

Donor-Promoted 1,2-Hydrogen Migration from Silicon to a Saturated Ruthenium Center and Access to Silaoxiranyl and Silaiminyl Complexes

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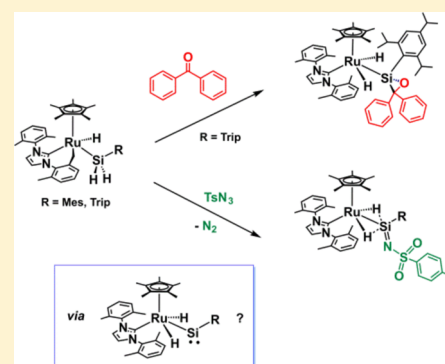
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S Supporting Information

ABSTRACT: Masked silylene complexes $\text{Cp}^*(\text{IXy-H})(\text{H})\text{RuSiH}_2\text{R}$ ($\text{R} = \text{Mes}$ (**3**) and Trip (**4**); $\text{IXy} = 1,3\text{-bis}(2,6\text{-dimethylphenyl})\text{imidazol-2-ylidene}$; “ IXy-H ” is the deprotonated form of IXy) exhibit metallocarbene-like ($L_n\text{M}-\text{Si}-\text{R}$) reactivity, as observed in reactions of nonenolizable ketones, enones, and tosyl azides, to give unprecedented silaoxiranyl, oxasilacyclopentenyl, and silaiminyl complexes, respectively. Notably, these silicon-containing complexes are derived from the primary silanes MesSiH_3 and TripSiH_3 via activation of all three $\text{Si}-\text{H}$ bonds. DFT calculations suggest that the mechanism of formation for the silaoxiranyl complex $\text{Cp}^*(\text{IXy})(\text{H})_2\text{Ru}-\text{Si}(\text{OCPh}_2)\text{Trip}$ (**6**) involves coordination of benzophenone to a silylene silicon atom, followed by a single-electron transfer in which Si-bonded, non-innocent benzophenone accepts an electron from the reactive, electron-rich ruthenium center. Importantly, this electron transfer promotes an unusual 1,2-hydrogen migration to the resulting, more electron-deficient ruthenium center via a diradicaloid transition state.



INTRODUCTION

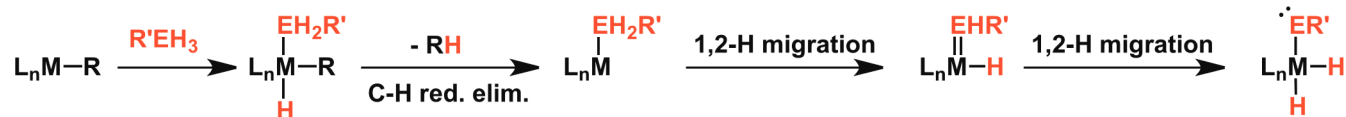
Transition metal–silicon chemistry has attracted considerable interest over many years, in the context of fundamental research on structure, bonding, and reactivity and with respect to applications in catalysis.^{1–4} Research in this area has identified a rich array of fundamental chemical transformations, involving several types of metal–silicon bonding interactions in key catalytic intermediates. Interesting species of the latter type involve unsaturated silicon fragments as ligands and metal–silicon multiple bonding. Prototypical are metal silylene complexes, $L_n\text{MSiRR}'$, that formally possess a metal–silicon double bond and are intermediates in a number of metal-catalyzed transformations involving organosilicon compounds.^{2–4} Several synthetic routes to silylene complexes have been established in recent years, which have greatly accelerated the discovery of new chemical transformations involving such species.^{3,4a} Of particular relevance to catalysis is a process that involves conversion of a silane substrate via activation of two $\text{Si}-\text{H}$ bonds, first by oxidative addition and then by 1,2-hydrogen migration, to produce a hydrido-silylene complex.^{4,5} An early example of this reactivity was identified in clean formation of the neutral silylene complex $[\text{PhB}(\text{CH}_2\text{PPh}_2)_3](\text{H})_2\text{Ir}=\text{SiMe}_2$ (and cyclooctene) by reaction of $[\text{PhB}(\text{CH}_2\text{PPh}_2)_3]\text{Ir}(\text{H})(\eta^3\text{-C}_8\text{H}_{13})$ with Me_2SiH_2 at 95 °C.^{4b}

Related metal–silicon species with a greater degree of unsaturation, referred to as silylyne complexes, formally contain a metal–silicon triple bond. This laboratory has reported the cationic silylyne complexes $[\text{Cp}^*(\text{dppe})(\text{H})\text{Mo}\equiv\text{SiMe}_3]^+$ and $[\text{Cp}^*(\text{Pr}_3\text{P})(\text{H})\text{Os}\equiv\text{SiTrip}]^+$ through anion abstraction chemistry, and the latter species engages in a number of cycloaddition reactions.^{6,7} Also, Filippou and co-workers have used abstraction methods to obtain $\text{Cp}(\text{CO})_2\text{Mo}\equiv\text{Si}(2,6\text{-Trip}_2\text{C}_6\text{H}_3)^8$ and $[\text{Cp}^*(\text{CO})_2\text{Cr}\equiv\text{Si}(\text{SIPr})]^+$ ($\text{SIPr} = 1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazolidin-2-ylidene}$).⁹ Although little is known about the chemistry of silylyne complexes, they appear to be potentially reactive species; however, they have so far not been available via the simple, direct reaction of a silane with a transition-metal complex.

Closely related to silylyne complexes are metallocsilylenes, $L_n\text{M}-\text{Si}-\text{R}$, which are formally differentiated from silylynes by possessing only a metal–silicon single bond and a lone pair localized on the divalent silicon center. Indeed, these two structure types may be interconverted by changes in the electron count at the metal, as demonstrated for the only isolated example of a metallocsilylene, $[\text{Cp}^*(\text{CO})_3\text{Cr}-\text{Si}(\text{SIPr})]^+$, prepared by addition of CO to the corresponding silylyne complex $[\text{Cp}^*(\text{CO})_2\text{Cr}\equiv\text{Si}(\text{SIPr})]^+$.⁹ Despite the

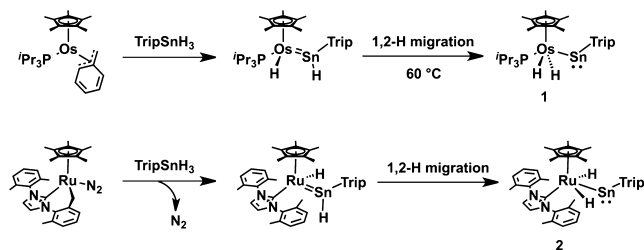
Received: May 29, 2015

Published: July 2, 2015

Scheme 1. Possible and Generalized Pathway for R'EH₃ Activation (E = Group 14 Element)

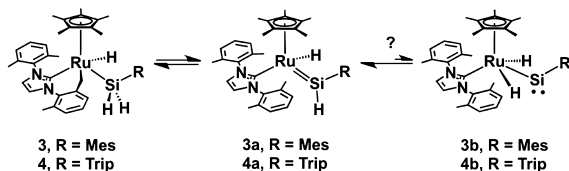
paucity of metallocenes, heavier group 14 analogs, the metallo-ylenes L_nM-E-R ($E = Ge, Sn, Pb$),¹⁰ have been known for some years since for these elements, appropriate divalent synthons of the type $R-E-X$ are readily available.

