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Organolutetium Complexes in σ-Bond Metathesis Reactions Involving Silicon. Catalysts for the Hydrogenolysis of Si−C Bonds

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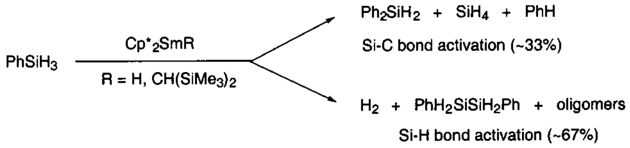
The lutetium hydride complex [Cp*$_2$Lu(μ-H)]$_2$ (**1**) efficiently cleaves the Si−C bond of PhSiH$_3$ to produce benzene and cross-linked polysilanes (SiH$_x$)$_y$. The Si−C bond cleavage appears to proceed via the lutetium phenyl complex Cp*$_2$LuPh (**2**). This is supported by the reaction of PhSiH$_3$ with **2**, which results in the formation of benzene. Moreover, activation of the Si−C bond of C$_6$F$_5$SiH$_3$ by **1** yields the related lutetium aryl complex Cp*$_2$LuC$_6$F$_5$ (**4**) and oligosilanes. The reaction of **1** with *o*-MeOC$_6$H$_4$SiH$_3$, on the other hand, results in the formation of dihydrogen and the neutral lutetium silyl complex Cp*$_2$LuSiH$_2$(*o*-MeOC$_6$H$_4$) (**5**). The solid-state structure of **5** was determined by X-ray crystallography. Reactions of arylsilanes with the lutetium methyl complex [Cp*$_2$LuMe]$_2$ (**3**) are less selective than the corresponding reactions of **1** and lead to competitive Si−C and Si−H bond activations. Complex **1** acts as an efficient catalyst for organosilane hydrogenolysis. Thus, addition of excess phenyl- or hexylsilane to solutions of **1** under an atmosphere of dihydrogen at 75 °C results in formation of benzene or hexane, respectively, along with cross-linked polysilanes.

Introduction

Organometallic f-element chemistry is associated with reactive metal−carbon and metal−hydrogen bonds, which readily participate in σ-bond metathesis processes.[1,2] It therefore seems that the f-elements are potentially useful in developing new chemical transformations that feature element−hydrogen and element−element bond activations.[1,3] Recent investigations of organosamarium−silicon systems revealed that Si−C bond activation (silane redistribution) competes with the expected dehydrocoupling of Si−H bonds in reactions of Cp*$_2$SmR[4] derivatives with PhSiH$_3$ [R = H, CH(SiMe$_3$)$_2$, Scheme 1].[5] Such processes are of interest in that direct observations of Si−C bond cleavage by transition or f-block metal complexes are extremely rare.[5,6] For example, Si−C bonds do not readily undergo oxidative addition, except in strained rings.[7] We recently reported direct observations of Si−C bond cleavage via σ-bond metathesis, in (for example) the reaction of [Cp*$_2$SmH]$_2$ with C$_6$F$_5$SiH$_3$, to give SiH$_4$ and Cp*$_2$SmC$_6$F$_5$.[5c]

Scheme 1



Additional interest in the activation of Si−C bonds, which generally do not participate in σ-bond metathesis

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[1] For recent examples see: (a) Fryzuk, M. D.; Jafarpour, L.; Kerton, F. M.; Love, J. B.; Patrick, B. O.; Rettig, S. J. *Organometallics* **2001**, *20*, 1387. (b) Douglass, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 1824. (c) Gountchev, T. I.; Tilley, T. D. *Organometallics* **1999**, *18*, 5661. (d) Dash, A. K.; Wang, J. Q.; Eisen, M. S. *Organometallics* **1999**, *18*, 4724. (e) Gountchev, T. I.; Tilley, T. D. *Organometallics* **1999**, *18*, 2896. (f) Arredondo, V. M.; Tian, S.; McDonald, F. E.; Marks, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 3633. (g) Tian, S.; Arredondo, V. M.; Stern, C. L.; Marks, T. J. *Organometallics* **1999**, *18*, 2568. (h) Arredondo, V. M.; McDonald, F. E.; Marks, T. J. *Organometallics* **1999**, *18*, 1949. (i) Molander, G. A.; Corrette, C. P. *J. Org. Chem.* **1999**, *64*, 9697. (j) Schumann, H.; Keitsch, M. R.; Demtschuk, J.; Molander, G. A. *J. Organomet. Chem.* **1999**, *582*, 70.

[2] For reviews see: (a) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57. (b) Bercaw, J. E. *Pure Appl. Chem.* **1990**, *62*, 1151. (c) Davis, J. A., Watson, P. L., Liebman, J. F., Greenberg, A., Eds.; *Selective Hydrocarbon Activation*; VCH Publishers: New York, 1990. (c) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51.

[3] Examples: (a) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175. (b) Reichl, J. A.; Berry, D. H. *Adv. Organomet. Chem.* **1999**, *43*, 197. (c) Gauvin, F.; Harrod, J. F.; Woo, H.-G. *Adv. Organomet. Chem.* **1998**, *42*, 363. (d) Molander, G. A.; Dowdy, E. D.; Noll, B. C. *Organometallics* **1998**, *17*, 3754. (e) Tilley, T. D. *Comments Inorg. Chem.* **1990**, *10*, 37.

[4] Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091.

[5] (a). Radu, N. S.; Tilley, T. D.; Rheingold, A. L. *J. Organomet. Chem.* **1996**, *516*, 41. (b) Radu, N. S.; Hollander, F. J.; Tilley, T. D.; Rheingold, A. L. *Chem. Commun.* **1996**, 2459. (c) Castillo, I.; Tilley, T. D. *Organometallics* **2000**, *19*, 4733.

[6] For example: (a) Nakano, T.; Nakamura, H.; Nagai, Y. *Chem. Lett.* **1989**, 83. (b) Hoffman, P.; Heiss, H.; Neiteler, P.; Müller, G.; Lachmann, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 880. (c) Horton, A. D.; Orpen, A. G. *Organometallics* **1992**, *11*, 1193. (d) Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 419. (e) Steenwinkel, P.; James, S. L.; Grove, D. M.; Kooijman, H.; Spek, A. L.; van Koten, G. *Organometallics* **1997**, *16*, 513. (f) Koizumi, T.; Osakada, K.; Yamamoto, T. *Organometallics* **1998**, *17*, 5721. (g) Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1999**, *18*, 4660.

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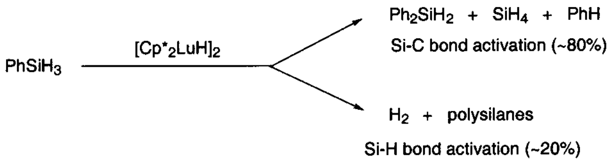
Scheme 2



processes, stems from the possible development of new transformations for organosilicon compounds and a better understanding of related C−C bond activations.[8] Within the context of organosilicon chemistry, compounds with Si−C bonds are readily available on a commercial scale by the direct process.[9] On the other hand, compounds with Si−H bonds (hydrosilanes) are not generally available via inexpensive chemical routes. This is unfortunate, since hydrosilanes possess a rich reaction chemistry which makes them versatile chemical intermediates.[3a,7d,9] A catalytic method for producing Si−H bonds from readily available Si−C bonded compounds would therefore be of interest.

