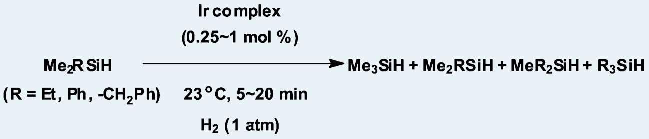
ACS Catalysis
Research Article
pubs.acs.org/acscatalysis

Redistribution of Trialkyl Silanes Catalyzed by Iridium Silyl Complexes

Sehoon Park,[†] Bong Gon Kim,[‡] Inigo Göttker-Schnetmann,[§] and Maurice Brookhart*[,†]

[†]Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, United States
[‡]Department of Chemistry Education, Gyeongsang National University, Jinju 660-701, Republic of Korea
[§]Department of Chemistry, University of Konstanz, Universitätstrasse 10, D-78457 Konstanz, Germany

Supporting Information



ABSTRACT: $[Ir(COE)_2Cl]_2$ reacts with Et_3SiH at 23 °C to form a binuclear iridium complex $(Et_3Si)_2(H)_2Ir(\mu\text{-}Cl)_2Ir(H)_2(SiEt_3)_2$, **1**. Complex **1** reacts further with Et_3SiH at 60 °C to form a second binuclear iridium complex, $Et_3Si(H)_2Ir(\mu\text{-}SiEt_2)_2Ir(H)_2SiEt_3$, **2**, containing bridging Et_2Si groups. Activation of **2** with H_2 produces trace quantities of a very highly reactive but unobservable species which rapidly and efficiently catalyzes alkyl redistribution reactions of silanes, RR′R″SiH. D_2 and silane exchange experiments establish reactivity features of both **2** and the reactive intermediate. The intermediate cannot be observed, but it is likely a monomeric iridium silyl silylene complex that catalyzes alkyl scrambling via silane exchanges coupled with 1,3-alkyl migrations between silicon centers. DFT calculations support such a mechanism.

KEYWORDS: *iridium, bridged silylene complexes, redistribution of silanes, H_2-triggered catalysis, 1,3-alkyl migration, low-T NMR spectroscopy*

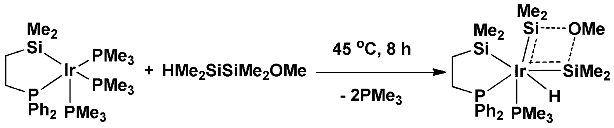
■ INTRODUCTION

Metal silylene complexes of the type $L_nM{=}SiR_2$[1−11] have been proposed as key intermediates in stoichiometric and catalytic transformations including catalytic redistribution of silanes,[12−16] various silylene-transfer reactions,[17−25] and dehydrogenative silane couplings.[26−32] Pannel reported Cp(CO)(L)Fe−$SiMe_3$ (L = CO, PPh_3) catalyzes the thermal isomerization of $HSiMe_2SiMe_2R$ at 120 °C to produce a mixture of $HSiMe_2SiMe_2R$ and $HSiMeRSiMe_3$.[33] This transformation was proposed to occur as shown in Scheme 1 with the redistribution occurring through a combination of reactions involving 1,2-shifts of $-SiMe_2R$ between iron and silicon in Cp(CO)Fe−$SiMe_2SiMe_2R$ and 1,3-shifts of alkyl groups between silicon centers in the proposed iron silylene intermediates, $Cp(CO)Fe{=}SiR_2(SiR'_3)$.[33−39]

The key step to permit formation of a silyl(silylene) complex as an intermediate is the creation of a coordinatively unsaturated metal center via dissociation of labile ligands such as CO and PPh_3, which allows α-elimination and production of an iron silylene complex. Isolation by Tilley,[40−53] et al. of numerous base-free transition metal silylene complexes gives credence to the proposal of an iron silyl(silylene) intermediate.

Ogino has reported similar chemistry. The silyliridium(I) complex $\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}Ir(PMe_3)_3$ (20 mol %),[54] catalyzes the redistribution of methyl groups in $HMe_2SiSiMe_2Ph$ at 45 °C to lead to the formation of a mixture of $HPhMeSiSiMe_3$ and $HMe_2SiSiMe_2Ph$ in a ratio of 2:3; the catalytically active species decays during the scrambling.[55] Ogino suggested that, similar to the processes shown in Scheme 1, this mixture of hydrodisilanes results from reversible formation of an iridium silyl(silylene) intermediate via a 1,2-silyl shift coupled with a 1,3-Me shift in the silyl silylene intermediate (Scheme 2).

Evidence for the silyl silylene intermediate is provided by the stoichiometric reaction of the silyliridium(I) complex with $HMe_2SiSiMe_2OMe$ at 45 °C for 8 h to afford the methoxy-bridged bis(silylene) complex:[55−60]

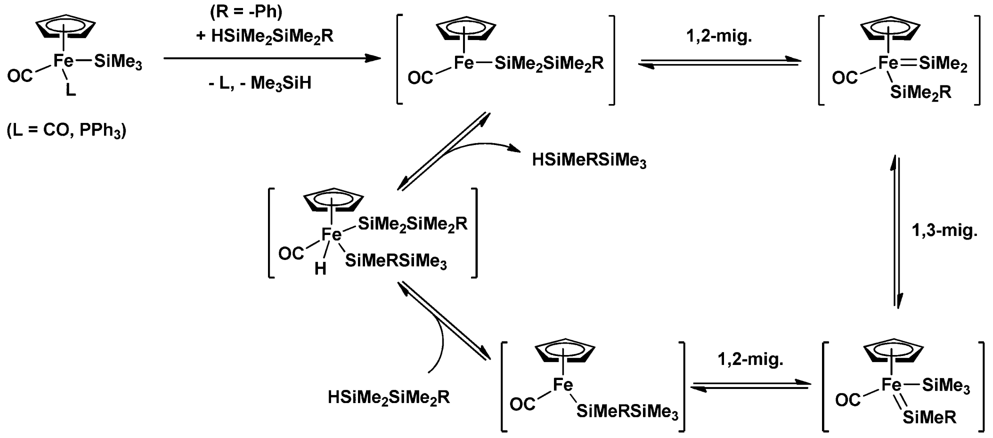


In related chemistry, Tamao found that $Pd(PPh_3)_4$ catalyzes a chemoselective skeletal rearrangement of (alkoxy)oligosilanes, which is proposed to involve 1,3-alkoxy shifts in a palladium silylene intermediate.[61]

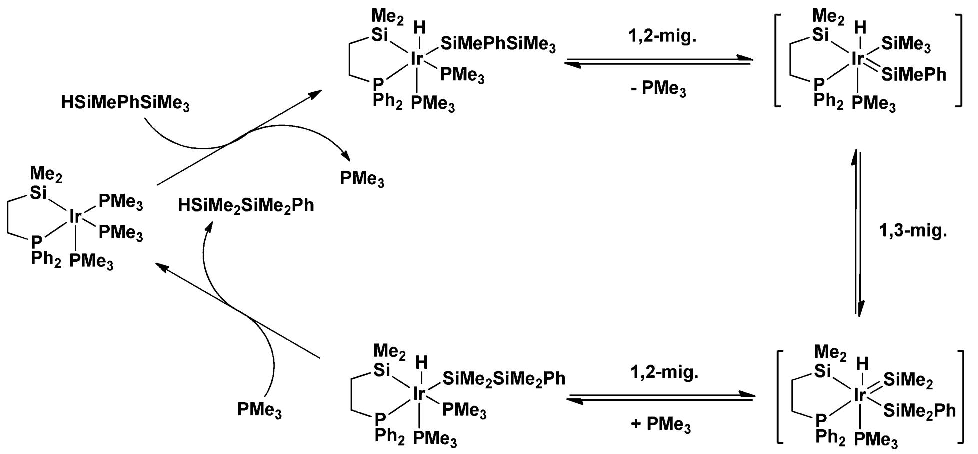
Despite observations of catalytic redistribution reactions of organodisilanes, there are no reports of catalytic alkyl redistribution reactions of simple trialkyl silanes, RR′R″SiH, via metal silylene intermediates. We describe here synthetic and mechanistic details of an efficient catalytic redistribution of trialkyl silanes employing a "ligand-free" dimeric silyliridium complex as a precatalyst. This catalyst system shows high catalytic activity at low catalyst loading (0.25 mol %) under a

Received: December 1, 2011
Revised: January 10, 2012
Published: January 10, 2012

Scheme 1. Proposed Mechanism of Thermal Isomerization of a Hydrodisilane Catalyzed by an Iron Silyl Complex at 120 °C[33]



Scheme 2. Iridium-Catalyzed Redistribution of Hydrodisilanes



H_2 atmosphere for the redistribution of trialkyl silanes to give an equilibrium mixture of scrambling products in 20 min at 23 °C. Mechanistic studies show that only a trace amount of the precatalyst undergoes activation by H_2 to form the active catalyst. On the basis of the studies cited above, we suggest that this active species is likely a monomeric silyl(silylene) iridium complex.