Recently, a new synthetic route to metallo-stannylenes was described, based on activations of all three $Sn-H$ bonds of the primary stannane $TripSnH_3$, to generate osmium (**1**)^{11a} and ruthenium (**2**)^{11b} examples. As shown in Schemes 1 and 2, this

Scheme 2. Formation of Metallostannylenes **1** and **2**

reaction sequence features an unusual type of 1,2-hydrogen migration in an electronically saturated stannylene complex. Significantly, this type of transformation provides synthetic access to metallo-ylene species from simple group 14-based compounds and potentially enables catalytic transformations that feature metallo-ylene species as intermediates. Thus, it is of interest to explore the generality of this route to metallo-ylenes, and herein we describe related chemistry involving a metal-silicon system. In particular, the masked silylene complexes $Cp^*(IXy-H)(H)RuSiH_2R$ ($R = Mes$ (**3**), $Trip$ (**4**); $IXy-H$ is the deprotonated form of IXy)¹² exhibit metallocene character in reactions with a variety of organic substrates to give unprecedented metallo-silaoxiranes, -silaoxacyclopentenes, and -silaimines. These new compounds are striking in that they are derived from metal-mediated transformations of primary silanes ($MesSiH_3$ and $TripSiH_3$) with various substrates involving three $Si-H$ bond activations (*vide infra*).

As described in an earlier report, complex **4** reacts with an enolizable ketone (e.g., 4-bromoacetophenone) by way of isomerization to the silylene hydride form (**4a**, Scheme 3).¹² Thus, treatment of **4** with the deuterated acetophenone $PhCOCD_3$ exclusively afforded the deuterated silyl enol ether complex $Cp^*(IXy)(H)(D)RuSi[OC(=CD_2)Ph]Trip$, indicating that a $C-H(D)$ bond was activated by addition across the $Ru=Si$ bond of the more reactive isomer **4a**, presumably via a silylene-ketone adduct.¹²

Scheme 3. Possible Formation of **3b** or **4b** via α -Hydrogen Migrations

RESULTS AND DISCUSSION

Reactions of complexes **3** and **4** with nonenolizable ketones did not result in the formation of hydrosilylation products¹³ but instead gave the cycloaddition products **5** and **6** (Scheme 4). Thus, the reaction of **3** with 1 equiv of α,α,α -trifluoroacetophenone in benzene at 24 °C over 6 h resulted in formation of the silaoxirane **5** in 49% isolated yield as a pale yellow solid (quantitative yield in benzene- d_6 solution by ¹H NMR spectroscopy). The reaction of **4** with 1 equiv of benzophenone under the same conditions was significantly slower, requiring 72 h for complete formation of **6** (in benzene- d_6), isolated in 63% yield. The ¹H NMR spectra of **5** and **6** indicate C_1 symmetry for these complexes, each of which possesses chemically inequivalent hydrides ($\delta = -9.61$ and -9.81 for **5**; -8.97 and -9.71 for **6**) as a consequence of the chiral silicon centers. No silicon satellites were detected for the hydride resonances of **5** and **6** via ²⁹Si-filtered ¹H NMR experiments, suggesting the absence of significant interactions between the hydride ligands and the silicon centers. The ²⁹Si resonances at 7.9 ppm for **5** and -9.3 ppm for **6** are downfield-shifted relative to those reported for silaoxiranes with pentacoordinate silicon centers (ca. -100 ppm).^{14a-c} The molecular structures of **5** and **6** (Figure 1) clearly reveal that the three-membered silaoxirane rings are bound to Ru, with $Ru-Si$ bond distances of 2.298(2) and 2.341(1) Å, respectively. The hydride ligands were all located in the Fourier maps to give $Ru-H$ bond lengths of ~ 1.5 Å and average $Ru-H\cdots Si$ distances of about 2.0 Å for both **5** and **6**. Otherwise, the bond lengths and angles within the silaoxirane rings of **5** and **6** are comparable to those reported for nonmetal-containing silaoxiranes.¹⁴

Well-established routes to silaoxiranes involve addition of a transient or isolated silylene to an organic carbonyl compound.¹⁴ For example, Ando et al. prepared the first isolated silaoxirane by reaction of a photochemically generated silylene $Mes_2Si:$ with the bulky ketone 1,1,3,3-tetramethyl-2-indanone.^{14a} Recent access to a range of isolated silylenes, including some that are base-stabilized, has provided routes to additional silaoxiranes.^{14b-d} For example, the internally base-stabilized silylene $PhC(N^tBu)_2SiCl$,^{14b,d} with three-coordinate silicon, and the dichlorosilylene carbene adduct $IPrSiCl_2$ ($IPr = 1,3$ -bis(2,6-diisopropylphenyl)imidazol-2-ylidene)^{14b} react with carbonyl compounds to produce silaoxiranes. Note that silaoxiranes derived from stable base-stabilized silylenes possess five-coordinate silicon centers, and this is likely responsible for their distinctly upfield ²⁹Si resonances.

It therefore seemed that complexes **5** and **6**, which represent the first examples of transition-metal-stabilized silaoxiranes, might form via trapping of metallocene isomers of **3** and **4** (**3b** and **4b**, respectively) by the ketone. In principle, these metallocenes could exist in equilibrium with the corresponding silyl (**3**, **4**) and silylene (**3a**, **4a**) isomers (Scheme 3), especially given the recent precedent involving an analogous ruthenostannylene (**2**), which formed by an unusual type of migration in the isomeric stannylene complex (Scheme 2). However, the formation of a divalent silicon species should be much less favorable, and it was therefore of interest to