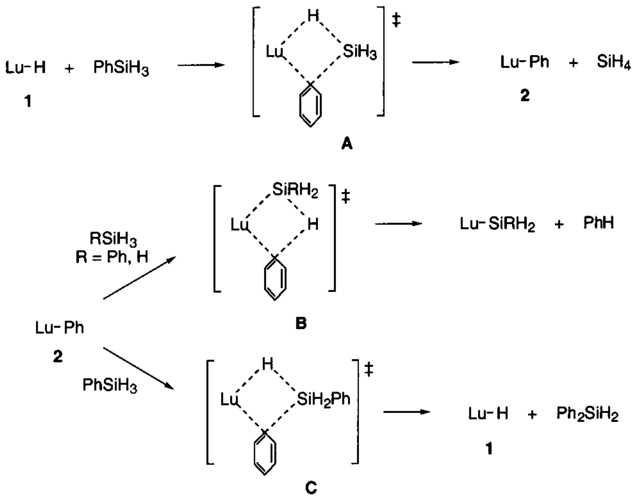
Lutetium complexes seem well-suited for activation of otherwise unreactive σ-bonds, since $[Cp^*_2LuMe]_2$ has been observed to activate even the C−H bond of methane.[10] The remarkable reactivity of organolutetium complexes toward C−H bonds in hydrocarbon−metal chemistry[10,11] suggested that complexes of lutetium could act as efficient silane dehydropolymerization catalysts, via activation of the more reactive Si−H bond. As in the case of the samarium systems, however, the poor catalytic performance of lutetium complexes toward silane dehydropolymerization implies the presence of a competitive Si−C bond activation pathway.[12]

To allow comparisons between the characteristics of samarium and lutetium in σ-bond metathesis reactions involving Si−H and Si−C bonds, we have undertaken a study of the $[Cp^*_2Lu(\mu\text{-}H)]_2/PhSiH_3$ system. One goal of this research is to identify selective bond activations. In addition, we have explored reactions of $[Cp^*_2Lu(\mu\text{-}H)]_2$ with various organosilanes R_2SiH_2 (R = H, alkyl, aryl) in attempts to develop useful transformations.

Results and Discussion

Reaction of $[Cp^*_2Lu(\mu\text{-}H)]_2$ (1) with Phenylsilane. To establish the reaction pathways that characterize the interaction of phenylsilane with the lutetium hydride complex $[Cp^*_2Lu(\mu\text{-}H)]_2$ (**1**),[4] we studied the reaction between **1** and 1 equiv of $PhSiH_3$ in cyclohexane-d_{12}. The colorless solution of **1** turned bright yellow immediately upon addition of $PhSiH_3$. Analysis of the reaction mixture by ^1H NMR spectroscopy revealed complete consumption of $PhSiH_3$ after 5 min, accompanied by the formation of Si−C bond cleavage products. Thus, benzene was produced in 80% yield (by ^1H NMR spectroscopy, Scheme 2) along with trace amounts of Ph_2SiH_2 (no other products giving rise to Si−H resonances were observed). The identities and quantities of the benzene and Ph_2SiH_2 produced were confirmed by GC−mass spectrometry. The amount of Si−H activation, which yields dehydrocoupling products, was therefore limited to the remaining 20% of $PhSiH_3$ consumed (Scheme 2). Although dehydrocoupling products such as PhH_2SiSiH_2Ph could not be identified, it is expected that such species would react further with SiH_4, generated by the redistribution of $PhSiH_3$. This is supported by the appearance of small amounts of H_2 and broad SiH resonances (at δ 4.48 and 3.32 in the ^1H NMR spectrum, respectively), which are consistent with dehydrocoupling products. We attribute the SiH resonance to a sparingly soluble white material, which appears to be cross-linked polysilane. Unlike the samarium-phenylsilane system, which allows the isolation of samarium hydrosilyl complexes,[5] these reactions were characterized by the formation of several unidentified lutetium-containing products.

Scheme 3



In the samarium system, activation of the Si−C bond of phenylsilane was proposed to occur by initial attack of the metal hydride on the unhindered silicon center via a four-centered transition state, yielding SiH_4 and a samarium phenyl complex.[5c] We suggest that this occurs in the lutetium system as well, such that the lutetium phenyl complex Cp^*_2LuPh (**2**)[11a] and silane are initially generated via transition state **A** (Scheme 3). Complex **2** would then rapidly react with 1 equiv of SiH_4 (or $PhSiH_3$), via H atom transfer, to give benzene and $Lu-SiH_3$ (or $Lu-SiH_2Ph$) via transition state **B** (Scheme 3). Alternatively, complex **2** could arylate $PhSiH_3$ through transition state **C** in Scheme 3, yielding Ph_2SiH_2 and regenerating the lutetium hydride **1**. The reaction pathway involving transition state **C** is a minor one in this system, however, since only trace amounts of Ph_2SiH_2 were observed. This result is in contrast to the considerable amount of diphenylsilane observed, relative to benzene, in the analogous samarium-mediated reaction (approximately 1:2).[5c]

In the lutetium system, activation of Si−H bonds represents an alternative reaction manifold, which consumes about 20% of the phenylsilane. Dehydrocoupling of $PhSiH_3$ and SiH_4 likely occurs via the intermediate lutetium silyl complexes $Cp^*_2LuSiH_2Ph$ and $Cp^*_2LuSiH_3$. Although these complexes were not observed

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(12) Tilley, T. D.; Radu, N. S.; Walzer, J. F.; Woo, H.-G. *Polym. Prepr. (ACS Div. Polym. Chem.)* **1992**, *33* (1), 1237.

(by ^{1}H NMR spectroscopy), this is not surprising since Lu−Si bonds are expected to be very reactive toward dehydrocoupling with $PhSiH_3$ or SiH_4.

Reaction of Cp*$_2$LuPh (2) with Phenylsilane. Cleavage of the Si−C bond of phenylsilane by **1** is proposed to proceed through lutetium phenyl complex Cp*$_2$LuPh (**2**).[11a] The preparation of reasonably pure samples of **2** in cyclohexane-d_{12} was accomplished by mixing [Cp*$_2$LuMe]$_2$ (**3**)[11b] and 2 equiv of benzene with a catalytic amount of **1**, as previously described by Watson. Heating the reaction mixture to 80 °C for about 5 days in a sealed NMR tube produced **2** via the elimination of methane. Small amounts (ca. 5%) of the phenylene-bridged dilutetium complex Cp*$_2$Lu(μ-1,4-C_6H_4)LuCp*$_2$[11a] were also formed in such reactions, but this compound did not seem to interfere in the reaction with $PhSiH_3$.