■ RESULTS AND DISCUSSION

In Situ Catalytic Redistribution of Trialkyl Silanes with $[Ir(COE)_2Cl]_2$. In a preliminary experiment, we found that Me_2EtSiH undergoes alkyl scrambling catalyzed by $[Ir(COE)_2Cl]_2$ (COE = cyclooctene) (1.3 mol %) at 60 °C to result in a mixture of Et_2MeSiH, Me_2EtSiH, Me_3SiH, and Et_3SiH in 3.5 h (eq 1). The ^1H NMR spectrum of the reaction

$$Me_2EtSiH \xrightarrow[\text{toluene, 60 °C, 3.5 h}]{[Ir(COE)_2Cl]_2\ (1.3\ mol\%)} \underset{1}{Et_2MeSiH} + \underset{2}{Me_2EtSiH} + \underset{1}{Me_3SiH} + \underset{0.1}{Et_3SiH} \quad (1)$$

mixture exhibits four multiplets at δ 4.13, 4.03, 3.93, and 3.84 that are assigned to the $-Si\mathit{H}$ of Me_3SiH, Me_2EtSiH, Et_2MeSiH, and Et_3SiH, respectively (Figure 1).

On the basis of the peak intensities of these signals, the relative ratios of Me_3SiH, Me_2EtSiH, Et_2MeSiH, and Et_3SiH are estimated as 1:2:1:0.1. This ratio is essentially unchanged overnight, suggesting a complete scrambling of alkyl groups and production of a thermodynamic mixture of silanes. As expected, the $^{13}C\{^1H\}$ NMR spectrum shows a total of nine singlets due to Me_3SiH, Me_2EtSiH, Et_2MeSiH, and Et_3SiH. The $^{29}Si\{^1H\}$ NMR spectrum of this mixture shows three main signals at δ −5.6, −11.2, and −16.4 due to Et_2MeSiH, Me_2EtSiH, and Me_3SiH, respectively, and a small signal due to Et_3SiH (~3%) at δ −0.1. No signals due to di- and tetraalkyl silanes are observed by NMR spectroscopy, suggesting a Si−H group is necessary for scrambling, which results in chemoselectivity during the scrambling reaction. Similar to Me_2EtSiH, the catalytic reaction of Me_2PhSiH under the same conditions leads to an equilibrium mixture of Me_3SiH, Me_2PhSiH, and $MePh_2SiH$ in 5 h. The observation of signals due to free COE

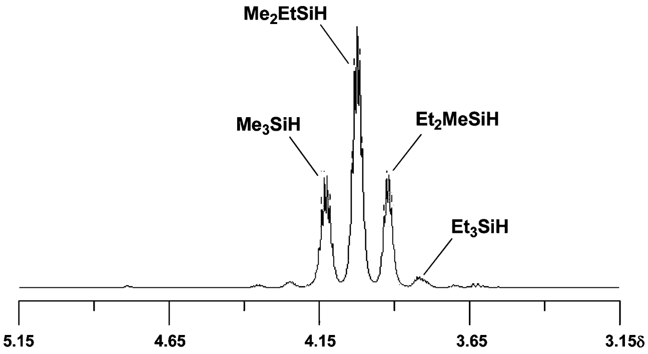
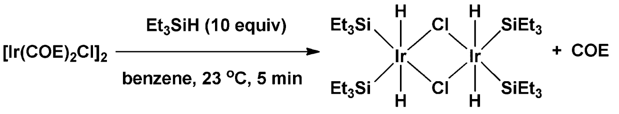


Figure 1. ^1H NMR (toluene-d_8) spectrum of the alkyl redistribution products obtained from Me_2EtSiH.

and of several iridium hydride signals at $\delta \sim -5.5$ (m), -7.5 (m), and -12.8 (m) in the ^1H NMR spectrum during the catalysis implies that trialkyl silanes displace COE from iridium to form silyl iridium hydride species, which catalyze the alkyl redistribution reaction.[62]

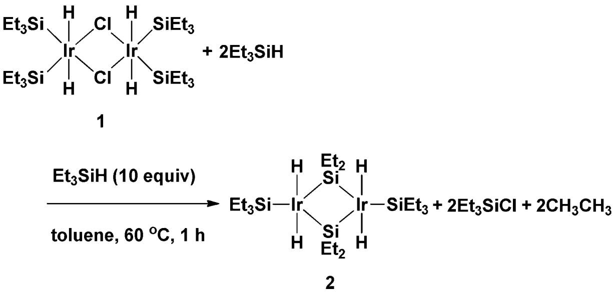
Synthesis and Characterization of a “Ligand-Free” Iridium Silyl Complex 1. To probe the structure of the active iridium catalyst, we carried out a stoichiometric reaction of $[Ir(COE)_2Cl]_2$ with Et_3SiH (eq 2). Treatment of $[Ir(COE)_2Cl]_2$ with 10 equiv of Et_3SiH in benzene at 23 °C quantitatively yields $[(Et_3Si)_2IrH_2(Cl)]_2$, **1**, which could be isolated as a yellow oil. Complete characterization of **1** was accomplished by ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectroscopy as well as by elemental analysis. The iridium hydride appears as a singlet at δ −21.1, and triethyl silyl groups are observed at δ 1.07 as a multiplet in the ^1H NMR spectrum of **1**. The integral ratio of Et_3Si protons to Ir−H is ∼15, which is consistent with the proposed structure of **1**. Two ^{13}C resonances at δ 11.5 and 8.6 and a single ^{29}Si resonance at δ 46.5 for the triethyl silyl groups of **1** indicate equivalence of all triethyl silyl groups on iridium. In addition, elemental analysis of **1** supports either a monomeric or dimeric structure. Several attempts to recrystallize **1** from pentane at −30 °C were unsuccessful; however, we have synthesized an analogue of complex **1**, $[(Et_2PhSi)_2IrH_2(Cl)_2]_2$, **1′**, in a quantitative NMR yield by reaction of $[Ir(COE)_2Cl]_2$ with Et_2PhSiH (molar ratio 1:2.5) at 23 °C (see the Experimental Section for NMR spectroscopic data for **1′**). Slow evaporation of pentane containing **1′** at −30 °C gave, over 5 days, yellow crystals that were subjected to an X-ray diffraction study. Although the crystal structure of **1′** exhibits disorder of the ethyl groups, the data clearly confirmed a chloro-bridged dimeric structure. These results strongly suggest a dimeric structure for **1**, as shown, rather than a monomeric structure.



(2)

1

Thermal Reaction of 1 with Et₃SiH To Give 2. Heating a solution of **1** with Et_3SiH (10 equiv) at 60 °C affords a new complex, **2**, as a red oil in 83% NMR yield in 1 h (eq 3).



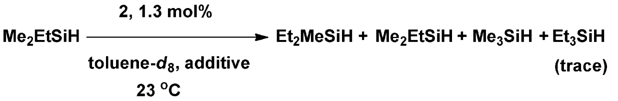
(3)

Complex **2** is assigned to the dimeric structure shown below. Following the reaction by GC/mass spectroscopy of the head space gas in the reactor shows that ethane is increasingly formed as the reaction proceeds. In addition to **2**, ^1H and ^{13}C NMR analysis indicates the formation of Et_3SiCl (^{13}C signals at δ 7.2 and 6.5); the ^{13}C peak integral ratio of the Si−Et groups on **2** to Et_3SiCl is ∼1:1, which is consistent with the stoichiometry shown in eq 3 and indicates no chloride remains in **2**. Complex **2** exhibits an iridium hydride signal at δ −13.0 (singlet). The ^1H integral ratio of ethyl groups on silicon to iridium hydride is 12.5:1, which is in excellent agreement with structure **2**. The $^{13}C\{^1H\}$ NMR spectrum of **2** shows two types of Si−Et groups: δ 20.9 ($-CH_2$), 16.2 ($-CH_2$), 11.0 ($-CH_3$), and 9.5 ($-CH_3$) assigned via an HSQC spectrum (see the Supporting Information). The most compelling evidence for the bridging structure comes from the $^{29}Si\{^1H\}$ NMR spectrum, which exhibits two signals at δ22 and 132.1. The former peak is clearly assignable to a normal $Ir-SiEt_3$ group.[63]

The later shift, δ 132.1, is a highly unusual low-field ^{29}Si shift. A terminal iridium silylene moiety, $Ir{=}SiEt_2$, would be expected to exhibit a shift in the range of δ 225−265.[64] Thus, **2** does not appear to be a terminal silylene. Such species are highly electrophilic,[65,66] and further evidence against a terminal silylene is the inertness of **2** toward nucleophiles such as acetonitrile and Et_3N.

We could find no good models for the ^{29}Si shift in a “bridging” iridium silylene complex; however, the low-field shifts in rhodium[67] and iron[68,69] bridging silylene species suggest large downfield ^{29}Si shifts for such bridged silylenes are reasonable. Thus, we propose a bridging structure for **2**. Unfortunately, complex **2** is not stable in solution without excess Et_3SiH and is soluble even in pentane. For those reasons, to date, we have been unable to recrystallize this highly soluble complex.