Scheme 4. Reactivity of Complexes 3 and 4 with Organic Substrates

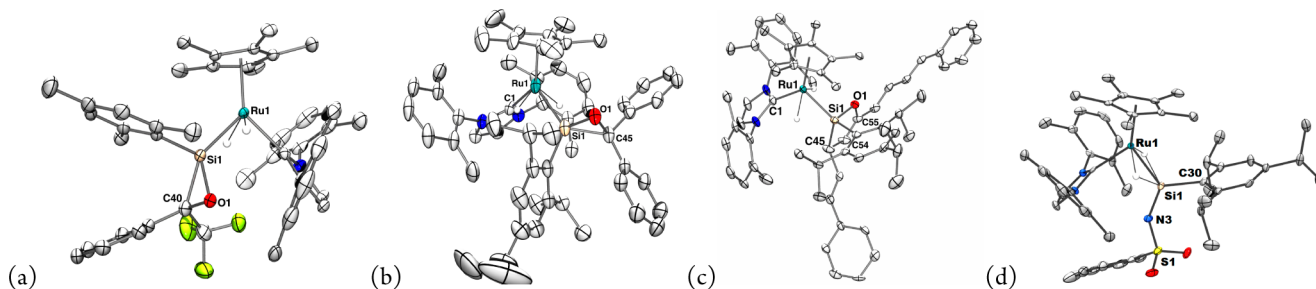
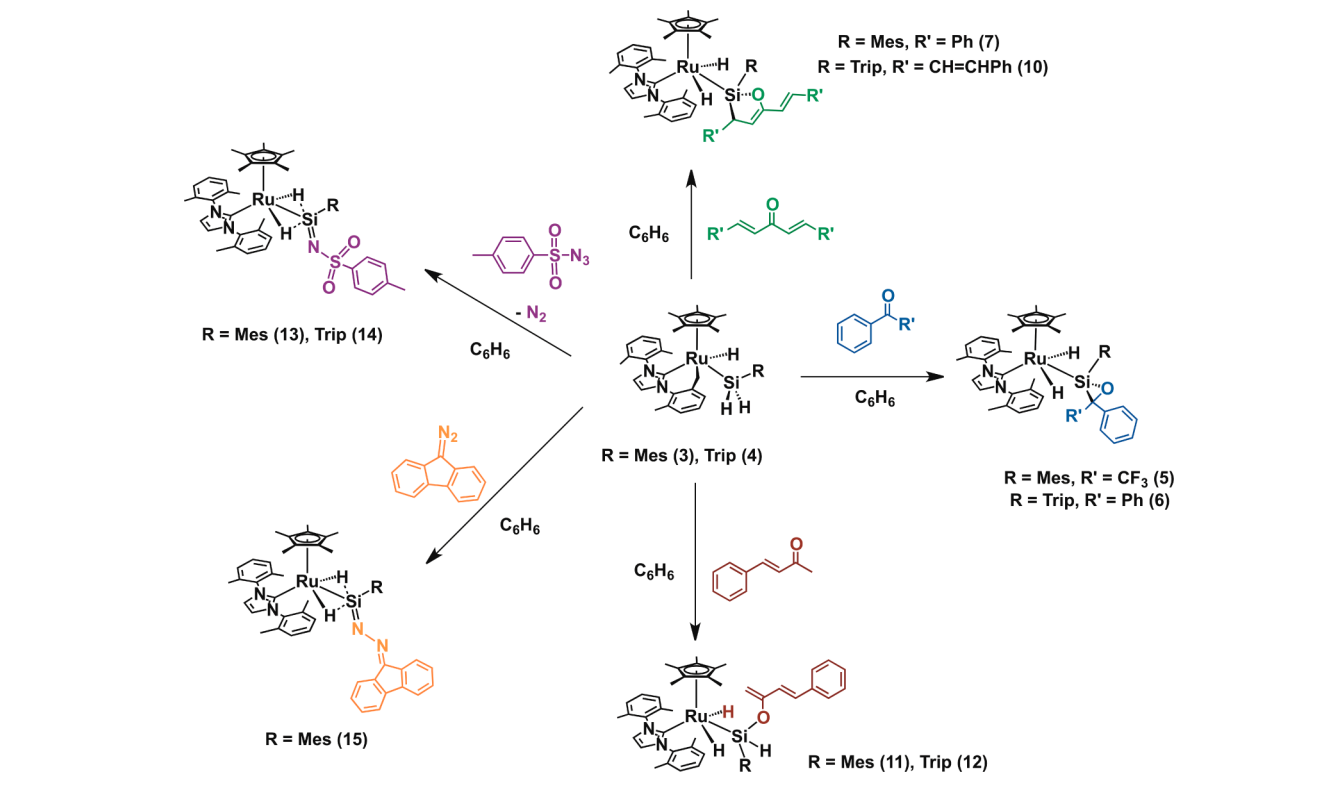
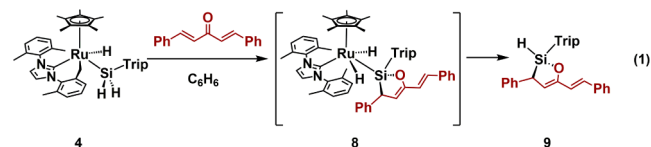


Figure 1. Molecular structure of 5 (a), 6 (b), 10 (c), and 14 (d) displaying thermal ellipsoids at the 50% probability level. Selected H atoms have been omitted for clarity.

investigate the mechanism by which 5 and 6 are generated. To probe electronic effects in this transformation, reaction rates were determined by monitoring reactions of 4 with a variety of 4,4'-substituted benzophenones ($p\text{-XC}_6\text{H}_4$)₂CO (X = H, Me, Br and Cl) by ¹H NMR spectroscopy. First, experiments under pseudo-first-order reaction conditions with various concentrations of benzophenone (0.19–1.12 M) and 0.019 M of 4 indicate first-order dependence on the concentrations of both benzophenone and 4. Moreover, more electron-withdrawing Br and Cl groups greatly enhance the reaction rate, as exemplified by the reaction of 4,4'-dichlorobenzophenone with 4 (to give 6-Cl₂), which was complete within 4 h.

Further reactivity studies were designed to investigate the possible trapping of metallocylenes in reactions of 3 and 4. For example, α,β -unsaturated enones are known to trap silylenes to give cycloaddition products, namely oxasilacyclopentenes.¹⁵ In fact, treatment of 3 with 1 equiv of dibenzylideneacetone (dba) in benzene at 24 °C afforded complex 7 as an off-white solid in 46% yield (Scheme 4). In addition, the clean formation of complex 8 was observed from the reaction of 4 with 1 equiv of dba in benzene-*d*₆ (by ¹H NMR spectroscopy). While isolation

of 8 was unsuccessful, compound 9 was obtained upon attempted crystallization of 8 from pentane at –30 °C. This compound was characterized by X-ray crystallography as the oxasilacyclopentene shown in eq 1 (see the Supporting

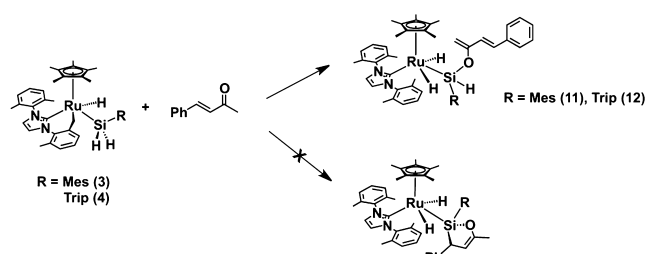


Information (SI)), suggesting that reductive elimination from an intermediate ruthenium complex (8) had occurred. Similarly, complex 10 was synthesized from dicinnamalacetone (1 equiv) in 58% yield as an orange powder (Scheme 4), and X-ray crystallography unambiguously confirmed the molecular structure of 10 with an oxasilacyclopentene ring bound to the Cp*(IXy)Ru(H)₂ fragment, with a Ru–Si bond distance of 2.349(1) Å (Figure 1c). Complexes 7 and 10 both exhibit two hydride resonances (–10.26 and –10.53 ppm for 7; –10.61 and –10.89 ppm for 10) with no observable silicon satellites in

the ^1H NMR spectra (benzene- d_6) and ^{29}Si resonances at 26.7 (for **7**) and 68.9 (for **10**) ppm. For comparison, the ruthenostannylene (**2**) exhibits analogous reactivity toward *E*-1,3-diphenyl-2-propen-1-one and forms the cycloaddition product $\text{Cp}^*(\text{IXy})(\text{H})_2\text{RuSn}(\kappa^2\text{-O,C-OCPhCHCHPh})\text{Trip}$.¹⁶ Taken together, this reactivity suggests that metallocsilylenes **3b** and **4b** (Scheme 4) might be intermediates in the formation of cycloaddition products **7** and **10**.

Additionally, complexes **11** and **12** were obtained in 97 and 77% yields, respectively, by treatment of **3** or **4** with 1 equiv of benzylideneacetone in benzene at 24 °C (Scheme 4). The ^1H NMR spectra of **11** and **12** both exhibit one Si–H resonance ($\delta = 6.49$ for **11** and 6.45 for **12**), resonances for two vinylic hydrogens located between δ 4 to 5 ppm, and two Ru–H signals resonating at about -10 ppm, indicating that **11** and **12** are enolate derivatives resulting from formal addition of the ketone methyl group across the $\text{Ru}=\text{Si}$ bonds of the silylene isomers of **3** and **4**. These reactions are analogous to that of masked silylene **4** toward acetophenone, in which the C–H bond activation occurred, presumably via a silylene-ketone adduct.¹² Thus, enolizable 1,3-enones appear to preferentially react to form enolates, rather than by cycloaddition to give five-membered silaoxacyclopentene complexes (Scheme 5).