Examination of the reaction between solutions of **2** and an equimolar amount of $PhSiH_3$ provides support for the fundamental steps presented in Scheme 3. Thus, addition of 1 equiv of $PhSiH_3$ to colorless cyclohexane-d_{12} solutions of **2** at room temperature led to the production of benzene (67%) as the main product, and only trace amounts of Ph_2SiH_2 were observed after 10 min (by ^{1}H NMR spectroscopy). The remaining phenyl groups (33%) were probably incorporated into polysilanes in dehydrocoupling processes catalyzed by the lutetium species in solution. This process leads to a number of lutetium-containing products, which could not be identified (by ^{1}H NMR spectroscopy).

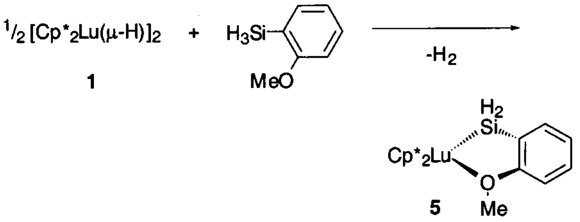
The preference for hydrogen transfer from silicon to the phenyl ligand of **2** is in contrast to the previously reported preference for phenyl ligand transfer to silicon by the analogous Sm−Ph complex.[13] Thus, the former reaction yields mostly benzene, while the latter one yields mostly diphenylsilane. Moreover, in the lutetium system approximately one-third of the phenylsilane seems to be consumed by dehydrocoupling, whereas in the samarium system[13] no phenylsilane was consumed by this process.

Reactions of 1 with Arylsilanes. To investigate the electronic effects of substituted arylsilanes on the chemoselectivity for Si−C vs Si−H bond activations by **1**, we examined its reactivity with $C_6F_5SiH_3$ and o-$MeOC_6H_4SiH_3$. Electron-poor $C_6F_5SiH_3$ and electron-rich o-$MeOC_6H_4SiH_3$ had proven useful in related studies involving samarium.[13]

Reaction of $C_6F_5SiH_3$ with benzene-d_6 solutions of **1** resulted in quantitative Si−C bond activation within 10 min (by ^{1}H NMR spectroscopy), producing the lutetium complex Cp*$_2$LuC_6F_5 (**4**, eq 1). This reaction is analogous to that observed between [Cp*$_2$Sm(μ-H)]$_2$ and $C_6F_5SiH_3$, for which SiH_4 was detected as the only byproduct.[13] In the lutetium system, however, no SiH_4 was observed, and instead a broad Si−H resonance at δ 3.83 seems to indicate the formation of $(SiH_x)_y$ species. Complex **4** gives rise to a single resonance in its ^{1}H NMR spectrum at δ 1.72 corresponding to the Cp* group. In the ^{19}F NMR spectrum, three sets of resonances in a 2:1:2 ratio can be assigned to the o-, p-, and m-F atoms in the $-C_6F_5$ ligand. Analytically pure samples of **4** were obtained as colorless crystals from concentrated, cold pentane solutions.

$$\underset{\mathbf{1}}{{}^1\!/_2[\mathrm{Cp^*_2Lu}(\mu\text{-H})]_2} + \mathrm{C_6F_5SiH_3} \rightarrow \underset{\mathbf{4}}{\mathrm{Cp^*_2LuC_6F_5}} + \text{oligosilanes} \quad (1)$$

In contrast to the clean Si−C bond activation of $C_6F_5SiH_3$, the reaction of benzene-d_6 solutions of **1** with o-$MeOC_6H_4SiH_3$ led to the lutetium silyl complex Cp*$_2\overline{\mathrm{LuSiH_2}(o\text{-MeO}}\mathrm{C_6H_4})$ (**5**) within 10 min, produced by quantitative Si−H activation (by ^{1}H NMR spectroscopy, eq 2). Compound **5** was identified by ^{1}H NMR spectroscopy chiefly by its Si−H resonance at δ 4.71, which integrates to 2 protons relative to the Cp* resonance (δ 1.95, 30 H). The $^1J_{SiH}$ coupling constant of 140 Hz is consistent with bonding of silicon to an electropositive element,[14] in this case lutetium. The IR spectrum of **5** is also consistent with this formulation, since the ν_{SiH} stretching frequencies at 2034 and 2013 cm^{-1} are significantly lower than that of the parent silane (2159 cm^{-1}), indicative of a Lu−Si bond.[5,15]



(2)

In contrast to its samarium counterpart, complex **5** is stable for at least one week in benzene-d_6 solution. The stability of **5** allowed its isolation from concentrated pentane solutions upon cooling to −35 °C. Colorless crystals suitable for X-ray diffraction studies were obtained in this fashion. Complex **5** represents the first structurally characterized, neutral lutetium-silyl derivative. The one Lu−Si bonded compound to be structurally characterized previously is the ion pair [Li(DME)$_3$][Cp$_2$Lu(SiMe$_3$)$_2$] (DME = dimethoxyethane, Cp = η^5-C_5H_5).[16] The crystal structure of **5** presents disorder in one of the Cp* rings. The Cp* ligand was thus modeled as having in-plane displacements, pivoting about one of the ring carbon atoms C(19). As a result, two of the methyl groups were modeled in two positions of 50% occupancy and refined isotropically. The remaining methyl groups on the Cp* ring presented large thermal parameters, except for the one bound to C(19).

The solid-state structure of **5** confirms the presence of a Lu−Si bond characterized by a distance of 2.82 Å, which can be compared to the Lu−Si bond length of 2.89 Å in [Li(DME)$_3$][Cp$_2$Lu(SiMe$_3$)$_2$]. The lutetium atoms in both compounds are in a pseudo-tetrahedral environment, with the coordination sphere of the lutetium metallocene in [Li(DME)$_3$][Cp$_2$Lu(SiMe$_3$)$_2$] complemented by two formally anionic silyl ligands, whereas that of **5** contains one silyl ligand and an oxygen donor.

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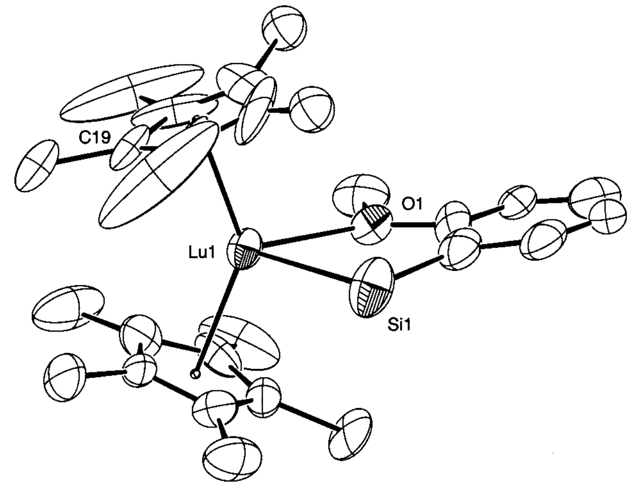


Figure 1. ORTEP diagram of $Cp^*_2[LuSiH_2(o\text{-}MeOC_6H_4)$ (**5**).