Redistribution of Me₂EtSiH Catalyzed by 2 and Promoted by Various Additives. The redistribution reaction of Me_2EtSiH with **2** as a catalyst was carried out with pure **2** and with **2** in combination with various additives (eq 4). Contrary to our expectations, the redistribution reaction of Me_2EtSiH in the presence of pure **2** (1.3 mol %) proceeded at a very slow rate. For example, after 2.5 h at 23 °C, only 10 mol % of scrambling products ($Et_2MeSiH + Me_3SiH + Et_3SiH$) were produced relative to total silanes. During the reaction, the δ −13 Ir−H singlet of **2** splits up into several singlets closely spaced around δ −13, which are ascribed to various analogues of **2** in which methyl groups have, through the scrambling reaction, replaced ethyl groups to various degrees. Since **2** contains two Et_3Si- groups, there are a large number of Et/Me combinations that can give rise to minor variations in the Ir−H shifts.



$$Me_2EtSiH \xrightarrow[\substack{\text{toluene-}d_8\text{, additive} \\ 23\ ^\circ C}]{\mathbf{2}\text{, 1.3 mol\%}} Et_2MeSiH + Me_2EtSiH + Me_3SiH + \underset{(\text{trace})}{Et_3SiH} \quad (4)$$

Outside of the group of singlets centered around δ −13, no other Ir−H resonances are evident. Traces of siloxane compounds are observed in the reaction, which must come from hydrolysis of the silane by traces of water present to form siloxanes and H_2.[70,71] This observation led us to speculate whether **2** was activated by water or H_2. Indeed, the reaction in the presence of H_2O (2.6 mol %, 2 equiv) is greatly accelerated and achieves complete scrambling of alkyl groups in only 10 min. Subsequent addition of more Me_2EtSiH (75 equiv) to this reaction mixture results in further scrambling to achieve an equilibrium mixture within 10 min. During the catalysis, multiple iridium hydride signals are again observed at ∼δ −13. Carrying out the scrambling reaction in the presence of either Et_2O or Et_3N in place of water does not accelerate the reaction, suggesting that water is not functioning as a Lewis base in accelerating the scrambling.

Since addition of water generates some H_2, we further investigated the scrambling under an atmosphere of H_2.

Remarkably, the redistribution of Me_2EtSiH with **2** (1.3 mol %) under H_2 (1 atm) proceeds to achieve complete scrambling in less than 5 min. Upon addition of further Me_2EtSiH (75 equiv), the scrambling reaction resumes with a rate similar to the first cycle.[72] Dropping the catalyst loading to 0.25 mol % of **2** still catalyzes redistribution of Me_2EtSiH at 23 °C to yield an equilibrium mixture of scrambling products in 20 min. Figure 2 summarizes the effects of additives on the redistribution reactions shown in eq 4. On the basis of the results of screening experiments, we conclude that the key to the acceleration of the scrambling reaction is activation of **2** by H_2.

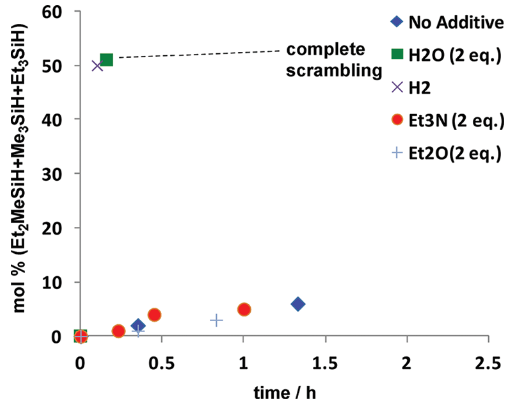
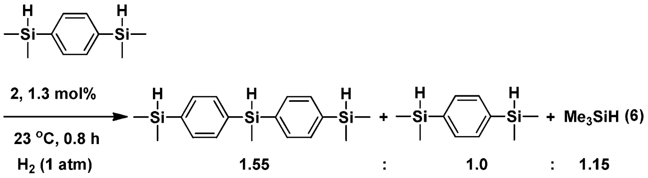


Figure 2. Effect of additives on the rate of alkyl group redistribution of Me_2EtSiH with 1.3 mol % 2 at 23 °C.

Complex **2** (1.3 mol %) under H_2 (1 atm) is also highly active for the catalytic redistribution reactions of Me_2PhSiH and Me_2BzSiH at 23 °C, which result in mixtures of the silane products in 0.1 and 0.8 h, respectively, as shown in eq 5, below

$$\underset{(R = Ph,\ Bz)}{Me_2RSiH} \xrightarrow[\text{toluene-}d_8,\ H_2\ (1\ atm),\ 23\ ^\circ C,\ 0.1\ or\ 0.8\ h]{2,\ 1.3\ mol\%} \underset{1}{R_2MeSiH} + \underset{2}{Me_2RSiH} + \underset{1}{Me_3SiH} \quad (5)$$

(no R_3SiH silanes, R = −Ph or $-CH_2Ph$, were detected). Interestingly, 1,4-bis(dimethylsilyl)benzene undergoes a selective disproportionation to afford a mixture of Me_2SiH-(1,4-phenyl)-SiMeH-(1,4-phenyl)-Me_2SiH, 1,4-bis(dimethylsilyl)-benzene, and Me_3SiH in a ratio of 1.55:1.0:1.15 in 0.8 h under the same conditions (eq 6).



NMR Investigations of the Catalytic Redistribution of Me_2EtSiH Employing 2 under H_2 (1 atm).

We have monitored the scrambling reaction of Me_2EtSiH with **2** (0.9 mol %) at −20 °C under H_2 (1 atm) by ^1H NMR spectroscopy (eq 7).The reaction yields 45 mol % conversion of Me_2EtSiH to Et_2MeSiH (21 mol %), Me_3SiH (21 mol %), and Et_3SiH (3 mol %) as scrambling products in 4 h, in which only a *single* signal at δ −13.1 due to Ir−H for **2** appears throughout this conversion (Figure 3).

$$Me_2EtSiH \xrightarrow[\text{toluene-}d_8,\ H_2\ (1\ atm),\ -20\ ^\circ C,\ 4\ h]{2,\ 0.9\ mol\%} \underset{21\%}{Et_2MeSiH} + \underset{55\%}{Me_2EtSiH} + \underset{21\%}{Me_3SiH} + \underset{3\%}{Et_3SiH} \quad (7)$$

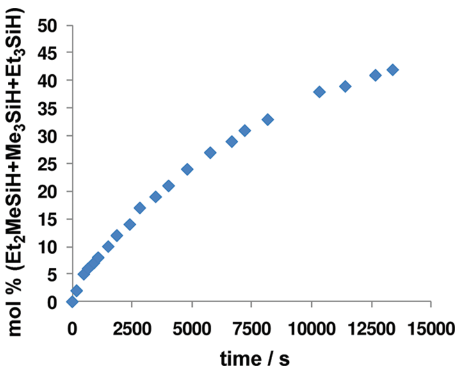


Figure 3. Plot of new scrambling products of Et_2MeSiH (mol %) versus reaction time at −20 °C under H_2 (1 atm), 0.9 mol % 2, toluene-d_8.

Upon warming to 23 °C, the singlet for **2** splits into several singlets between δ −12.7 and −13.1 over the course of 4.3 h. As noted above, these closely spaced singlets are assignable to analogues of **2** bearing different combinations of methyl and ethyl groups due to exchange of the Et_3Si- groups with Et_2MeSi, $EtMe_2Si-$, and Me_3Si- groups. These results again imply that **2** is inactive and that the active species for the catalytic scrambling can be generated from **2** under H_2 (1 atm), even at −20 °C. The fact that no new Ir−H signals (in addition to that **2** at δ −13.1) appear during the catalysis at −20 °C suggests that undetectable amounts of a highly active iridium species are formed from **2** under H_2 (1 atm) and that this active species is capable of redistributing alkyl groups faster than trialkyl silyl groups scramble into **2** from Me_2EtSiH, Et_2MeSiH, and Me_3SiH.

A series of NMR experiments were carried out to assess the stability of the catalytically active species, as summarized in eqs 8 and 9. Me_2EtSiH was treated with **2** (1.3 mol %) in toluene-d_8 under 1 atm H_2 at 23 °C (eq 8a). Scrambling was completed in 4 min. At that point the solution was purged with argon for 5 min to remove excess H_2. An additional 75 equiv of Me_2EtSiH was added to this solution and monitored by NMR spectroscopy over 20 min (eq 8b). Only a trace of additional

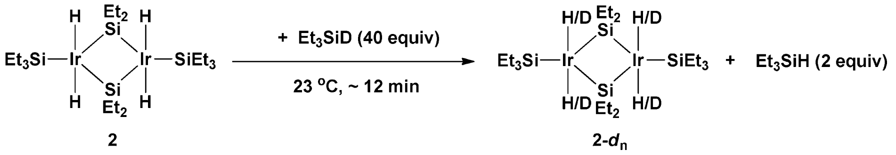
$$Me_2EtSiH \xrightarrow[23\ ^\circ C,\ 4\ min,\ H_2\ (1\ atm)]{2,\ 1.3\ mol\%} \underbrace{Et_2MeSiH + Me_2EtSiH + Me_3SiH}_{\text{complete scrambling}} + \underset{(trace)}{Et_3SiH} \quad (8a)$$

$$\xrightarrow[23\ ^\circ C,\ 5\ min]{1)\ \text{purged with Ar}} \xrightarrow[23\ ^\circ C,\ 20\ min]{2)\ Me_2EtSiH\ (75\ equiv)} \text{trace scrambling} \quad (8b)$$

$$\xrightarrow[<20\ min]{H_2\ (1\ atm)} \underbrace{Et_2MeSiH + Me_2EtSiH + Me_3SiH}_{\text{complete scrambling}} + \underset{(trace)}{Et_3SiH} \quad (8c)$$

$$2 \xrightarrow[-25\ ^\circ C,\ 5\ min]{1)\ H_2} \xrightarrow[-40\ ^\circ C,\ 5\ min]{2)\ \text{purged with Ar}} \xrightarrow[-40\ ^\circ C \to 23\ ^\circ C,\ 10\ min]{Me_2EtSiH\ (75\ equiv)} \text{complete scrambling} \quad (9)$$