Scheme 5. Exclusive Formation of **11** and **12** Rather than Cycloaddition Products



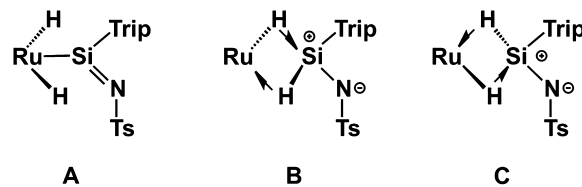
As described above, both **3** and **4** exhibit metallocsilylene-like properties upon treatment with nonenolizable ketones. This raised the possibility of utilizing the silylene-like reactivity of a putative $\text{M}-\text{Si}-\text{R}$ intermediate in the synthesis of novel ligands possessing silicon–heteroatom multiple bonds, as in a metallocsilimine complex ($\text{M}-\text{Si}(\text{R})=\text{NR}'$). Stable, base-free silimines were first isolated independently by Wiberg^{17a} and Klingebiel^{17b} using a salt-elimination strategy, and subsequently silimines were generated in reactions of stable silylenes with bulky azides.^{17c–i} With the goal of kinetically stabilizing silimines with steric protection, complexes **3** and **4** were treated with bulky azides, such as 2,6-($\text{Pr}_2\text{C}_6\text{H}_3$) N_3 and adamantyl azide, but unfortunately these reactions gave only complex mixtures that resisted purification. Due to the significant electronegativity difference between nitrogen and silicon, a $\text{Si}=\text{N}$ bond is expected to be highly polarized toward the nitrogen atom ($\text{Si}^{\delta+}-\text{N}^{\delta-}$) and therefore stabilized by electron-withdrawing groups at the nitrogen atom. Indeed, the synthesis of metallocsilimines $\text{Cp}^*(\text{IXy})\text{Ru}(\mu\text{-H})_2\text{Si}(\text{NTs})\text{R}$ (**13**, $\text{R} = \text{Mes}$; **14**, $\text{R} = \text{Trip}$; Scheme 4) was achieved by treatment of **3** or **4** with 1 equiv of tosyl azide (TsN_3 , *p*- $\text{MeC}_6\text{H}_4\text{SO}_2\text{N}_3$) in benzene at 24 °C, and these reactions were complete within 10 min. Complexes **13** and **14** were isolated as off-white solids in 95 and 77% yields, respectively. Additional information about the formation of **14** was obtained from variable temperature NMR experiments. The generation of

complex **14** occurred at -30 °C from a toluene- d_8 mixture of **4** and 1 equiv of TsN_3 , suggesting a relatively low barrier for this reaction.

Complexes **13** and **14** possess C_s symmetry as indicated by their ^1H NMR spectra; both exhibit a single resonance corresponding to two Ru–H hydrides at -10.50 ($J_{\text{SiH}} = 51.0$ Hz) and -10.47 ($J_{\text{SiH}} = 54.1$ Hz) ppm, respectively. Rather downfield-shifted ^{29}Si resonances (154 ppm for **13** and 145 ppm for **14**) are observed relative to those reported for silimines ($^{29}\text{Si} \sim -100$ to -20 ppm).¹⁷ The X-ray structure of **14**, shown in Figure 1d, reveals a planar environment about the sp^2 silicon center (summation of bond angles at Si = $360.1(0)^\circ$), and bond lengths to silicon of 2.266(3) (Ru–Si) and 1.634(8) (Si–N) Å that are slightly longer than those of reported nonmetal-containing silimines (1.56–1.60 Å).¹⁷ For complexes **13** and **14**, the electron-withdrawing Ts group appears to stabilize the electron-rich nitrogen atom, while the $\text{Cp}^*(\text{IXy})(\text{H})_2\text{Ru}$ fragment donates electron density from two Ru–H bonds to the electropositive silicon ($\text{Si}^{\delta+}$), as evidenced by close $\text{Si}\cdots\text{H}$ contacts (1.71(8), 2.1(1) Å) and relatively large J_{SiH} coupling constants of ca. 50 Hz.

An NBO analysis carried out for the DFT-optimized structure of **14** (see SI), which is very similar to the solid-state structure, indicates that the $\text{Ru}(\mu\text{-H})_2\text{Si}$ moiety possesses two three-center, two-electron bonds for which the Ru–H bond order of 0.5 is larger than that of the Si–H bond (0.32), and the Ru–Si bonding interaction is relatively small (bond order = 0.09). This supports a bonding picture for the $\text{Ru}(\mu\text{-H})_2\text{Si}$ moiety that is similar to that of diborane. There are three lone pairs associated with the ruthenium center in the $\text{Cp}^*(\text{IXy})\text{Ru}(\text{H})$ unit, suggesting a formal oxidation state of Ru(II). In the remaining $\text{SiH}(\text{NTs})\text{Trip}$ fragment, the silicon atom has a high charge of +1.6, attributed to a highly polarized Si–N bond and a weak Si–H bond. The electron-deficient silicon is slightly stabilized by one of two lone pairs on the nitrogen atom, which possesses a charge of -1.44 ; the other lone pair on N donates into the σ^*_{SO} orbitals of the Ts group. The slight donation from a lone pair on nitrogen to silicon would indicate some $\text{Si}=\text{N}$ bond character, as shown in structure A of Scheme 6. However, valence bond structures B

Scheme 6. Selected Representations of the Bonding in the $\text{Ru}(\mu\text{-H})_2\text{Si}(\text{NTs})\text{Trip}$ Portion of Complex **14**



and C better represent **14**, as evidenced by two strong Ru–H–Si interactions, the $\text{Si}^{\delta+}-\text{N}^{\delta-}$ polarity, the presence of two lone pairs on nitrogen, and the absence of a Si–N π -bond. Note that the recently reported ruthenostannimine $\text{Cp}^*(\text{IXy})(\text{H})_2\text{RuSn}(\kappa^2\text{-N,O-NSO}_2\text{C}_6\text{H}_4\text{Me})\text{Trip}$ features coordination of the oxygen atom of the Ts group to stabilize the electron deficient $\text{Sn}=\text{N}$ moiety. This is probably due to less effective Ru–H bond donation to the tin center owing to a longer Ru–Sn distance.¹⁶

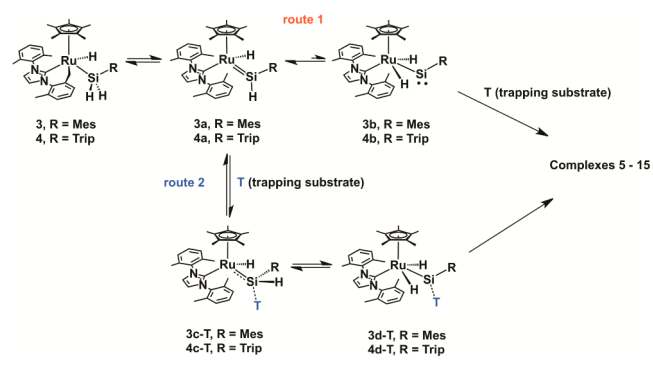
The successful isolation of ruthenosilimines **13** and **14** motivated efforts to generate analogous metallocsilene derivatives ($\text{M}-\text{Si}(\text{R})=\text{CR}_2$). An attempt to prepare a ruthenosilene

by treatment of **3** with 1 equiv of the carbene transfer reagent 9-diazafluorene (N_2Flu) in benzene at 24 °C instead gave $Cp^*(IXy)(H)_2RuSi(N_2Flu)Mes$ (**15**; see Scheme 4) as an orange powder in 88% yield. A single hydride resonance was found in the 1H NMR spectrum of **15** ($\delta = -9.84$; $J_{SiH} = 38.2$ Hz), suggesting C_s symmetry for complex **15**. The large J_{SiH} coupling constant for **15** might be associated with stabilization of the polarized Si–N bond by two Ru–H bonds, as discussed above for complexes **13** and **14**. Dinitrogen elimination from complex **15** was not observed in benzene- d_6 after 24 h at 70 °C or upon irradiation (Hg-xenon lamp) at 60 °C over 6 h. Note that Sen et al. reported analogous reactivity of the silylene $PhC(N^tBu)_2SiCl$ with trimethylsilyldiazomethane, $N_2CH(SiMe_3)$, to give the dimer $\{PhC(N^tBu)_2Si(Cl)[N_2CH(SiMe_3)]\}_2$.¹⁸ This presumably involves formation of the monomeric intermediate $PhC(N^tBu)_2Si(Cl)[N_2CH(SiMe_3)]$ (structurally similar to **15**) which dimerizes due to the polarized nature of the Si–N bond and the absence of any bulky substituents at the α -nitrogen atom. Attempts to grow high-quality single crystals have been unsuccessful; however, a single-crystal diffraction study on a poorly diffracting crystal of **15** provided a low-resolution structure consistent with the formulation established by spectroscopy (see Figure S4 in SI).

