **2** in this study. They form bilayer membranes[8,9] and are suitable as monolayer components.

As shown in Figure 1,[10] the naphthalene amphiphile produces a condensed monolayer on pure water with molecular area of 0.50 $nm^2 \cdot molecule^{-1}$ and collapse pressure of 40 $mN \cdot m^{-1}$. A somewhat expanded monolayer is formed (molecular area, 0.58 $nm^2 \cdot molecule^{-1}$) in the presence of dextran sulfate (DEX) in the subphase. Carboxymethylcellulose (CMC) in the subphase produces a much more expanded monolayer (molecular area, ca. 0.80 $nm^2 \cdot molecule^{-1}$). Similar polyanion effects have been found for monolayers of azobenzene-derived, single-chain ammonium amphiphiles.[12,13] These specific $\pi$-A changes are produced by polyion complex formation at the air–water interface, and this technique would have a general usefulness for controlling the molecular packing in charged monolayers.

Monolayer **1** gives a structured fluorescence spectrum (Figure 2a) which was characteristic of the crystalline aqueous bilayer membrane.[8] This spectral pattern does not change with the progress of compression, and the intensity fluctuation is observed in the low pressure region (ca. 2 $mN \cdot m^{-1}$). These data indicate that the crystalline monolayer island is formed on water even without compression.

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[10] The surface pressure area isotherms ($\pi$-A curve) were obtained with a computer-controlled film balance (San-esu Keisoku, Japan, Model FSD-20)[11] at a compression rate of 6 × $10^{13}$ $nm^2 \cdot s^{-1}$ at 20 °C on pure water (Milli-Q II system, Millipore Co.). Amphiphiles were dissolved (10 mg/10 mL) in a 7:1:2 mixture of benzene, $CH_2Cl_2$, and ethanol and spread on water evenly. Fluorescence spectra of surface monolayers were measured with an intensified multichannel photodetector system (Otsuka Electronics, Japan, Model IMUC 7000). A Xenon lamp with a band pass filter ($\lambda_{max}$ 278 nm, half band width 14 nm) was used as light source. The incident light through an optical fiber was directed at an angle of 45° against water surface, and emission was detected by a vertically positioned optical fiber. The sampling time of a whole spectrum was 5 or 10 s.

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