Scheme 3. Stoichiometric Reaction of 2 with Et_3SiD in a Ratio of 1:40 at 23 °C



scrambling was observed. At this point, the solution was purged with H_2 and rapid scrambling of the added Me_2EtSiH was observed with complete equilibrium occurring in less than 20 min (eq 8c). These results suggest that the active species decays rapidly at 23 °C. To assess the lifetime of the active species at lower temperatures, the following experiment was carried out (eq 9). Since we have established that the active species can be generated by reaction of **2** with H_2 at −20 °C (eq 7), a solution of **2** in toluene-d_8 was purged with H_2 for 5 min at −25 °C,[73] and the temperature was lowered to −40 °C. This solution was then purged with argon for 5 min to remove H_2. To this solution was added 75 equiv of Me_2EtSiH. The solution was warmed to 23 °C and examined by NMR spectroscopy. Complete scrambling was observed. In contrast to observations above (eqs 8a−c), these experiments suggest that the active species has a significant lifetime at low temperature. The pathway for decay of the active species is not clear. One option is that it simply thermally decays to other inactive species. A second option is that the active species is in equilibrium with **2** and that removal of H_2 from solution drives the active species back to **2**. We favor the former explanation.[74]

Silane and Hydrogen Exchange Experiments. Results described above indicate that under catalytic conditions, the scrambled trialkyl silanes produced get incorporated into **2** and provide a number of alkyl-substituted analogues of **2** that exhibit slight differences in chemical shifts of the Ir−H signals. To test whether exchange of these groups are mediated by the intermediate responsible for scrambling, we examined exchange reactions of 2 in the absence of H_2. The reaction of 2 with Et_3SiD (40 equiv) was carried out at 23 °C in the presence of mesitylene (5 equiv) as an internal standard (Scheme 3).

The ^1H NMR analysis showed that ~2 equiv of Et_3SiH was eliminated from **2**, accompanied by incorporation of Et_3SiD into **2**, resulting in **2**-d_n in 12 min (Figure 4a). Unexpectedly, prolonged reaction times up to 45 h resulted in catalytic exchange between D and the α-hydrogen on free Et_3SiD to produce $HSi[C(H/D)_2CH_3]_3$ which is confirmed by ^1H and ^2H NMR spectroscopy (see Figure S17 of the Supporting Information; also note the growth of the Si−H resonance in Figure 4b resulting from exchange of Si−D with $-SiCH_2-$).

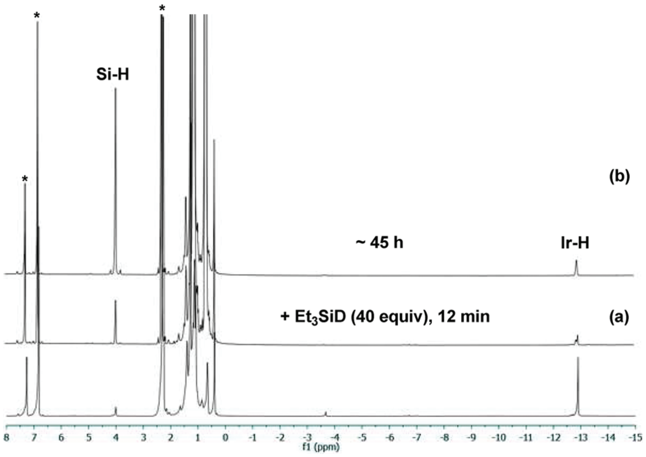
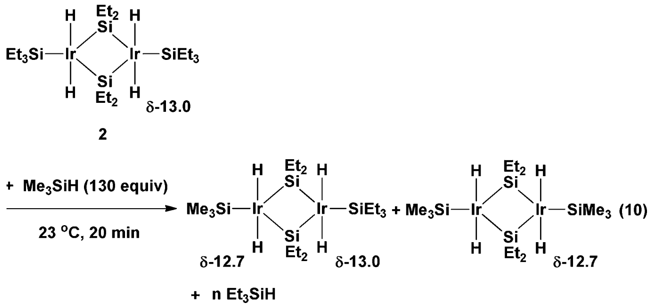


Figure 4. ^1H NMR (C_6D_6, 23 °C) spectra of **2** in the presence of Et_3SiD after 12 min (a) and 45 h (b). The growth in the Si−H signal (δ 3.98) at long times is the result of exchange with the $Si-CH_2$ protons (see text).



The result of the Et_3SiD exchange experiment in the absence of H_2 shows that the silane exchange in **2** is independent of the catalytic alkyl redistribution reaction. To further establish this, we carried out exchange of Me_3SiH with **2** in the absence of H_2. Treatment of **2** with 130 equiv of Me_3SiH at 23 °C in C_6D_6 results in incorporation of Me_3Si groups into **2** as shown in eq 10. The new Ir−H signal appears at δ −12.7 in 20 min together with the observation of the Ir−H signal of **2** at δ −13.0. Again, this shows the exchange is independent of the alkyl scrambling process. Reaction of 2 with D_2 (1 atm) in the presence of Et_3SiH (5 equiv) has been found to give **2**-d_n and excess Et_3SiD in 5 min by ^2H NMR spectroscopy (Figure 5a). This result supports exchange of D_2 with the Ir−H of **2**, followed by the facile exchange between terminal triethyl silyl groups on **2** and free Et_3SiH at 23 °C. Further reaction up to 2 h does not bring any remarkable change in the intensity ratio of the signals at δ 3.9 and δ −12.9 (Figure 5b). The ^2H spectrum of the reaction mixture in 0.5 h, after adding Me_2EtSiH (30 equiv), exhibits new ^2H signals at δ 4.25−3.75 and δ 0.61 as well as the signal due to Ir−D at δ −12.9 (Figure 5c). The δ 4.25−3.75 signals are assigned to Si−D resonances of scrambling products containing Me_3SiD, Me_2EtSiD, and Et_2MeSiD, and the δ 0.61 signal is attributed to deuterium incorporated into the methylene groups of the silanes. This result is consistent with the methylene exchange reaction described above.

Reaction of Me_2EtSiH (80 equiv) with **2** under D_2 (1 atm) has been carried out over the temperature range −70 to 23 °C in toluene-d_8 to gain further insights into the exchange processes in this system. The experiments are summarized in eq 11. Exposure of the Me_2EtSiH/toluene-d_8/**2** solution to D_2 at −70 °C results in partial deuteration of Me_2EtSiH over 15 min, but no deuterium incorporation into **2**. This experiment suggests that D_2 reacts with **2** to produce the intermediate responsible for alkyl silane redistribution and that this intermediate initiates a catalytic exchange between Me_2EtSiH and D_2 to yield Me_2EtSiD, even at −70 °C. Upon increasing the temperature to −30 °C, the scrambling reaction of alkyl groups at silicon occurs to yield $Et_2MeSiH(D)$ and $Me_2EtSiH(D)$, whereas

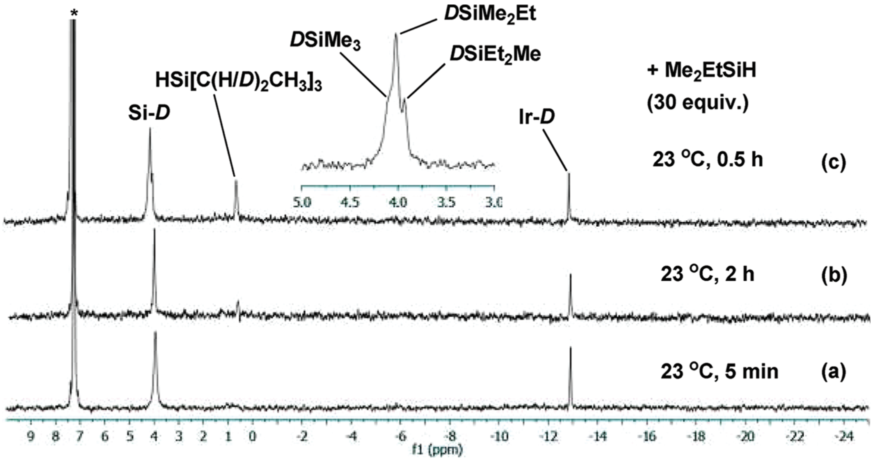
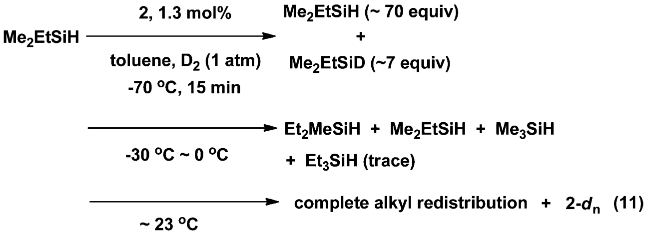


Figure 5. ^{2}H NMR (C_6H_6) spectra of **2** under 1 atm of D_2 in the presence of Et_3SiH (5 equiv) at 23 °C after 5 min (a), after 2 h (b), and followed by addition of Me_2EtSiH (30 equiv) (c).



$$\mathrm{Me_2EtSiH} \xrightarrow[\text{toluene, } D_2 \text{ (1 atm)}, -70\ ^\circ\text{C, 15 min}]{\mathbf{2}\text{, 1.3 mol\%}} \mathrm{Me_2EtSiH}\ (\sim 70\text{ equiv}) + \mathrm{Me_2EtSiD}\ (\sim 7\text{ equiv})$$

$$\xrightarrow[-30\ ^\circ\text{C} \sim 0\ ^\circ\text{C}]{} \mathrm{Et_2MeSiH} + \mathrm{Me_2EtSiH} + \mathrm{Me_3SiH} + \mathrm{Et_3SiH}\ \text{(trace)}$$

$$\xrightarrow[\sim 23\ ^\circ\text{C}]{} \text{complete alkyl redistribution} + \mathbf{2}\text{-}d_n \qquad (11)$$

deuterium incorporation into **2** is still not observed by ^{2}H NMR spectroscopy, even at temperatures up to 0 °C. Eventually, **2**-d_n begins to appear at ~23 °C, at which point the alkyl redistribution reaction has been completed. Complex **2** under D_2 (1 atm) in toluene-d_8 shows no deuterium incorporation between −70 and 0 °C. Upon warming the solution to 10 °C, **2**-d_n is formed via exchange with D_2 (Figure 6).