The metallocosilylene-like reactivity of **3** and **4** is reminiscent of the thermodynamically favored formation of ruthenostannylene $Cp^*(IXy)(H)_2Ru-Sn-Trip$ (**2**) via a low-barrier α -H migration in the electronically saturated Ru stannylene complex $Cp^*(IXy)(H)Ru=SnHTrip$, which is mainly driven by replacement of the Sn–H bond with a stronger Ru–H bond. This migration may be viewed as a pivoting of the stannylene ligand, by way of Ru donation of a lone pair into an empty 3p orbital of Sn, to eventually position the Sn–H bond for addition to the Ru center.^{11b} However, theoretical results suggest that formation of metallocosilylenes **3b** and **4b** from **3a** and **4a** is unfavorable; the reaction is endoergic (~ 16 kcal mol⁻¹), as Si–H bonds are significantly stronger than Sn–H bonds.¹⁹ This trend is consistent with the successful isolation of complex **2**, while **3b** and **4b** have eluded isolation. In addition, the Ru=Si bond is significantly stronger than the Ru=Sn bond, and thus cleavage of the Ru=Si bond must occur at a relatively high energy cost. The role of the metal–element bond strength in such migrations is also apparent in comparison of the ruthenium stannylene complex **2** (Scheme 1), which undergoes a spontaneous and unimolecular isomerization to the corresponding metallocosilylene, and the osmium stannylene $Cp^*(Pr_3P)(H)Os=SnHTrip$, which requires heat, light or catalysis by a radical species for transformation to the metallocosilylene $Cp^*(Pr_3P)(H)_2Os-Sn-Trip$.^{11b} Beyond these thermodynamic considerations, the absence of an “inert lone pair” at the lighter silicon atom results in a significantly higher kinetic barrier for migration compared to that for the analogous tin complexes.^{11,20} Thus, metallocosilylenes **3b** and **4b** would not appear to spontaneously form via simple 1,2-hydrogen migration, as indicated by route 1 of Scheme 7.

It is therefore surprising that metallocosilylene-like reactivity is observed in reactions of **3** and **4** with organic substrates (e.g., ketones and azides). Note that an alternative pathway to the observed products might involve Si–H migration in silylene-substrate adducts (**3c-T/4c-T**, T = trapping substrates; route 2 in Scheme 7). This postulate is consistent with isolation of complexes **11** and **12**, since these compounds implicate the intermediacy of a silylene adduct that adds an enolizable C–H

Scheme 7. Possible Routes for Formation of Complexes 5–15



bond in a manner observed for other silylene complexes.^{12,13a,b,21} Such processes are examples of the general pathway involving intermediate **3c-T** (Scheme 7) prior to formation of the final products.

The postulated reaction pathway for formation of the silaoxirane complex **6** was further examined by DFT calculations using the PBE0-D3BJ functional corrected for dispersion, the SDD ECP for Ru and Def2-TZVP//Def2-SVP basis sets (See SI), starting from the putative silylene species **4a** (**I**) and benzophenone. The Gibbs free energy profile for transformation to the silaoxirane complex **IV** is shown in Figure 2. The coordination of benzophenone to **I** results in strong electronic reorganization. The intermediate **II** (with a free energy of 9.1 kcal mol⁻¹ above the free energy reference of **I** + benzophenone) has an open-shell singlet electronic structure (obtained at the DFT level with an unrestricted method) and is thus a diradicaloid. Benzophenone coordination to Si involves homolytic cleavage of the Ru–Si $d_{\pi}-p_{\pi}$ interaction to leave an electron on ruthenium and transfer an electron into the LUMO of the coordinated benzophenone, in accordance with the exceptional one-electron-accepting ability for aromatic ketones.²² The transition state **TS II–III** (located at 20.9 kcal mol⁻¹ above the energy reference) possesses an open-shell singlet electronic state (giving also a diradicaloid character to **TS II–III**) and proceeds to the η^3 -silylene complex **III** via combined 1,2-hydrogen (Si to Ru) migration and movement of the Ru-bonded hydride toward Si. The electron-rich nature of **4a** (**I**) appears to be an important factor in formation of the Lewis acid adducts $Cp^*(IXy)(H)Ru(\mu-MOTf)SiHTrip$ (M = Cu, Ag).¹² This aspect of the mechanism explains the lack of observed reactions of **3** and **4** with 2,3-dimethyl-1,3-butadiene, a commonly employed trap for silylenes and stannylens but a poor electron acceptor. In addition, this electron-transfer event provides an explanation for the significant rate acceleration observed with electron-withdrawing groups in substituted benzophenones.

Calculations of open shell singlets with methods such as DFT require careful validation. The current system is too large for a multiconfigurational calculation so instead, several tests were carried out. The results obtained from the closed-shell method strengthen the results obtained with the unrestricted method. Extrema located for **II** and **TS II–III**, with a singlet closed-shell structure gave much higher energies (**II** and **TS II–III** are 27 and 34 kcal mol⁻¹ above the reference) but indicated a strong delocalization of electron density from **I** toward the benzophenone moiety. A triplet electronic state was also identified for **II** and **TS II–III**. The structures for the

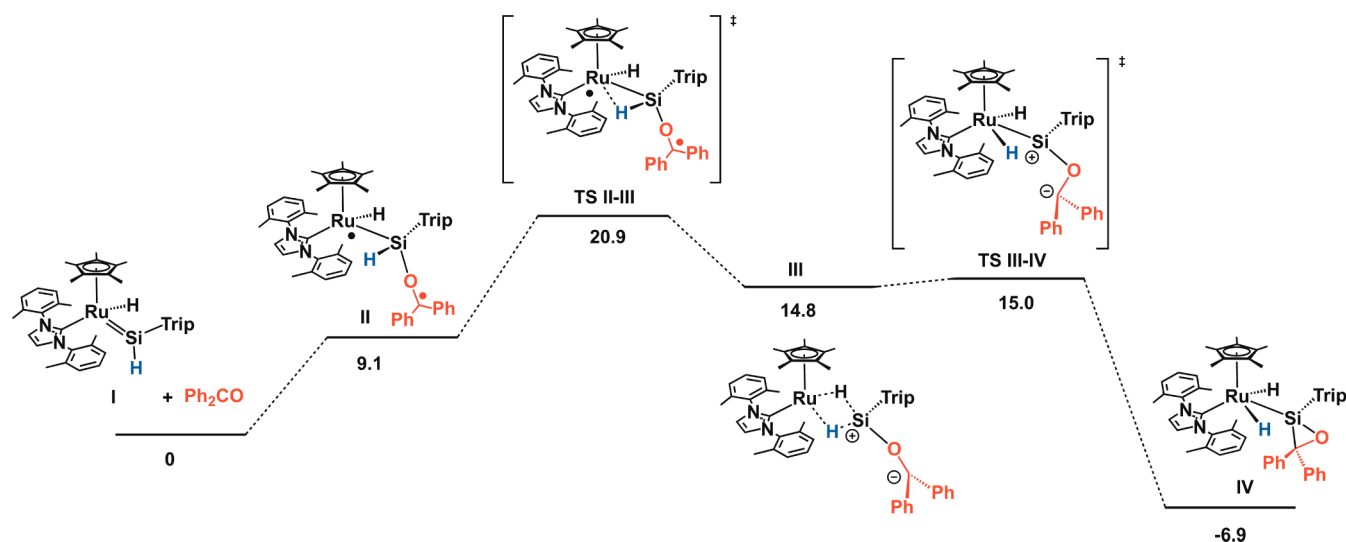


Figure 2. Gibbs energy profile (kcal mol⁻¹) for the reaction of benzophenone with I.