Table 1. Summary of Crystallographic Data for 5

formula	$C_{27}H_{39}SiOLu$
MW	582.66
cryst color, habit	colorless, rodlike
cryst dimens, mm	0.28 × 0.11 × 0.10
cryst syst	monoclinic
cell determination (2θ range)	2732 (4.0° − 45.0°)
lattice params	$a = 10.0247(4)$ Å $b = 12.8302(5)$ Å $c = 20.0541(7)$ Å $\beta = 92.144(2)°$ $V = 2577.5(1)$ Å^3
space group	$P2_1/c$ (#14)
Z value	4
D_{calc}	1.501 g/cm^3
μ(Mo Kα)	38.92 cm^{-1}
diffractometer	Siemens SMART
radiation	Mo Kα
temperature	−117.0 °C
scan type	ω(0.3° per frame)
no. of reflns measd	11 333
no. of reflns obsd	1928 ($I > 3.00\sigma(I)$)
solution	direct methods (SAPI91)
refinement	full-matrix least-squares
R; R_w	0.035; 0.041
max. peak in diff map	0.64 e$^-$/Å^3
min. peak in diff map	−1.01 e$^-$/Å^3

Despite the differences in the electronic nature of the ligands about lutetium in $[Li(DME)_3][Cp_2Lu(SiMe_3)_2]$ and **5**, the Lu−Si distances are surprisingly similar. Moreover, the Lu−Cp* centroid distance of 2.32 Å in **5** is identical to the corresponding distance in $[Li(DME)_3]$-$[Cp_2Lu(SiMe_3)_2]$, despite the differences in steric properties between the Cp* and Cp ligands. Finally, the centroid−Lu−centroid angle of 139.6° in **5** is significantly larger than the 131.6° angle of the anionic lutetium complex, indicative of the larger steric demand of the two $SiMe_3$ ligands in the latter and the Cp* ligands of the former. An ORTEP diagram of **5** is presented in Figure 1. The crystallographic data are summarized in Table 1, and selected bond distances and angles are presented in Table 2.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 5

(a) Bond Distances

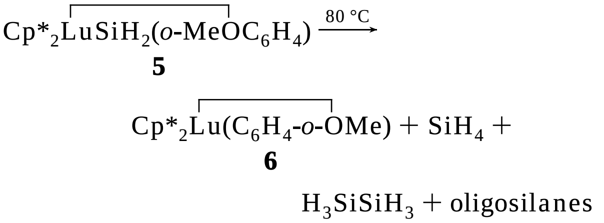
Lu(1)	Cp*(1)[a]	2.3217(5)	Lu(1)	Si(1)	2.823(5)
Lu(1)	Cp*(2)	2.3163(6)	Lu(1)	O(1)	2.389(8)

(b) Bond Angles

Cp*(1)	Lu(1)	Cp*(2)	139.62(2)	Si(1)	Lu(1)	O(1)	72.6(2)
O(1)	Lu(1)	Cp*(1)	106.0(2)	Si(1)	Lu(1)	Cp*(1)	106.5(1)
O(1)	Lu(1)	Cp*(2)	106.0(2)	Si(1)	Lu(1)	Cp*(2)	106.2(1)

[a] Cp* denotes the centroid of the ring.

Although **5** is stable in benzene-d_6 solution at ambient temperature, heating to 80 °C for approximately 4 h led to relatively clean (73%) conversion to the lutetium complex $Cp^*_2Lu(C_6H_4\text{-}o\text{-}OMe)$ (**6**, eq 3). Compound **6** was identified by its ^{1}H NMR spectrum, which lacks a resonance associated with an Si−H group. The chemical shifts of the Cp* and OMe resonances of **6** coincide with those of **5**, but a set of distinct aromatic resonances confirms the presence of a new lutetium product. This reaction was also characterized by the appearance of SiH_4 and H_3SiSiH_3 (at δ 3.10 and 3.21 in the ^{1}H NMR spectrum, respectively), as well as other unidentified silanes, which give rise to Si−H resonances at δ 3.22 and 3.27. Once again, this reactivity is reminiscent of that observed in analogous samarium systems.[13]



$$\underset{\mathbf{5}}{Cp^*_2LuSiH_2(o\text{-}MeOC_6H_4)} \xrightarrow{80\ °C} \underset{\mathbf{6}}{Cp^*_2Lu(C_6H_4\text{-}o\text{-}OMe)} + SiH_4 + H_3SiSiH_3 + \text{oligosilanes} \tag{3}$$

As has been previously observed for samarium, the substituents on the aryl ring of an arylsilane have a profound effect on the chemoselectivity of bond activation chemistry. The perfluorophenyl group gives rise to robust Ln−C_6F_5 complexes (Ln = Sm,[13] Yb,[17] Lu) in which the anionic character of the lanthanide-bound carbon atom is increased by the inductive effect of the fluorine atoms. This results in facile activation of the Si−C bond of $C_6F_5SiH_3$. The *o*-methoxy group of *o*-$MeOC_6H_4SiH_3$, on the other hand, directs the formation of five-membered metallacycles by selective Si−H activation.

Reactions of $[Cp^*_2LuMe]_2$ (3) with Arylsilanes. To characterize the reactivity of a Lu-Me group toward Si−H and Si−C bonds, the lutetium complex **3** was examined. As in the case of **1**, addition of 1 equiv of $PhSiH_3$ to colorless benzene-d_6 solutions of **3** resulted in immediate formation of bright yellow solutions. In these reactions, however, activation of the Si−C bond of $PhSiH_3$ was accompanied by a significant amount of Si−H activation. Thus, both benzene (67%) and methane (29% in solution) were observed as products (by ^{1}H NMR spectroscopy). The reaction is relatively complex, in that a number of Si-H resonances were observed. Two resonances (quartets at δ 3.30 and 4.47) were assigned to trace amounts of $MeSiH_3$ and $PhMeSiH_2$, respectively. The presence of $PhMeSiH_2$ and benzene was confirmed by GC−mass spectrometry (volatile methane and $MeSiH_3$ evaporated during sample preparation). Multiplets centered at δ 3.95 and 4.03, which are probably due to other hydrosilane species, could not be

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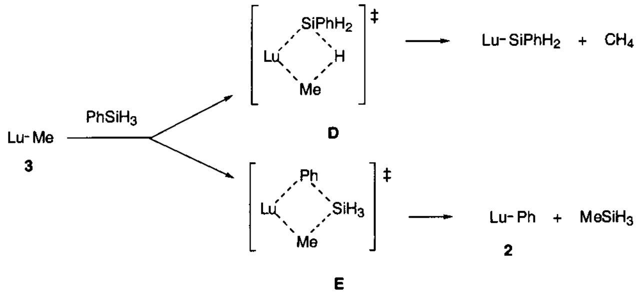
[17] Burns, C. J.; Andersen, R. A. *Chem. Commun.* **1989**, 136.