At this point, we can summarize the implications of the above experiments as follows: (1) Complex **2** is activated by H_2 to yield low levels of a very highly active species, which catalyzes redistribution of alkyl groups in trialkyl silanes. A Si−H group is required for scrambling. (2) The lifetime of the active species is quite short at 23 °C, but has a significant lifetime (at least minutes) at low temperatures (−40 °C to −20 °C). Concentrations of the active species cannot be built up by extensive purging with H_2, and the decay pathway of this species is unknown. (3) Exposure of complex **2** to silanes results in exchange in the absence of H_2. This exchange reaction does not proceed through the active species responsible for alkyl redistribution. (4) The iridium hydrides in **2** exchange with D_2 at 23 °C in the absence of added silanes. (5) The species active for alkyl redistribution can also catalyze D_2 incorporation into silanes faster than D_2 can be incorporated into silanes via, first, deuteration of **2** then transfer of deuterium to free silanes via silane exchange with **2**. The remaining major question is what is the active species? We can only speculate at this point, but in light of the results of Pannell and Ogino cited above and the requirement for an Si−H group for alkyl redistribution, it seems likely that an unstable but highly reactive iridium trialkylsilyl dialkylsilylene complex is formed, which can undergo rapid exchange of trialkyl silanes with iridium trialkylsilyl hydrides in addition to rapid, effectively degenerate, 1,3-migrations of alkyl groups between the silicon centers of the dialkyl silylene and the trialkyl silane. One possible pathway to such a reactive species is shown in Scheme 4. Hydrogenolysis of the bridging Ir−Si bond by H_2 could produce the monobridged complex A. The α-elimination of Si−H would split A into the monomer units, B and C, shown. It is easy

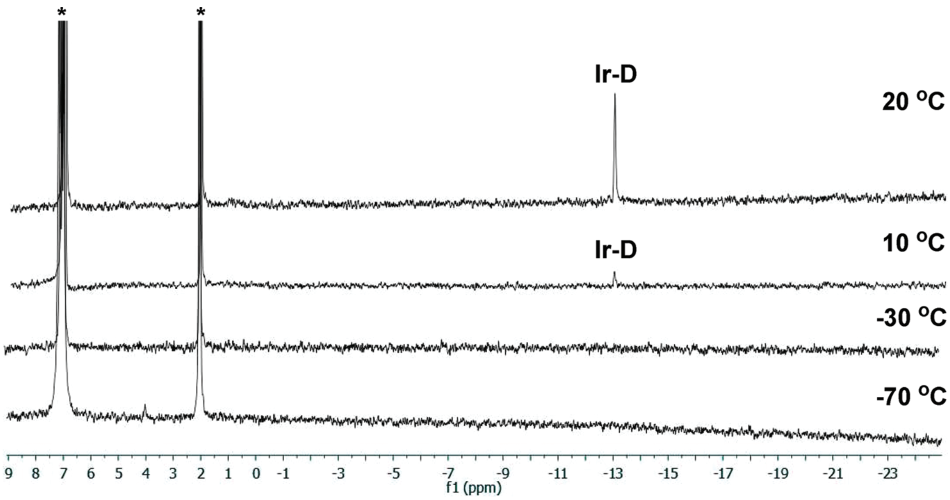
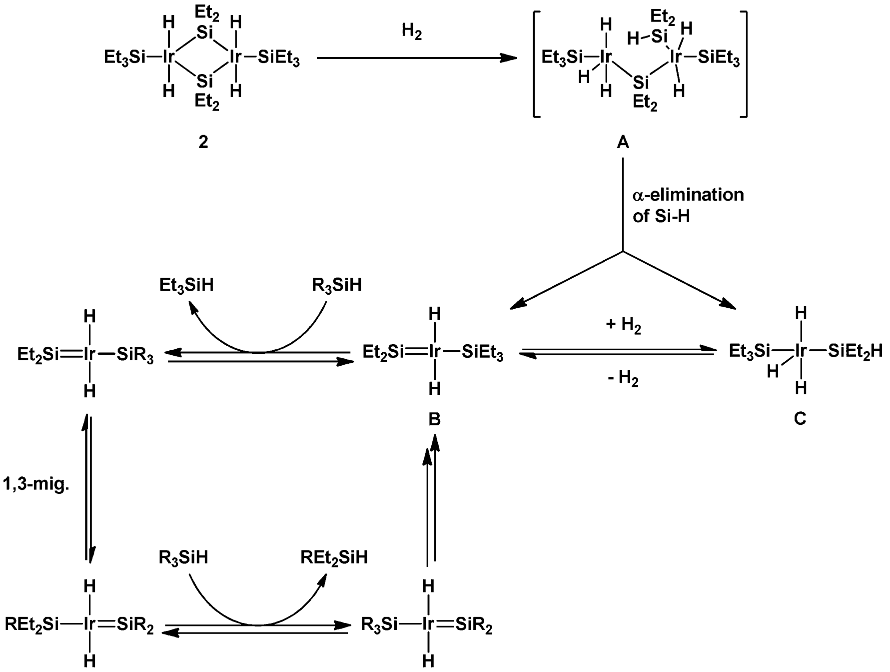


Figure 6. ^{2}H NMR (toluene) spectrum of **2** under D_2 (1 atm) at variable temperatures.

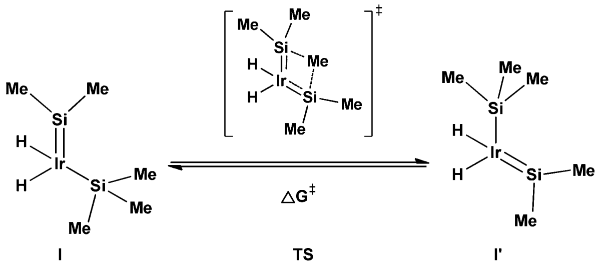
Scheme 4. Possible Mechanism of the Ir-Catalyzed Redistribution of Trialky Silane



to imagine that B could exhibit facile silane exchange reactions and either B or C could catalyze D_2 exchange with silanes.

DFT calculations were carried out on a model complex, $Ir(SiMe_3)H_2(SiMe_2)$, **3**, for B, $Ir(SiEt_3)H_2(SiEt_2)$, in which ethyl groups were replaced by methyl groups to probe whether the barrier for 1,3-alkyl migrations in such species was sufficiently low to be consistent with experimental observations. Calculations were performed with the Gaussian 09 suite of programs[75] with a tight self-consistent field convergence threshold for both gradient and wave function convergence. Several geometric isomers are possible for complex **3**. We have considered all possible isomers to identify the optimized structure of **3**: a distorted "see-saw"-like octahedral structure with two empty cis sites, a tetrahedral structure, and a square planar structure. The tetrahedral structure is paramagnetic so it was excluded. Two minima were found, **I** and **II**, both seesaw structures which differ in the H–Ir–H bond angles (85° and 178°) (see the Supporting Information). Frequency calculations were carried out on all minimum structures, and all the resulting frequencies had positive values. All geometries were fully optimized at the DFT level using both the hybrid B3LYP exchange correlation functional[76−80] and the newly developed m06-2x methods.[81] The double-ζ quality 6-311+G* and LanL2DZ basis sets were employed for the lighter nonmetallic atoms in ligands (C, Si, and H atoms) and the Ir atom, respectively. A relativistic effective core potential (ECP) for the Ir atom replaces the inner core electrons, leaving the outer layer ($5s^25p^6$) electrons and the ($5d^6$) valence electrons.[82−84] A continuum solvent model with a conductor-like polarizable continuum model of electrostatics (CPCM) was used to account for solvent effects.[85]

The calculated 1,3-methyl migration barriers ($\Delta G^{\ddagger}$) in the gas phase were 16.7 and 9.8 kcal/mol using B3LYP and m06-2x methods, respectively (eq 12). Corrections for solvation had little impact on the barriers, which were predicted to be 16.5 and 10.3 kcal/mol, respectively. These barriers correspond to half-lives for this process of ~0.1 s and 2×10^{-6} s, either of which is fully consistent with migrations occurring on a time scale of minutes in intermediates formed from **2** in low concentrations.