triplet and singlet open-shell states are similar for both **II** and **TS II–III**, and the two electronic states give parallel energy profiles, which are both below that for the closed-shell singlet. The open-shell singlet, found to be energetically below the triplet, has small spin contaminations ($S^2 = 0.33$ and 0.22 for **II** and **TS II–III**, respectively, close to the ideal value of 0 expected for a pure singlet state), which further validates the calculations of the open-shell singlet. The preference for an open-shell singlet is likely due to the coupling of electrons through the Si–O bond. Related coupling has been suggested to account for the unusual stability of singlet biradicals, which are thus best viewed as diradicaloids.²³ Final validation of the order of these three electronic states is obtained by calculating **II**, **TS II–III**, and **III** with a number of functionals (GGA, hybrid metaGGA, long-range corrected hybrid density functional, see SI). All functionals give the same results, namely an order open-singlet < triplet < closed-shell singlet for **II**, a preference for an open-shell singlet for **TS II–II**, and a preference for a closed-shell singlet for **III**. At **TS II–III**, the Si–H bond is weakened, and an NBO analysis gives a null charge at the migrating H. The 1,2-hydrogen migration (**II** to **III**) can thus be understood as being assisted by the electron-transfer process, such that the hydrogen atom is migrating to an electron-deficient Ru center. The hydrogen migration to form **III** depletes electron density at silicon, which therefore develops unpaired electron density that is coupled to that on the benzophenone. This gives a closed-shell ground state for **III**, which collapses with essentially no free energy barrier to the silaoxirane **IV** (see SI for all energy signatures, E, E + ZPE, enthalpy, and free Gibbs energies). The electronic structure of **III** is similar to that of complex **14** according to NBO analysis, in which ruthenium and silicon atoms are held together mostly through the bridging hydrogens. Furthermore, the benzophenone carbonyl carbon atom of **TS III–IV** is electron rich, while the Si atom is electron poor, and this facilitates formation of the Si–C bond. Although the single-electron-transfer (SET) mechanism of Figure 2 may not account for the formation of all complexes **5–16**, it demonstrates that Lewis acidic or electron-accepting substrates may act to create an electron-deficient ruthenium center, and this facilitates intramolecular hydrogen migration that causes silylene complex **4a** to exhibit metallosilylene-like reactivity.

CONCLUDING REMARKS

In summary, successful isolation of metallo-silaoxiranes, -silacyclopentenes, and -silamines from masked silylene complexes **3** and **4** demonstrates the ability of the transition-metal fragment Cp*(IXy)(H)₂Ru to stabilize a variety of unusual silicon-based entities. In particular, the Cp*(IXy)(H)₂Ru fragment provides both steric and electronic stabilization to these silicon-based ligands, leading to new chemical transformations in transition-metal main group chemistry. The reaction proceeds through an unconventional electron-transfer mechanism from the electron-rich Ru to the electrophilic substrate bonded to the silicon center. Interestingly, the non-innocent ketone substrates play a dual role in this chemistry, in stabilizing an electron-poor silicon center by electron donation, while acting as an electron acceptor through the presence of low-lying empty orbitals to render the ruthenium center more electrophilic. Increasing the electron-accepting ability of the substrate by introducing electron-withdrawing groups promotes the overall reaction. This reaction chemistry also emphasizes the activation of all three Si–H bonds of a primary silane and suggests the possibility of developing catalytic processes that produce novel silicon-containing species from common silane reagents.

EXPERIMENTAL SECTION

General Procedures. All experiments were conducted under nitrogen using standard Schlenk techniques or in a N₂-filled drybox. Nondeuterated solvents were distilled under N₂ from appropriate drying agents and stored in PTFE-valved flasks or obtained from solvent purification systems manufactured by Vacuum Atmospheres or JC Meyers Phoenix SDS. Benzene-*d*₆ was dried by vacuum distillation from Na/K alloy and deaerated with multiple freeze–pump–thaw cycles. Toluene-*d*₈ was dried by vacuum distillation from Na/benzophenone and similarly deaerated. Compounds **3** and **4** were prepared according to literature procedures.¹² All other chemicals were purchased from commercial sources and used without further purification. NMR spectra were recorded using Bruker AV-500 or AV-600 spectrometers equipped with a 5 mm BB probe. Spectra were recorded at room temperature and referenced to the residual protio solvent resonances for ¹H NMR spectra. ¹³C{¹H} NMR spectra were calibrated internally with the solvent resonance relative to tetramethylsilane. For ¹³C{¹H} NMR spectra, resonances obscured by the solvent signal are omitted.²⁹ Si NMR spectra were referenced

relative to a tetramethylsilane standard and obtained via 2D ^1H ^{29}Si HMBC experiments. All spectra were recorded at room temperature unless otherwise noted. Complex multiplets are noted as “m” and broad resonances as “br”.

Synthesis of Complexes 5–15. $Cp^*(IXy)(H)_2RuSi(OCPhCF_3)Mes$ (**5**). A 1 mL benzene solution of α,α,α -trifluoroacetophenone (0.008 g, 0.045 mmol) was added to a 6 mL benzene solution of **1** (0.030 g, 0.045 mmol), and the resulting solution was stirred at ambient temperature for 6 h, during which the color turned to pale yellow. All volatile materials were removed under vacuum; the resulting solid was washed with 10 mL of pentane and then dissolved in 0.5 mL of toluene. Slow vapor diffusion of pentane into the toluene solution at -30 °C afforded 0.019 g of **5**. Yield: 49%. ^1H NMR (C_6D_6 , 600 MHz): δ 7.26 (d, $J_{\text{HH}} = 8.15$ Hz, 1 H), 7.07–6.95 (m, 6 H), 6.88 (d, $J_{\text{HH}} = 6.91$ Hz, 1 H), 6.84 (t, $J_{\text{HH}} = 7.41$ Hz, 1 H), 6.63 (s, 1 H, ArH), 6.27 (s, 1 H, ArH), 6.19 (d, $J_{\text{HH}} = 1.86$ Hz, 1 H, NCHCHN), 5.91 (d, $J_{\text{HH}} = 1.86$ Hz, 1 H, NCHCHN), 2.99 (s, 3 H), 2.58 (s, 3 H), 2.35 (s, 3 H), 2.29 (s, 3 H), 2.09 (s, 3 H), 1.98 (s, 3 H), 1.69 (s, 3 H), 1.24 (s, 15 H, C_5Me_5), -9.61 (s, 1 H, RuH), -9.81 (s, 1 H, RuH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 150.9 MHz): δ 185.7 (NCN), 143.9, 141.7, 141.5, 140.2, 139.0, 138.6, 138.3, 137.9, 137.2, 135.8, 130.9, 130.6, 129.4, 127.6, 127.4, 126.8, 126.3, 125.0, 124.7, 124.0, 123.8, 96.3 (C_5Me_5), 66.6 (SiCO, $^2J_{\text{CF}} = 34.5$ Hz), 24.0, 22.7, 22.2, 22.0, 21.6, 21.2, 21.1, 20.6, 11.0 (C_5Me_5). ^{29}Si NMR (C_6D_6 , 99.4 MHz): δ 7.90. ^{19}F NMR (C_6D_6 , 376.5 MHz): -59.9 . Anal. calcd for $C_{51}H_{64}N_2F_3OSiRu$: C, 67.52; H, 7.11; N, 3.09. Found: C, 67.30; H, 6.67; N, 3.16.