Scheme 4



assigned. Observation of methane as a product in the reaction between $PhSiH_3$ and **3** is consistent with direct activation of a Si−H bond by the lanthanide−methyl bond via transition state **D** (Scheme 4). This type of reaction had not been observed previously,[5a] but it likely represents the first step in the silane dehydropolymerization catalyzed by **3**.[18] Formation of benzene as the main product likely proceeds through complex **2**. We tentatively propose that lutetium phenyl complex **2** is formed via exchange of hydrocarbyl groups between **3** and $PhSiH_3$, to produce **2** and $MeSiH_3$ through transition state **E** (Scheme 4). Subsequent reaction of **2** with the Si−H bonds of hydrosilanes present in the reaction mixture can account for benzene generation.

In reactions between benzene-d_6 solutions of **3** and $C_6F_5SiH_3$, predominant Si−C bond activation led to the formation of complex **4** (60% by ^1H and ^{19}F NMR spectroscopy), as well as lutetium hydride **1** (14%), and unidentified lutetium-containing products after 10 min (eq 4). Observation of methane in the reaction mixture implies that Si−H bonds were activated, but lutetium silyl complexes of the type $Cp^*_2LuSiH_2C_6F_5$ were not observed. A single broad resonance at δ 4.22 in the ^1H NMR spectrum could be due to $(C_6F_5)MeSiH_2$, but this could not be confirmed by GC−mass spectrometry. Although the silicon-based products were not identified, dehydrocoupling chemistry mediated by $Cp^*_2LuSiH_2C_6F_5$ could be responsible for the formation of insoluble polysilanes.

$$\underset{\mathbf{3}}{Cp^*_2LuMe} + C_6F_5SiH_3 \rightarrow 0.6\ \underset{\mathbf{4}}{Cp^*_2LuC_6F_5} + 0.14\ \underset{\mathbf{1}}{Cp^*_2LuH} + CH_4 + \text{oligosilanes} \quad (4)$$

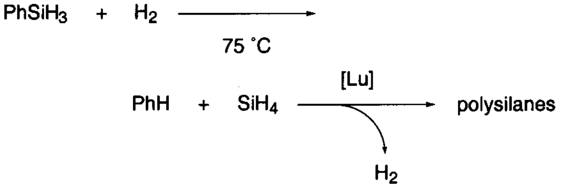
Finally, the reaction of benzene-d_6 solutions of **3** with o-$MeOC_6H_4SiH_3$ resulted in Si−H activation to give complex **5** and methane after 10 min (by ^1H NMR spectroscopy, eq 5). The yield of **5** in this case is rather moderate (52%), and unidentified lutetium-based products were also formed (by ^1H NMR spectroscopy). Among the dissolved silicon-containing products that were formed, SiH_4 (0.15 equiv) and H_3SiSiH_3 (0.05 equiv) were identified by their Si−H resonances in ^1H NMR spectra of the reaction mixtures. The remaining hydrosilane products were probably consumed in dehydrocoupling processes.

$$\underset{\mathbf{3}}{Cp^*_2LuMe} + o\text{-}MeOC_6H_4SiH_3 \rightarrow 0.52\ \underset{\mathbf{5}}{Cp^*_2LuSiH_2(o\text{-}MeOC_6H_4)} + CH_4 + SiH_4 + H_2SiSiH_3 + \text{oligosilanes} \quad (5)$$

Thus, complexes **1** and **3** react similarly with the arylsilanes that have been examined. The lutetium methyl system, however, seems to be more complex due to the indiscriminate activation of both Si−C and Si−H bonds, independent of the electronic properties of the arylsilane. This is best exemplified by comparing the reactions of $C_6F_5SiH_3$ with **1** and **3**. While **1** gives exclusive Si−C bond activation, producing quantitative yields of the aryl complex **4** (and no H_2 in solution), **3** gives both Si−C and Si−H bond activation, with generation of moderate yields of **4** (along with methane). It is important to note that the reactions of **3** are probably complicated by initial formation of highly reactive Lu−H and Lu−Si species, which should then participate in reactions with the added hydrosilane.

Catalytic Organosilane Hydrogenolyses. The selectivity for Si−C bond cleavage observed in stoichiometric reactions of **1** with phenylsilane suggested the possibility of catalytic Si−C bond hydrogenolyses. This is supported by the fact that the lutetium phenyl complex **2** does not transfer its phenyl group to $PhSiH_3$ (to give redistribution products), but instead reacts rapidly with Si−H bonds to produce benzene in high yield. To test this possibility, we initially examined reactions of **1** with excess $PhSiH_3$. When 10 equiv of $PhSiH_3$ was added to cyclohexane-d_{12} solutions of **1**, analysis of the reaction mixtures by ^1H NMR spectroscopy after 1 h revealed the presence of large amounts of unreacted $PhSiH_3$ (6 equivs) and the previously described Si−C and Si−H activation products (benzene, H_2, polysilanes).

Reactions of 10 equiv of $PhSiH_3$ and **1** in cyclohexane-d_{12} under an atmosphere of dihydrogen in sealed NMR tubes at 75 °C result in effective hydrogenolysis of the Si−C bond. Thus, benzene was produced in high yields (>90% by ^1H NMR spectroscopy and GC−mass spectrometry), along with an insoluble white solid attributed to polysilanes (broad resonance at δ 4.37 in the ^1H NMR spectrum). Monitoring the disappearance of the Si−H resonance of $PhSiH_3$ by ^1H NMR spectroscopy allowed determination of initial turnover frequencies for **1** of 4.3(5) $mol^{-1}\ h^{-1}$. Although rates diminished considerably after the first 4 h of the reaction, complete conversion to products was observed after approximately 24 h. This reaction therefore represents a rare example of catalytic cleavage of an unstrained Si−C bond (eq 6).



(6)

In organosamarium systems, related Si−C bond activations had been limited to the Si−C(sp^2) bonds of

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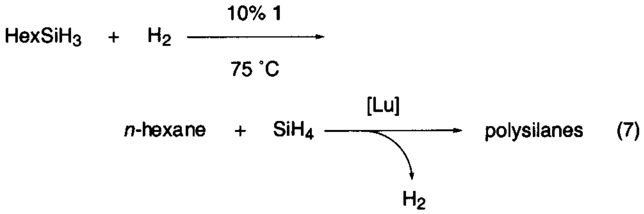
[18] (a) Watson, P. L.; Tebbe, F. N. U. S. Patent 4,965,386, Oct 23, 1990. (b) Watson, P. L.; Tebbe, F. N. *Chem. Abstr.* **1991**, *114*, 123331.

arylsilanes.[13] On the basis of the high reactivity of lutetium species toward σ-bond metathesis, it seemed that **1** might activate the Si−C(sp^3) bonds of alkylsilanes. Addition of a stoichiometric amount of *n*-hexylsilane to cyclohexane-d_{12} solutions of **1** did in fact lead to Si−C bond activation to give *n*-hexane (95%) and di-*n*-hexylsilane (5% by ^{1}H NMR spectroscopy). Both products were identified by GC−mass spectrometry, and Hex_2SiH_2 (Hex = *n*-hexyl) was also identified by its Si−H ^{1}H NMR resonance at δ 3.72.