(12)

■ SUMMARY

A highly active catalytic system has been developed for alkyl redistribution reactions of trialkyl silanes. The binuclear iridium complex, **2**, can be conveniently prepared from $[Ir(COE)_2Cl]_2$ and triethyl silane. Under 1 atm H_2, a small fraction of **2** is converted to a highly active species that catalyzes the alkyl redistribution reaction. For example, 0.25 mol % **2** under 1 atm H_2 converts Me_2EtSiH to a thermodynamic mixture of all possible trialkyl silanes in ~20 min at 23 °C. Similar rates of scrambling were observed for Me_2PhSiH and Me_2BzSiH. A Si–H functionality is required; tetraalkyl silanes are not scrambled. The nature of the reactive intermediate could not be determined, but it is likely to be a monomeric iridium silyl silylene complex. DFT calculations suggest a very low barrier to 1,3-alkyl migrations required for alkyl redistribution catalyzed by such a silyl silylene complex.

■ EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out using standard Schlenk, high-vacuum, and glovebox techniques. Argon and nitrogen were purified by passing through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves. THF was distilled under a nitrogen atmosphere from sodium benzophenone ketyl prior to use. Toluene was passed through columns of activated alumina[86,87] and degassed by either freeze−pump−thaw methods or by purging with argon. Benzene and acetonitrile were dried with 4 Å molecular sieves and degassed by freeze−pump−thaw methods. $\mathrm{Et_3SiH}$, $\mathrm{Me_2EtSiH}$, $\mathrm{Me_2PhSiH}$, $\mathrm{Me_2BzSiH}$, and $\mathrm{Et_2SiH_2}$ were dried with $\mathrm{LiAlH_4}$ or 4 Å molecular sieves and vacuum-transferred into sealed flasks, except $\mathrm{Me_2PhSiH}$ and $\mathrm{Me_2BzSiH}$. $\mathrm{Et_2PhSiH}$ was synthesized in 95% isolated yield by the reaction of EtMgBr (2.2 equiv) with $\mathrm{PhSi(OEt)_3}$ (1 equiv) in refluxing THF, followed by reduction by lithium aluminum hydride in $\mathrm{Et_2O}$.[88] Unless otherwise stated, all of the other substrates were purchased from Sigma-Aldrich and were used without purification. Deuterated solvents ($\mathrm{C_6D_5CD_3}$, $\mathrm{C_6D_5Cl}$, $\mathrm{C_6D_6}$) for NMR and pentane were dried with $\mathrm{CaH_2}$ or 4 Å molecular sieves and vacuum-transferred into sealed flasks.

NMR spectra were recorded on Bruker spectrometers (DRX-400, Avance-400, AMX-300, and DRX-500). ^{1}H and ^{13}C NMR spectra were referenced to residual protio solvent peaks. $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ chemical shifts were referenced to external $\mathrm{Et_3SiH}$. Gas chromatography was performed on a Varian 450-GC in combination with a Varian 220-MS ion trap mass spectrometer and was used for detection of ethane formed during the reaction of **1** with $\mathrm{Et_3SiH}$.

Synthesis of Complex 1. $\mathrm{Et_3SiH}$ (20 equiv, 0.4 mmol, 64 μL) was added to a solution of $[\mathrm{Ir(COE)_2Cl}]_2$ (0.02 mmol, 18 mg) in 2 mL of benzene in a 25 mL Schlenk flask, and the contents were stirred at 23 °C for 5 min. The volatile material was removed to afford **1** as an analytically pure yellow oil (16 mg, 99%). ^{1}H NMR ($\mathrm{C_6D_6}$, 400 MHz, 23 °C): δ 1.09−1.05 (m, 60H, $-\mathrm{Si}Et_3$), −21.3 (s, 4H, $\mathrm{Ir}-H$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$, 100.6 MHz, 23 °C): δ 11.5 ($-\mathrm{SiE}t_3$), 8.6 ($-\mathrm{Si}Et_3$). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ DEPT 45 ($\mathrm{C_6D_6}$, 79 MHz, 23 °C): δ 46.5 ($-Si\mathrm{Et_3}$). Anal. Calcd. for $\mathrm{C_{24}H_{64}Cl_2Ir_2Si_4}$: C, 31.32; H, 7.01; Cl, 7.70. Found: C, 31.07; H, 6.82; Cl, 6.80.

In Situ Synthesis of Complex 1′. $\mathrm{Et_2PhSiH}$ (2.5 equiv, 0.05 mmol, 8.2 mg) was added to a solution of $[\mathrm{Ir(COE)_2Cl}]_2$ (0.02 mmol, 18 mg) in 2 mL of toluene in a 25 mL Schlenk flask at 0 °C, and the contents were stirred at 0 °C for 10 min. The volatile material was removed to afford **1′** as a yellow oil in quantitative NMR yield. ^{1}H NMR (toluene-d_8, 400 MHz, 23 °C, selected data): δ 1.12−0.97 (m, 40H, $-\mathrm{Si}Et_2\mathrm{Ph}$), −20.3 (s, 4H, $\mathrm{Ir}-H$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (toluene-d_8, 100.6 MHz, 23 °C, selected): δ 11.0 ($-\mathrm{Si}Et_2\mathrm{Ph}$), 8.4 ($-\mathrm{Si}Et_2\mathrm{Ph}$). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ DEPT 45 (toluene-d_8, 79 MHz, 23 °C): δ −5.1 ($-Si\mathrm{Et_2Ph}$).

Synthesis of Complex 2. A solution of **1** (0.02 mmol, 18 mg) in the presence of $\mathrm{Et_3SiH}$ (10 equiv, 0.2 mmol, 32 μL) in 2 mL of toluene was allowed to heat at 60 °C for 1 h. The volatile material was removed to afford **2** as a red oil (83% NMR yield based on an internal standard, mesitylene). $\mathrm{Et_3SiCl}$ and ethane as side products were observed by $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR and GC/MS spectroscopy, respectively. ^{1}H NMR (toluene-d_8, 400 MHz, 23 °C): δ 1.32 (m, 12H, $-\mathrm{IrSi}Et_3$), 1.18 (br s, 26H, $-\mathrm{IrSi}Et_3$ and $-\mathrm{IrSiEt_2}$), 1.07 (m, 12H, $-\mathrm{Ir-SiEt_2}$), −13.0 (s, 4H, $\mathrm{Ir}-H$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (toluene-d_8, 100.6 MHz, 23 °C): δ 20.9 ($-\mathrm{IrSi}Et_3$), 16.2 ($-\mathrm{IrSi}Et_2$), 11.0 ($-\mathrm{IrSi}Et_2$), 9.5 ($-\mathrm{IrSi}Et_3$). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ DEPT 45 (toluene-d_8, 79 MHz, 23 °C): δ 132.1 ($-\mathrm{Ir}Si\mathrm{Et_2}$), 22.0 ($-\mathrm{Ir}Si\mathrm{Et_3}$). 35.8 ($\mathrm{Et_3}Si\mathrm{Cl}$, volatile).

General Procedure for the Catalytic Redistribution of $\mathrm{Me_2RSiH}$ (R = Et, Ph, Bz) and 1,4-Bis(dimethylsilyl)-benzene with 2 under 1 atm $\mathrm{H_2}$. Hydrosilane (1.5 mmol, 75 equiv) was added to a solution of **2** (0.02 mmol, 16 mg, 1.3 mol %) in 0.4 mL of toluene-d_8 or $\mathrm{C_6D_6}$ in a NMR tube with a screw cap. $\mathrm{H_2}$ (1 atm) was purged through the solution of **2** and silane at 23 °C for seconds. This mixture was allowed to stand at 23 °C. The progress was followed by NMR spectroscopy. The relative ratios of scrambling products were calculated on the basis of the peak intensity of the ^{1}H signal due to $-\mathrm{Si}H$ or $-\mathrm{Si}Me$.

For $\mathbf{Me_2EtSiH}$, ^{1}H NMR (toluene-d_8, 400 MHz, 23 °C, selected data): δ 4.03 (m, 1H, $-\mathrm{Si}H$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (toluene-d_8, 100.6 MHz, 23 °C): δ 7.6 ($-\mathrm{SiMe_2}Et$), 5.9 ($-\mathrm{SiMe_2}Et$), −5.4 ($-\mathrm{Si}Me_2\mathrm{Et}$). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ DEPT 45 (toluene-d_8, 79 MHz, 23 °C): δ −11.2 ($-Si\mathrm{Me_2Et}$).

For $\mathbf{Et_2MeSiH}$, ^{1}H NMR (toluene-d_8, 400 MHz, 23 °C, selected data): δ 3.93 (m, 1H, $-\mathrm{Si}H$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (toluene-d_8, 100.6 MHz, 23 °C): δ 7.8 ($-\mathrm{Si}Et_2\mathrm{Me}$), 4.1 ($-\mathrm{Si}Et_2\mathrm{Me}$), −7.6 ($-\mathrm{SiEt_2}Me$). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ DEPT 45 (toluene-d_8, 79 MHz, 23 °C): δ −5.6 ($-Si\mathrm{Et_2Me}$).