$Cp^*(IXy)(H)_2RuSi(OCPh)_2Trip$ (**6**). A 3 mL benzene solution of benzophenone (0.015 g, 0.083 mmol) was added to a 6 mL benzene solution of **2** (0.056 g, 0.075 mmol), and the resulting solution was stirred at ambient temperature for 3 days, during which the color turned to colorless from pale purple. All volatile materials were removed under vacuum, and the resulting solid was extracted with 10 mL of pentane. Concentration of the pentane solution to ca. 5 mL followed by cooling in a -30 °C refrigerator for 2 days afforded 0.044 g of **6**. Yield: 63%. ^1H NMR (C_6D_6 , 600 MHz): δ 7.94 (d, $J_{\text{HH}} = 6.63$ Hz, 2 H), 7.44 (d, $J_{\text{HH}} = 7.96$ Hz, 1 H), 7.32 (s, 1 H, ArH), 7.24 (m, 3 H), 7.20 (m, 3 H), 6.96 (m, 4 H), 6.85 (d, $J_{\text{HH}} = 7.96$ Hz, 1 H), 6.81 (d, $J_{\text{HH}} = 6.60$ Hz, 2 H), 6.70 (s, 1 H, ArH), 6.07 (d, $J_{\text{HH}} = 1.85$ Hz, 1 H, NCHCHN), 5.91 (d, $J_{\text{HH}} = 1.85$ Hz, 1 H, NCHCHN), 4.25 (septet, $J_{\text{HH}} = 6.53$ Hz, 1 H, $CHMe_2$), 3.31 (septet, $J_{\text{HH}} = 6.84$ Hz, 1 H, $CHMe_2$), 2.89 (septet, $J_{\text{HH}} = 6.53$ Hz, 1 H, $CHMe_2$), 2.85 (s, 3 H, xyllyl CH_3), 1.94 (d, $J_{\text{HH}} = 6.84$ Hz, 3 H, $CHMe_2$), 1.85 (s, 3 H, xyllyl CH_3), 1.77 (s, 3 H, xyllyl CH_3), 1.46 (d, $J_{\text{HH}} = 6.84$ Hz, 3 H, $CHMe_2$), 1.37 (d, $J_{\text{HH}} = 6.53$ Hz, 6 H, $CHMe_2$), 1.35 (s, 3 H, xyllyl CH_3), 1.32 (s, 15 H, C_5Me_5), 0.80 (d, $J_{\text{HH}} = 6.53$ Hz, 3 H, $CHMe_2$), 0.50 (d, $J_{\text{HH}} = 6.53$ Hz, 3 H, $CHMe_2$), -8.97 (s, 1 H, RuH), -9.71 (s, 1 H, RuH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 150.9 MHz): δ 189.0 (NCN), 155.2, 152.3, 151.3, 150.7, 149.0, 146.5, 142.3, 141.5, 138.7, 137.2, 136.6, 136.0, 133.6, 132.4, 130.6, 130.1, 129.7, 129.2, 129.1, 129.0, 128.9, 128.7, 128.1, 126.8, 126.1, 124.2, 124.0, 123.3, 122.3, 120.0, 120.4, 96.7 (C_5Me_5), 71.1 (SiCO), 35.1, 34.8, 34.4, 28.8, 26.3, 26.0, 25.0, 24.9, 23.1, 22.1, 20.2, 19.4, 11.0 (C_5Me_5). ^{29}Si NMR (C_6D_6 , 99.4 MHz): δ -9.3 . Anal. calcd for $C_{57}H_{70}N_2OSiRu$: C, 73.75; H, 7.60; N, 3.02. Found: C, 73.59; H, 7.57; N, 2.75.

$Cp^*(IXy)(H)_2RuSi(k^2-O,C-OC(CH=CHPh)=CHCH(CH=CHPh))Mes$ (**7**). A 4 mL benzene solution of dibenzylideneacetone (0.009 g, 0.038 mmol) was added to a 6 mL benzene solution of **3** (0.025 g, 0.037 mmol), and the resulting solution was stirred at ambient temperature for 6 h. All volatile materials were removed under vacuum, and the solid was washed three times with 2 mL of pentane followed by removal of solvent under vacuum to afford a white powder. Yield: 0.016 g (46%). Anal. calcd for $C_{55}H_{62}N_2OSiRu$: C, 73.71; H, 6.97; N, 3.13. Found: C, 74.02; H, 6.99; N, 3.01.

$Cp^*(IXy)(H)_2RuSi[OC(CH=CHC=CHPh)=CHCH(CH=CHPh)]Trip$ (**10**). A 4 mL benzene solution of dicinnamalacetone (0.012 g, 0.043 mmol) was added to a 6 mL benzene solution of **4** (0.027 g, 0.036 mmol), and the resulting solution was stirred at ambient temperature for 6 h. All volatile materials were removed under vacuum, and the resulting solid was washed three times with 2 mL of pentane followed by removal of solvent under vacuum to afford an

orange powder. X-ray quality crystals were grown from a dilute pentane solution at -30 °C. Yield: 0.022 g (58%). ^1H NMR (C_6D_6 , 600 MHz): δ 7.30 (m, 3 H), 7.22 (br 2 H), 7.13 (m, 3 H), 7.08 (br, 3 H), 7.04 (t, $J_{\text{HH}} = 7.46$ Hz, 2 H), 7.01 (br, 2 H), 6.96 (br, 2 H), 6.87 (m, 2 H), 6.78 (d, $J_{\text{HH}} = 15.54$ Hz, 1 H), 6.47 (m, 2 H), 6.24 (d, $J_{\text{HH}} = 15.54$ Hz, 1 H), 5.93 (s, 1 H, NCHCHN), 5.89 (s, 1 H, NCHCHN), 5.24 (br, 1 H), 5.06 (br, 1 H), 3.42 (septet, $J_{\text{HH}} = 6.09$ Hz, 1 H, $CHMe_2$), 3.06 (br, 1 H, $CHMe_2$), 2.81 (septet, $J_{\text{HH}} = 6.09$ Hz, 1 H, $CHMe_2$), 2.55 (br, 3 H), 2.36 (br, 3 H), 2.06 (br, 3 H), 1.83 (br, 3 H), 1.62 (br, 3 H), 1.50 (br, 18 H, C_5Me_5 , and one methyl group), 1.30 (br, 3 H), 1.25 (m, 3 H), 0.79 (br, 3 H), -10.21 (s, 1 H, RuH), -10.39 (s, 1 H, RuH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 150.9 MHz): δ 187.9 (NCN), 155.9, 155.2, 147.8, 141.5, 140.7, 139.6, 138.0, 137.8, 136.1, 135.4, 134.8, 131.6, 130.0, 129.5, 129.2, 128.7, 128.5, 128.4, 128.2, 128.1, 127.2, 127.1, 126.9, 126.3, 125.8, 125.6, 123.7, 122.9, 95.2 (C_5Me_5), 33.2, 30.0, 28.7, 23.9, 22.3, 20.3, 20.0, 20.0, 19.3, 10.6 (C_5Me_5), 10.5. ^{29}Si NMR (C_6D_6 , 99.4 MHz): δ 68.9. Anal. calcd for $C_{65}H_{78}N_2OSiRu$: C, 75.61; H, 7.61; N, 2.71. Found: C, 75.41; H, 7.91; N, 2.64.