As in the case of $PhSiH_3$ described above, catalytic cleavage of the Si−C bond was achieved by heating cyclohexane-d_{12} solutions of $HexSiH_3$ and **1** under an atmosphere of dihydrogen (eq 7). These reactions produced nearly quantitative yields of *n*-hexane (by ^{1}H NMR spectroscopy and GC−mass spectrometry) and presumably polysilanes (broad resonance at δ 3.50 in the ^{1}H NMR spectrum). Although the small amount of polymeric material obtained from hydrogenolysis did not allow its complete characterization, analysis of the solid obtained from a preparatory scale reaction in cyclohexane is consistent with a cross-linked polysilane (ν_{SiH} 2105 cm^{-1}) with the formula $[Hex_{0.10}SiH_{0.35}]_n$. Monitoring the reaction by ^{1}H NMR spectroscopy afforded an initial turnover frequency of 4.8(5) h^{-1} mol^{-1} for **1**. This number is identical (within experimental error) to that obtained for the hydrogenolysis of $PhSiH_3$. Thus, hybridization at carbon (sp^2 vs sp^3) does not play an important role in determining the reaction rate. To our knowledge, this represents the first example of the catalytic hydrogenolysis of a Si−C(sp^3) bond.



(7)

In an attempt to hydrogenate the Si−C bond of a more hindered silane, we examined the reaction of **1** with cyclohexylsilane under the conditions described above. Extended heating (2 days) to temperatures up to 110 °C resulted in no changes in the ^{1}H NMR spectra of such samples. Upon raising the temperature to 140 °C, the appearance of broad resonances in the Si−H region (δ 3.51 and 3.56) of ^{1}H NMR spectra indicated the presence of dehydrocoupling products. After approximately 18 h, 73% of the $CySiH_3$ (Cy = cyclohexyl) was consumed, and only dehydrocoupling products were observed. Apparently, the Si−C bond of $CySiH_3$ is too sterically congested for approach of the lutetium center, which results in exclusive Si−H bond activation and concomitant Si−Si bond formation. The dehydropolymerization of $CySiH_3$ by **1** was not pursued further.

Finally, we wished to determine whether it is feasible to hydrogenate secondary silanes. For this purpose, 10 equiv of Ph_2SiH_2 was added to solutions of **1** under an atmosphere of dihydrogen. As in the hydrogenolysis of $PhSiH_3$, benzene was obtained as the main product, along with polysilanes. Initial turnover frequencies of 1.1(2) mol^{-1} h^{-1} were determined by following the reaction by ^{1}H NMR spectroscopy. The hydrogenolysis of Ph_2SiH_2 is rather slow, as expected for a hindered Si−C bond. Thus, small amounts of $PhSiH_3$ were observed during the course of the reaction (by ^{1}H NMR spectroscopy).

Conclusions

Organolutetium systems are highly active in σ-bond metathesis reactions with the Si−C and Si−H bonds of organosilanes. Lutetium hydride complex **1** reacts with $PhSiH_3$ by predominant Si−C bond activation to produce benzene in high yield. This Si−C bond cleavage appears to proceed through a four-centered transition state that produces SiH_4 and lutetium phenyl complex **2**. Intermediate **2** then reacts with the Si−H bonds of SiH_4 or $PhSiH_3$ to produce benzene. The independent synthesis of **2** demonstrated that its phenyl group rapidly reacts with Si−H bonds to generate benzene.

Substituted arylsilanes are also susceptible to Si−C bond cleavage. The polarized Si−C bond of $C_6F_5SiH_3$ seems to be particularly well-suited for activation by σ-bond metathesis, as demonstrated by its reaction with **1** to give the lutetium aryl complex **4**. In the case of *o*-$MeOC_6H_4SiH_3$, the *o*-methoxy substituent leads to reaction of the Si−H bond with formation of a base-stabilized lutetium silyl complex **5**. Compound **5** represents the first structurally characterized neutral lutetium silyl species.

The reactions of **1** with arylsilanes are similar to those of the samarium analogue $[Cp^*_2Sm(\mu\text{-}H)]_2$,[13] since both complexes can cleave the Si−C bonds of $PhSiH_3$ and $C_6F_5SiH_3$. Also, both hydrides selectively activate the Si−H bond of *o*-$MeOC_6H_4SiH_3$ to produce metal−silicon bonded species. Nonetheless, there are significant differences between the Lu and Sm systems. Thus, in the former system benzene formation is accompanied by only trace amounts of Ph_2SiH_2 in the reaction of **1** with $PhSiH_3$, whereas in the samarium reaction 25% of Ph_2SiH_2 is observed relative to benzene. The phenyl complexes **2** and $[Cp^*_2SmPh]_2$ exhibit the same trend, in that addition of $PhSiH_3$ to **2** produces exclusively benzene, whereas the Sm system produces mostly Ph_2SiH_2 (80%). A possible explanation for these differences in reactivity is the smaller radius of lutetium compared to samarium. Transfer of the phenyl group of **2** from lutetium to silicon could result in prohibitively crowded four-centered transition states, inhibiting the formation of diphenylsilane. This could also explain the enhanced thermal stability of **5** relative to its samarium silyl counterpart, in that the Sm−Si bond may be more readily available for reaction compared to the (presumably) more sterically protected Lu−Si bond of **5**.

The reactions of arylsilanes with the Lu−C bond of $[Cp^*_2LuMe]_2$ (**3**) resulted in predominant formation of the same products observed for **1**. The reactions of **3** were less selective than those of **1**, however, resulting in competitive Si−C and Si−H bond activations with all arylsilanes. This result is possibly due to the weaker Lu−C bond of **3**, relative to the Lu−H bond of **1**,[10,11,19] which leads to facile reaction of the methyl group with both Si−C and Si−H bonds. Thermodynamic considerations[19,20] favor the production of $PhMeSiH_2$ via methyl-group transfer from **3** to the silicon center of $PhSiH_3$,

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(19) Nolan, S. P.; Stern, D.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7844.

but only trace amounts of $PhMeSiH_2$ were observed. Therefore, the Lu−Me bond of **3** seems to react with $PhSiH_3$ via two major pathways: exchange of hydrocarbyl groups to produce **2** and $MeSiH_3$, and formal protonation of the methyl group to yield Cp*$_2$LuSiH$_2$Ph and methane. The direct σ-bond metathesis reaction of **2** with Si−H bonds probably accounts for the observed benzene product. Another postulated intermediate, Cp*$_2$LuSiH$_2$Ph, and other lutetium species could play a significant role in mediating dehydrocoupling reactions of $PhSiH_3$ and $MeSiH_3$ to polysilanes.