For $\mathbf{Me_3SiH}$, ^{1}H NMR (toluene-d_8, 400 MHz, 23 °C, selected data): δ 4.13 (m, 1H, $-\mathrm{Si}H$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (toluene-d_8, 100.6 MHz, 23 °C): δ −3.1 ($-\mathrm{Si}Me_3$). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ DEPT 45 (toluene-d_8, 79 MHz, 23 °C): δ −16.4 ($-Si\mathrm{Me_3}$).

For $\mathbf{Et_3SiH}$, ^{1}H NMR (toluene-d_8, 400 MHz, 23 °C, selected data): δ 3.79 (m, 1H, $-\mathrm{Si}H$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (toluene-d_8, 100.6 MHz, 23 °C): δ 8.0 ($-\mathrm{Si}Et_3$), 2.3 ($-\mathrm{Si}Et_3$). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ DEPT 45 (toluene-d_8, 79 MHz, 23 °C): δ −0.1 ($-Si\mathrm{Et_3}$).

For $\mathbf{Me_2PhSiH}$, ^{1}H NMR (toluene-d_8, 400 MHz, 23 °C, selected data): δ 4.60 (m, 1H, $-\mathrm{Si}H$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (toluene-d_8, 100.6 MHz, 23 °C, selected): δ −4.1 ($-\mathrm{Si}Me_2\mathrm{Ph}$). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ DEPT 45 (toluene-d_8, 79 MHz, 23 °C): δ −17.2 ($-SiMe_2Ph$).

For $\mathbf{Ph_2MeSiH}$, ^{1}H NMR (toluene-d_8, 400 MHz, 23 °C, selected data): δ 5.09 (m, 1H, $-\mathrm{Si}H$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (toluene-d_8, 100.6 MHz, 23 °C, selected): δ −5.3 ($-\mathrm{SiPh_2}Me$). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ DEPT 45 (toluene-d_8, 79 MHz, 23 °C): δ −17.7 ($-Si\mathrm{Ph_2Me}$).

For $\mathbf{Me_2BzSiH}$, ^{1}H NMR ($\mathrm{C_6D_6}$, 400 MHz, 23 °C, selected data): δ 4.10 (m, 1H, $-\mathrm{Si}H$), 2.09 (m, 2H, $-\mathrm{SiMe_2}Bz$), 0.06 (s, 6H, $-\mathrm{Si}Me_2\mathrm{Bz}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$, 100.6 MHz, 23 °C, selected): δ 24.1 ($-\mathrm{SiMe_2}Bz$), −4.9 ($-\mathrm{Si}Me_2\mathrm{Bz}$). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ DEPT 45 ($\mathrm{C_6D_6}$, 79 MHz, 23 °C): δ −12.5 ($-Si\mathrm{Me_2Bz}$).

For $\mathbf{Bz_2MeSiH}$, ^{1}H NMR ($\mathrm{C_6D_6}$, 400 MHz, 23 °C, selected data): δ 4.10 (m, 1H, $-\mathrm{Si}H$), 2.09 (m, 4H, $-\mathrm{Si}Bz_2\mathrm{Me}$), −0.01 (s, 3H, $-\mathrm{SiBz_2}Me$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$, 100.6 MHz, 23 °C, selected): δ 22.3 ($-\mathrm{Si}Bz_2\mathrm{Me}$), −2.9 ($-\mathrm{SiBz_2}Me$). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ DEPT 45 ($\mathrm{C_6D_6}$, 79 MHz, 23 °C): δ −8.3 ($-Si\mathrm{Bz_2Me}$).

For **1,4-bis(dimethylsilyl)benzene**, ^{1}H NMR ($\mathrm{C_6D_6}$, 400 MHz, 23 °C, selected data): δ 4.61 (m, 1H, $-\mathrm{Si}H\mathrm{Me_2}-$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$, 100.6 MHz, 23 °C, selected): δ −4.1 ($-\mathrm{SiH}Me_2-$). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ DEPT 45 ($\mathrm{C_6D_6}$, 79 MHz, 23 °C): δ −17.4 ($-Si\mathrm{HMe_2}-$).

For $\mathbf{Me_2SiH\text{-}(1,4\text{-}phenyl)\text{-}SiMeH\text{-}(1,4\text{-}phenyl)\text{-}Me_2SiH}$, ^{1}H NMR ($\mathrm{C_6D_6}$, 400 MHz, 23 °C, selected data): δ 5.12 (m, 1H, $-\mathrm{SiMe}H-$), 4.61 (m, 1H, $-\mathrm{Si}H\mathrm{Me_2}-$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$, 100.6 MHz, 23 °C, selected): δ −4.2 ($-\mathrm{SiH}Me_2-$), −5.4 ($-\mathrm{Si}Me\mathrm{H}-$). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ DEPT 45 ($\mathrm{C_6D_6}$, 79 MHz, 23 °C): δ −17.3 ($-Si\mathrm{HMe_2}-$), −17.8 ($-Si\mathrm{MeH}-$).

General Procedure for the Catalytic Redistribution of $\mathrm{Me_2EtSiH}$ with 2 under 1 atm $\mathrm{H_2}$ at −20 °C. $\mathrm{Me_2EtSiH}$ (2.2 mmol, 110 equiv, 0.29 mL) was added to a solution of **2** (0.02 mmol, 16 mg, 0.9 mol %) in 0.4 mL of toluene-d_8 in a NMR tube with a screw cap at ∼−70 °C. $\mathrm{H_2}$ (1 atm) was purged through the solution of **2** and $\mathrm{Me_2EtSiH}$ at ∼−70 °C for tens of seconds. This NMR tube was quickly placed in the probe, which was precooled to −20 °C. The reaction progress was followed by ^{1}H NMR spectroscopy. The relative ratios of scrambling products were calculated on the basis of the peak intensity of the ^{1}H signal due to $-\mathrm{Si}H$.

General Procedure for the Reaction of 2 under 1 atm D_2, Followed by Addition of Me_2EtSiH. Et_3SiH (0.1 mmol, 5 equiv, 16 μL) was added to a solution of **2** (0.02 mmol, 16 mg) in 0.6 mL of C_6H_6 in a NMR tube with a screw cap. D_2 (1 atm) was purged through the solution of **2** and Et_3SiH at 23 °C for seconds. This mixture was allowed to stand at 23 °C. The progress was followed by ^2H NMR spectroscopy for 2 h, and then Me_2EtSiH (30 equiv) was added to the catalyst solution under D_2 (1 atm) at 23 °C. The relative ratios of scrambling products were calculated on the basis of the peak intensity of the ^2H signal due to $-SiD$.

General Procedure for the Reaction of 2 under 1 atm D_2. A solution of **2** (0.02 mmol, 16 mg) was added to 0.6 mL of toluene in a NMR tube with a screw cap. D_2 (1 atm) was purged through the solution of **2** at ∼−70 °C for tens of seconds. This NMR tube was quickly placed in the probe, which was precooled to −70 °C. The reaction progress was monitored by ^2H NMR spectroscopy at variable temperatures.

General Procedure for the Catalytic Redistribution of Me_2EtSiH with 2 under 1 atm H_2, Followed by Purging with Argon and Readdition of Me_2EtSiH at 23 °C. Me_2EtSiH (1.5 mmol, 75 equiv, 0.2 mL) was added to a solution of **2** (0.02 mmol, 16 mg, 1.3 mol %) in 0.4 mL of toluene-d_8 in a NMR tube with a screw cap. H_2 (1 atm) was purged through the solution of **2** and Me_2EtSiH at 23 °C for seconds. This mixture was allowed to stand at 23 °C for 4 min to achieve a complete scrambling and then was purged with argon at 23 °C for 5 min to remove residual H_2 in the NMR tube. Another portion of Me_2EtSiH (1.5 mmol, 75 equiv, 0.2 mL) was added into this reaction mixture. Finally, the reaction mixture was exposed to H_2 (1 atm) again for seconds at 23 °C, and the reaction progress was followed by ^1H NMR spectroscopy. The relative ratios of scrambling products were calculated on the basis of the peak intensity of the ^1H signal due to $-SiH$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra contained include ^1H, ^{13}C, and ^{29}Si NMR spectra of scrambling reactions; ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectra of complex **1**; a HSQC spectrum of complex **2**; and a ^2H NMR spectrum of the reaction mixture of **2** with Et_3SiD. Details of the DFT calculation of the energy barrier for 1,3-methyl migration in complex **3** as a model compound for complex **B**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: mbrookhart@unc.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National Science Foundation (CHE 1010170) for support of this work and Prof. Don Tilley for useful comments. B. G. Kim thanks Gyeongsang National University for support of his sabbatical leave at the University of North Carolina at Chapel Hill.

■ REFERENCES

(1) Tilley, T. D. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; Chapters 9 and 10; pp 245 and 309.

(2) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 24, p 1415.

(3) Tilley, T. D. *Comments Inorg. Chem.* **1990**, *10*, 37.

(4) Pannell, K. H.; Sharma, H. K. *Chem. Rev.* **1995**, *95*, 1351.

(5) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175.

(6) Corey, J. Y. *Chem. Rev.* **2011**, *111*, 863.

(7) Eisen, M. S. In *The Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2; Chapter 35.

(8) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley-Interscience: New York, 2000.

(9) Okazaki, M.; Tobita, H.; Ogino, H. *J. Chem. Soc., Dalton Trans.* **2003**, 493.

(10) Ogino, H. *Chem. Rec.* **2002**, *2*, 291.

(11) Waterman, R.; Hayes, P. G.; Tilley, T. D. *Acc. Chem. Res.* **2007**, *40*, 712.

(12) Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213.

(13) Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1988**, 1411.

(14) Okinoshima, H.; Yamamota, K.; Kumada, M. *J. Organomet. Chem.* **1971**, *27*, C31.

(15) Hashimoto, H.; Tobita, H.; Ogino, H. *J. Organomet. Chem.* **1995**, *499*, 205.

(16) Radu, N. S.; Hollander, F. J.; Tilley, T. D.; Rheingold, A. L. *Chem. Commun.* **1996**, *21*, 2459.

(17) Yamamoto, K.; Okinoshima, H.; Kumada, M. *J. Organomet. Chem.* **1971**, *27*, C31.

(18) Seyferth, D.; Shannon, M. L.; Vick, S. C.; Lim, T. F. O. *Organometallics* **1985**, *4*, 57.

(19) Ishikawa, M.; Matsuzawa, S.; Higuchi, T.; Kamitori, S.; Hirotsu, K. *Organometallics* **1985**, *4*, 2040.

(20) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9263.

(21) Kerber, R. C.; Pakkanen, T. *Inorg. Chim. Acta* **1979**, *37*, 61.

(22) Lemanski, M. F.; Schram, E. P. *Inorg. Chem.* **1976**, *15*, 1489.

(23) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3879.

(24) Pannell, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. *Organometallics* **1986**, *5*, 1056.

(25) Carlson, C. W.; West, R. *Organometallics* **1983**, *2*, 1801.

(26) Yamamoto, K.; Pkinoshima, H.; Kumada, M. *J. Organomet. Chem.* **1970**, *23*, C7.

(27) Ojima, I.; Inaba, S.-I.; Kogure, T.; Nagai, Y. *J. Organomet. Chem.* **1973**, *55*, C7.

(28) Brown-Wensley, K. A. *Organometallics* **1987**, *6*, 1590.

(29) Corey, J. Y.; Chang, L. S.; Corey, E. R. *Organometallics* **1987**, *6*, 1595.

(30) Aitken, C.; Harrod, J. F.; Gill, U. S. *Can. J. Chem.* **1987**, *65*, 1804.

(31) Woo, H. G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 8043.

(32) Woo, H. G.; Walzer, J. F.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 7047.

(33) Pannell, K. H.; Burn, M. C.; Sharma, H.; Jones, K.; Sharma, S. *Organometallics* **1994**, *13*, 1075.

(34) Jones, K. L.; Pannell, K. H. *J. Am. Chem. Soc.* **1993**, *115*, 11336.

(35) Pannell, K. H.; Wang, L. J.; Rozell, J. M. *Organometallics* **1989**, *8*, 550.

(36) Pannell, K. H.; Rozell, J. M. Jr.; Hernandez, C. *J. Am. Chem. Soc.* **1989**, *111*, 4482.

(37) Tobita, H.; Ueno, K.; Ogino, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2797.

(38) Ueno, K.; Tobita, H.; Ogino, H. *Chem. Lett.* **1990**, 369.

(39) Haynes, A.; George, M. W.; Haward, M. T.; Poliakoff, M.; Turner, J. J.; Boag, N. M.; Green, M. *J. Am. Chem. Soc.* **1991**, *113*, 2011.

(40) Straus, D. A; Grumbine, S. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1990**, *112*, 7801.

(41) Grumbine, S. D.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 358.

(42) Grumbine, S. D.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 7884.

(43) Grumbine, S. D.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 5495.

(44) Mitchell, G. P.; Tilley, T. D. *J. Am. Chem. Soc.* **1997**, *119*, 11236.

(45) Grumbine, S. K.; Mitchell, G. P.; Straus, D. A.; Tilley, T. D.; Rheingold, A. L. *Organometallics* **1998**, *17*, 5607.

(46) Wanandi, P. W.; Glaser, P. B.; Tilley, T. D. *J. Am. Chem. Soc.* **2000**, *122*, 972.

(47) Peters, J. C.; Feldman, J. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1999**, *121*, 9871.

(48) Mork, B. V.; Tilley, T. D. *J. Am. Chem. Soc.* **2001**, *123*, 9702.

(49) Mitchell, G. P.; Tilley, T. D. *Angew. Chem., Int. Ed.* **1998**, *37*, 2524.

(50) Feldman, J. D.; Mitchell, G. P.; Nolte, J. O.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 11184.

(51) Klei, S. R.; Tilley, T. D.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 1816.

(52) Grumbine, S. K.; Tilley, T. D. *J. Am. Chem. Soc.* **1994**, *116*, 6951.

(53) Gavenonis, J.; Tilley, T. D. *Organometallics* **2004**, *23*, 31.

(54) Okazaki, M.; Tobita, H.; Ogino, H. *Organometallics* **1996**, *15*, 2790.

(55) Okazaki, M.; Tobita, H.; Ogino, H. *Chem. Lett.* **1997**, 437.

(56) Tobita, H.; Wada, H.; Ueno, K.; Ogino, H. *Organometallics* **1994**, *13*, 2545.

(57) Ueno, K.; Ogino, H. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1955.

(58) Tobita, H.; Ueno, K.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1990**, *112*, 3415.

(59) Takeuchi, T.; Tobita, H.; Ogino, H. *Organometallics* **1991**, *10*, 835.

(60) Ueno, K.; Seki, S.; Ogino, H. *Chem. Lett.* **1993**, 2159.

(61) Tamao, K.; Sun, G.-R.; Kawachi, A. *J. Am. Chem. Soc.* **1995**, *117*, 8043.

(62) The iridium hydride signal at δ −12.8 splits into several singlets, which are assigned to analogues of complex **2**, as explained later in the manuscript. The species observed at δ −5.5 and −7.5 convert to analogues of **2**, the thermodynamic product(s), upon heating.

(63) Calimano, E.; Tilley, T. D. *Dalton Trans.* **2010**, *39*, 9250.

(64) Calimano, E.; Tilley, T. D. *J. Am. Chem. Soc.* **2009**, *131*, 11161.

(65) Tilley reported a number of metal silylene complexes, in which electrophilicity character at silicon that promotes alkene binding has been suggested on the basis of the DFT calculation.

(66) Hayes, P. G.; Beddie, C.; Hall, M. B.; Waterman, R.; Tilley, T. D. *J. Am. Chem. Soc.* **2006**, *128*, 428.

(67) McBee, J. L.; Escalada, J.; Tilley, T. D. *J. Am. Chem. Soc.* **2009**, *131*, 12703.

(68) Ueno, K.; Hamashima, N.; Shimoi, M.; Ogino, H. *Organometallics* **1991**, *10*, 959.

(69) Ogino, H.; Tobita, H. *Adv. Organomet. Chem.* **1998**, *42*, 223.

(70) Li, Y.; Kawakami, Y. *Macromolecules* **1999**, *32*, 3540.

(71) Li, Y.; Kawakami, Y. *Macromolecules* **1999**, *32*, 6871.

(72) To exclude the possibility of the scrambling reaction catalyzed by iridium nanoparticles, we have conducted a redistribution of Me_2EtSiH with **2** (1.3 mol%) under H_2 (1 atm) in the presence of one drop of Hg at 23 °C. Complete scrambling is achieved in 0.1 h. An Ir−H signal (singlet) is observed at δ −12.93 for **2**, but no other Ir−H signals over the range of δ 0 to −30 are seen. This suggests a homogeneous catalytic redistribution of trialkyl silanes.

(73) In an attempt to build up the silyl(silylene) intermediate, the reaction of **2** under H_2 (1 atm) has been conducted in toluene-d_8 at −25 °C for 12 h; however, the solution turns into a heterogeneous solution with intractable precipitates.

(74) If **2** plus H_2 were to be in equilibrium with traces of the active species, then the back reaction (active species forming H_2 plus **2**) would seem to be faster than formation of the active species. This seems inconsistent with the observation that the active species can be formed at low temperature, but purging the solution to remove H_2 does not result in significant depletion of the active species.

(75) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision A.1*; Gaussian, Inc.: Wallingford, CT, 2009.

(76) Yang, J.; White, P. S.; Schauer, S. K.; Brookhart, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 4141.

(77) Paul, A.; Musgrave, C. B. *Angew. Chem., Int. Ed.* **2007**, *119*, 8301.

(78) Li, S.; Hall, M. B. *Organometallics* **2001**, *20*, 2153.

(79) Calimano, E.; Tilley, T. D. *J. Am. Chem. Soc.* **2008**, *130*, 9226.

(80) Liu, T.; Xia, B. H.; Zhou, X.; Zhang, H. X.; Pan, Q. J.; Gao, J. S. *Organometallics* **2007**, *26*, 143.

(81) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *119*, 215.

(82) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *87*, 270.

(83) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.

(84) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(85) Mennucci, B.; Tomasi, J.; Cammi, R.; Cheeseman, J. R.; Frisch, M. J.; Devlin, F. J.; Gabriel, S.; Stephens, P. J. *J. Phys. Chem. A* **2002**, *106*, 6102.

(86) Alaimo, P. J.; Peters, D. W.; Arnold, J.; Bergman, R. G. *J. Chem. Educ.* **2001**, *78*, 64.

(87) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(88) Woo, H. G.; Walzer, J. F.; Tilley, T. D. *Macromolecules* **1991**, *24*, 6863.