Despite the high reactivity of lutetium hydride **1** toward organosilanes, it displays good selectivity for Si−C over Si−H activation. Use of dihydrogen in the lutetium hydride-catalyzed Si−C activations provides a source of hydrogen atoms, which allow complete conversion of Si−C to Si−H and C−H bonds. Thus, under hydrogenolysis conditions, selective and catalytic Si−C bond cleavage can be achieved. Moreover, such activation reactions have been demonstrated for both Si−C(sp^2) and Si−C(sp^3) bonds, as well as for disubstituted silanes. The hydrogenolysis of *n*-hexylsilane, in particular, appears to represent the first example of catalytic cleavage of an unactivated (no adjacent π-system) and unstrained Si−C bond. This type of reactivity had not been observed in other organolanthanide systems, and it can be attributed to the high charge density of lutetium relative to the rest of the lanthanide metals. The hydrosilane products of the hydrogenolysis reactions seem to react further with Lu species in solution by dehydrogenative coupling, which does not allow the isolation of well-characterized Si−H compounds. Despite this limitation, these reactions are potentially useful in future developments of new catalytic reactions of organosilicon compounds.

Experimental Section

General Considerations. Unless otherwise specified, all manipulations were performed under a nitrogen or argon atmosphere using standard Schlenk techniques or an inert atmosphere drybox. Dry, oxygen-free solvents were employed throughout. Olefin-free pentane was obtained by treatment with concentrated H_2SO_4, then 0.5 N $KMnO_4$ in 3 M H_2SO_4, followed by $NaHCO_3$, and finally $MgSO_4$. Thiophene-free benzene and toluene were obtained by pretreating the solvents with concentrated H_2SO_4, followed by Na_2CO_3 and $CaCl_2$. Pentane, benzene, toluene, and diethyl ether were distilled from sodium/benzophenone and stored under nitrogen prior to use, whereas benzene-d_6 was vacuum distilled from Na/K alloy. Cyclohexane-d_{12} was vacuum distilled from Na and stored under nitrogen. Reagents were purchased from commercial suppliers and used without further purification unless otherwise specified. [Cp*$_2$Lu(μ-H)]$_2$,[4] [Cp*$_2$LuMe]$_2$,[11b] $C_6F_5SiH_3$,[21] and *o*-MeOC$_6$H$_4$SiH$_3$[13] were prepared by literature methods. NMR spectra were recorded on Bruker AMX-300, AMX-400, or DRX-500 spectrometers at ambient temperature unless otherwise noted. Elemental analyses were performed by the Microanalytical Laboratory in the College of Chemistry at the University of California, Berkeley. Infrared spectra were recorded on a Mattson Infinity 60 FT IR instrument. Samples were prepared as KBr pellets unless otherwise noted, and data are reported in units of cm^{-1}.

Caution: Extreme care must be taken in conducting reactions that produce SiH_4, which is a flammable and potentially explosive gas.

Cp*$_2$LuPh (2). To a solution of [Cp*$_2$LuMe]$_2$ (**3**) (5.0 mg, 0.01 mmol) and [Cp*$_2$Lu(μ-H)]$_2$ (**1**) (0.1 mg, 2×10^{-4} mmol) in ca. 0.7 mL of cyclohexane-d_{12} was added benzene (1.4 μL, 4×10^{-4} mmol) via microsyringe. The colorless mixture was placed in a J-Young equipped NMR tube and heated to 80 °C. Monitoring the reaction by ^{1}H NMR spectroscopy revealed the progressive liberation of methane with concomitant formation of **2** (>90%). After approximately 5 days, complexes **3** and **1** had been completely consumed and the only two lutetium-containing species detected were **2** and small amounts (<5%) of Cp*$_2$Lu(μ-1,4-C$_6$H$_4$)LuCp*$_2$.[11a] Both **2** and Cp*$_2$Lu(μ-1,4-C$_6$H$_4$)LuCp*$_2$ were identified by ^{1}H NMR spectroscopy, as attempts to isolate **2** from large-scale syntheses resulted in samples that were contaminated with considerable amounts of Cp*$_2$Lu(μ-1,4-C$_6$H$_4$)LuCp*$_2$. ^{1}H NMR (300 MHz, cyclohexane-d_{12}): δ 1.79 (s, 30 H, Cp*), 6.79 (d, 2 H, *o*-Ph), 6.93 (t, 1 H, *p*-Ph), 7.10 (t, 2 H, *m*-Ph).

Cp*$_2$LuC$_6$F$_5$ (4). A solution of [Cp*$_2$Lu(μ-H)]$_2$ (**1**) (0.08 g, 0.09 mmol) in ca. 5 mL of pentane was stirred vigorously in a Schlenk tube. In another Schlenk tube, $C_6F_5SiH_3$ (0.04 g, 0.17 mmol) was dissolved in ca. 3 mL of pentane. The latter solution was added via cannula to the colorless solution of **1**, which underwent an immediate color change to bright yellow. Formation of the yellow solution was accompanied by vigorous bubbling that continued for about 1 min. After approximately 15 min, the mixture slowly turned colorless again. At this point, the solution was cannula filtered into another Schlenk tube and concentrated to a volume of about 3 mL. Cooling to −35 °C afforded off-white crystalline **4** in 67% yield (0.07 g, 0.11 mmol). Mp: 147−149 °C. IR: 2968 (s), 2903 (s), 2912 (s), 2864 (s), 1749 (w, br), 1633 (w), 1602 (w), 1535 (m), 1495 (s), 1432 (s), 1382 (m), 1358 (w), 1307 (w), 1245 (m, sh), 1181 (w), 1079 (m), 1026 (s), 955 (w), 910 (s), 801 (w), 745 (w), 710 (w), 587 (w, sh), 532 (w, br). ^{1}H NMR (300 MHz, benzene-d_6): δ 1.72 (s, 60 H, Cp*). ^{13}C{^{1}H} NMR (126 MHz): δ 27.35 (C$_5$*Me*$_5$), 119.63 (*C*$_5$Me$_5$). ^{19}F NMR (376 MHz): δ −158.67 (m, 2 F, *o*-C$_6$F$_5$), −154.79 (t, 1 F, *p*-C$_6$F$_5$), −129.57 (m, 2 F, *m*-C$_6$F$_5$). Anal. Calcd for $C_{26}H_{30}F_5Lu$: C, 50.99; H, 4.94. Found: C, 51.22; H, 5.01.

Cp*$_2\overline{\text{LuSiH}_2(o\text{-MeO}}\text{C}_6\text{H}_4)$ (5). A solution of [Cp*$_2$Lu(μ-H)]$_2$ (**1**) (0.08 g, 0.09 mmol) in ca. 5 mL of pentane was stirred vigorously in a Schlenk tube. In another Schlenk tube, *o*-MeOC$_6$H$_4$SiH$_3$ (0.03 g, 0.18 mmol) was dissolved in ca. 3 mL of pentane. As in the synthesis of **4**, the latter solution was added via cannula to the colorless solution of **1**. In this case, the reaction mixture remained colorless upon addition of the silane, and gentle bubbling was observed for about 1 min. After further stirring for 5 min, colorless crystals of **5** began to form. The mixture was allowed to settle, and the supernatant solution was cannula filtered and concentrated to a volume of approximately 3 mL. A second crop of crystals was obtained upon cooling to −35 °C for a combined yield of 75% (0.08 g, 0.14 mmol). Mp: 189−192 °C (dec). IR: 3058 (w), 3036 (w), 2969 (s), 2903 (s), 2858 (s), 2725 (w), 2034 (s, br, ν_{SiH}), 2013 (s, br, ν_{SiH}), 1685 (w), 1584 (w), 1565 (m), 1458 (s), 1428 (s), 1378 (m), 1260 (m), 1240 (m), 1206 (m, sh), 1150 (s), 1128 (m), 1085 (w), 1059 (m, sh), 1022 (m), 1001 (s, sh), 953 (s), 920 (m), 852 (w, br), 779 (m), 756 (s), 730 (s), 673 (w, sh), 588 (w), 467 (w, br). ^{1}H NMR (500 MHz, benzene-d_6) δ 1.95 (s, 30 H, Cp*), 2.67 (s, 3 H, OMe), 4.71 (s, 2 H, Si*H*), 6.32 (d, 1 H, Ar), 6.94 (m, 1 H, Ar), 7.01 (m, 1 H, Ar), 8.09 (d, 1 H, Ar). ^{13}C{^{1}H} NMR (126 MHz): δ 12.29 (C$_5$*Me*$_5$), 54.08 (OMe), 110.34 (Ar), 117.98 (*C*$_5$Me$_5$), 124.00 (Ar), 133.42 (Ar), 143.49 (Ar), 163.54 (Ar). ^{29}Si NMR (99 MHz): δ −39.57. Anal. Calcd for $C_{27}H_{39}LuOSi$: C, 55.66; H, 6.75. Found: C, 55.29; H, 6.92.

Preparation of Samples for GC−Mass Spectrometry. The benzene-d_6 and cyclohexane-d_{12} solutions of silanes ob-

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(20) (a) Nolan, S. P.; Porchia, M.; Marks, T. J. *Organometallics* **1991**, *10*, 1450. (b) Forsyth, C. M.; Nolan, S. P.; Marks, T. J. *Organometallics* **1991**, *10*, 2543. (c) King, W. A.; Marks, T. J. *Inorg. Chim. Acta* **1995**, *229*, 343.

(21) Molander, G. A.; Corrette, C. P. *Organometallics* **1998**, *17*, 5504.

tained from the reactions of **1**, **2**, and **3** with organosilanes were quenched with ca. 1 mL of 3 N HCl. The biphasic mixtures were then diluted with 1 mL of pentane and shaken vigorously. After decanting, the organic phase was filtered through a short silica plug for analysis by GC−mass spectrometry. Cyclooctane present as an internal standard for ^{1}H NMR spectroscopy was also used as a standard for integration of the GC traces.

Silane Hydrogenolyses. Catalytic hydrogenolysis of silanes was achieved by preparing solutions of the appropriate silane (0.10 mmol) in ca. 0.7 mL of cyclohexane-d_{12} in J-Young equipped NMR tubes. Cyclooctane (1.5 μL, 0.01 mmol) was used as an internal standard for ^{1}H NMR spectroscopy and GC−mass spectrometry. After acquisition of ^{1}H NMR spectra to accurately determine the amount of silane present (relative to cyclooctane), solid **1** (5.0 mg, 0.01 mmol) was added to the NMR tubes. The samples were degassed by three freeze−pump−thaw cycles and placed under an atmosphere of dihydrogen. After analysis by ^{1}H NMR spectroscopy, the products were quenched with ca. 1 mL of a 3 N HCl aqueous solution. Addition of ca. 1 mL of pentane allowed phase separation, which was followed by filtration of the organic phase through a short silica plug. The organic phase separated in this fashion was then analyzed by GC−mass spectrometry.

Preparation of [Hex$_{0.10}$SiH$_{0.35}$]$_n$. To a solution of **1** (50 mg, 0.11 mmol) in ca. 5 mL of cyclohexane in a Schlenk tube was added *n*-hexylsilane (0.26 g, 2.24 mmol). The mixture was degassed by three freeze−pump−thaw cycles and placed under an atmosphere of dihydrogen. The reaction mixture was then heated to 75 °C while stirring with a magnetic stirbar for 36 h. Volatile materials were removed under vacuum, and the products were redissolved in ca. 5 mL of pentane. Methanol (3 mL) was added to the solution, which resulted in precipitation of a white solid. The supernatant solution was removed by cannula filtration, and the solid was washed with three portions of 3 mL of diethyl ether. Removal of any traces of solvent in vacuo yielded 0.04 g of cross-linked polysilane. IR: 2957 (s), 2925 (s), 2857 (s), 2105 (m, br, ν_{SiH}), 1843 (w, br), 1189 (m), 1032 (s, br), 797 (w, br), 520 (w), 465 (m). ^{1}H NMR (500 MHz, benzene-d_6): δ 3.50 (s, SiH). Anal. Calcd for $C_{0.60}H_{1.65}Si$: C, 19.49; H, 4.51. Found: C, 19.54; H, 4.45.

X-ray Crystal Structure Determination of 5. A colorless, rodlike crystal of approximate dimensions 0.28 × 0.11 × 0.10 mm was mounted on a glass capillary using Paratone N hydrocarbon oil and placed under a stream of cold nitrogen on a Siemens SMART diffractometer with a CCD area detector. Preliminary orientation matrix and unit cell parameters were determined by collecting 60 10-s frames. A hemisphere of data was collected at a temperature of −117 ± 1 °C using ω scans of 0.30° and a collection time of 10 s per frame. Frame data were integrated using SAINT. An absorption correction was applied using SADABS ($T_{\max} = 0.831$, $T_{\min} = 0.552$). The 11 333 reflections integrated were averaged in point group $P2_1/c$ to yield 4373 unique reflections ($R_{\mathrm{int}} = 0.058$). No correction for decay was necessary. The structure was solved using direct methods (SAPI91) and refined by full-matrix least-squares methods using teXsan. The number of variable parameters was 269, giving a data/parameter ratio of 7.17. The maximum and minimum peaks on the final difference Fourier map correspond to 0.64 and −1.01 e$^-$/Å^3: $R = 0.035$, $R_w = 0.041$, GOF = 1.16.

Acknowledgment is made to the National Science Foundation for their generous support of this work, and to Professor Richard Andersen for useful discussions.

Supporting Information Available: Tables of crystal, data collection and refinement parameters, atomic coordinates, bond distances, bond angles, and anisotropic displacement parameters for **5**. This material is available free of charge via the Internet at http://pubs.acs.org

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