$Cp^*(IXy)Ru(H)_2SiH[OC(=CH_2)CH=CHPh]Mes$ (**11**). A 4 mL benzene solution of benzylideneacetone (0.005 g, 0.036 mmol) was added to a 6 mL benzene solution of **3** (0.024 g, 0.036 mmol), and the resulting solution was stirred at ambient temperature for 6 h. All volatile materials were removed under vacuum, and the resulting solid was washed three times with 5 mL of pentane followed by removal of solvent under vacuum to afford a white powder. Yield: 0.028 g (97%). ^1H NMR (C_6D_6 , 600 MHz): δ 7.47 (d, $J_{\text{HH}} = 7.82$ Hz, 2 H), 7.24 (t, $J_{\text{HH}} = 7.82$ Hz, 2 H), 7.09–7.15 (m, 3 H), 7.03–7.08 (m, 2 H), 6.94–7.00 (m, 3 H), 6.85 (s, 2 H), 6.69 (d, $J_{\text{HH}} = 15.27$ Hz, 1 H, $OCH_2CHCHPh$), 6.49 (br, $J_{\text{SiH}} = 194.70$ Hz, 1 H, SiH), 6.03 (br, 2 H, NCHCHN), 4.58 (s, 1 H, $OCH_2CHCHPh$), 4.31 (s, 1 H, $OCH_2CHCHPh$), 2.65 (s, 6 H), 2.44 (s, 3 H), 2.24 (s, 3 H), 2.11 (s, 3 H), 2.00 (s, 3 H), 1.97 (s, 3 H), 1.51 (s, 15 H, C_5Me_5), -9.90 (s, 1H, RuH), -10.34 (s, 1H, RuH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 150.9 MHz): δ 189.0 (NCN), 158.9, 144.3, 142.0, 141.7, 140.0, 138.9, 138.3, 138.1, 137.0, 136.0, 135.7, 130.1, 129.9, 129.7, 129.5, 129.2, 129.0, 128.9, 127.6, 127.4, 123.3, 123.1, 94.8 (C_5Me_5), 23.4, 21.6, 20.4, 20.3, 20.1, 19.8, 11.4 (C_5Me_5). ^{29}Si NMR (C_6D_6 , 99.4 MHz): δ 25.5. Anal. calcd for $C_{48}H_{58}N_2OSiRu$: C, 71.34; H, 7.23; N, 3.47. Found: C, 71.67; H, 7.50; N, 3.29.

$Cp^*(IXy)Ru(H)_2SiH[OC(=CH_2)CH=CHPh]Trip$ (**12**). A 4 mL benzene solution of benzylideneacetone (0.007 g, 0.049 mmol) was added to a 6 mL benzene solution of **4** (0.036 g, 0.049 mmol), and the resulting solution was stirred at ambient temperature for 6 h. All volatile materials were removed under vacuum, and the resulting solid was washed three times with 5 mL of pentane followed by removal of solvent under vacuum to afford a white powder. Yield: 0.033 g (77%). ^1H NMR (C_6D_6 , 600 MHz): δ 7.60 (s, 1 H), 7.34–7.58 (m, 2 H), 7.20–7.33 (m, 3 H), 7.13 (t, $J_{\text{HH}} = 7.46$ Hz, 1 H), 7.00 (t, $J_{\text{HH}} = 7.26$ Hz, 1 H), 6.95 (d, $J_{\text{HH}} = 7.11$ Hz, 1 H), 6.88 (d, $J_{\text{HH}} = 6.47$ Hz, 1 H), 6.66 (br, 1 H), 6.45 (br, 1 H, SiH), 5.97 (s, 1 H, NCHCHN), 5.93 (s, 1 H, NCHCHN), 4.44 (br, 1 H, $OCH_2CHCHPh$), 4.26 (br, 1 H, $OCH_2CHCHPh$), 3.53 (br, 1 H, $CHMe_2$), 2.84–3.02 (m, 2 H, $CHMe_2$), 1.97 (s, 3 H), 1.84 (s, 3 H), 1.58 (br, 18 H, C_5Me_5 , and one methyl group), 1.30–1.40 (m, 9 H, $CHMe_2$), 1.07–1.29 (m, 9 H, $CHMe_2$), -10.44 (s, 1H, RuH), -11.04 (s, 1H, RuH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 150.9 MHz): δ 192.9 (NCN), 161.0, 153.6, 149.0, 141.0, 139.1, 138.6, 137.6, 135.7, 130.2, 130.0, 129.2, 129.1, 128.9, 127.5, 127.4, 127.3, 121.8, 121.6, 95.0 (C_5Me_5), 35.2, 27.1, 24.9, 24.8, 23.1, 20.6, 20.1, 14.6, 10.8 (C_5Me_5). ^{29}Si NMR (C_6D_6 , 99.4 MHz): δ 34.8. Anal. calcd for $C_{54}H_{70}N_2OSiRu$: C, 72.69; H, 7.91; N, 3.14. Found: C, 72.93; H, 8.20; N, 2.81.

$Cp^*(IXy)(H)_2RuSi(NSO_2C_6H_4Me)Mes$ (**13**). A 2 mL benzene solution of TsN_3 (0.006 g, 0.030 mmol) was added to a 5 mL benzene solution of **3** (0.020 g, 0.030 mmol), and the resulting solution was stirred at ambient temperature for 30 min. All volatile materials were removed under vacuum, and the resulting solid was washed three times with 5 mL of pentane followed by removal of solvent under vacuum to afford a white powder. Yield: 0.024 g (95%). ^1H NMR (C_6D_6 , 600 MHz): δ 7.90 (d, $J_{\text{HH}} = 7.9$ Hz, 2 H), 7.09 (d, $J_{\text{HH}} = 7.20$ Hz, 2 H), 6.98 (t, J_{HH}

= 7.9 Hz, 2 H), 6.87 (d, $J_{\text{HH}} = 7.2$ Hz, 2 H), 6.82 (d, $J_{\text{HH}} = 7.9$ Hz, 2 H), 6.67 (s, 2 H, ArH), 6.21 (s, 2 H, NCHCHN), 2.93 (s, 6 H), 2.63 (s, 6 H), 2.14 (s, 3 H), 2.08 (s, 3 H), 1.78 (s, 6 H), 1.13 (s, 15 H, C_5Me_5), -10.50 (s, $J_{\text{SiH}} = 51$ Hz, 2 H, RuH). $^{13}\text{C}\{\text{H}\}$ NMR (C_6D_6 , 150.9 MHz): δ 182 (NCN), 147.8, 140.9, 140.5, 139.9, 139.6, 138.9, 137.8, 135.7, 129.6, 127.1, 124.0, 94.7 (C_5Me_5), 22.5, 21.5, 21.3, 21.2, 19.5, 10.4 (C_5Me_5). ^{29}Si NMR (C_6D_6 , 99.4 MHz): δ 154 ($J_{\text{SiH}} = 51$ Hz). Anal. calcd for $\text{C}_{45}\text{H}_{55}\text{N}_3\text{O}_2\text{SSiRu}$: C, 65.03; H, 6.67; N, 5.06; S, 3.86. Found: C, 64.63; H, 7.02; N, 5.35; S, 3.71.

Cp*(IXy)(H)₂RuSi(NSO₂C₆H₄Me)Trip (14). A 2 mL benzene solution of TsN_3 (0.005 g, 0.028 mmol) was added to a 5 mL benzene solution of **4** (0.021 g, 0.028 mmol), and the resulting solution was stirred at ambient temperature for 30 min. All volatile materials were removed under vacuum, and the resulting solid was washed three times with 5 mL of pentane followed by removal of solvent under vacuum to afford a white powder. Yield: 0.020 g (77%). ^1H NMR (C_6D_6 , 600 MHz): δ 7.97 (d, $J_{\text{HH}} = 7.56$ Hz, 2 H), 7.15 (s, 2 H, ArH), 7.06 (d, $J_{\text{HH}} = 7.56$ Hz, 2 H), 6.98–6.92 (m, 4 H), 6.80 (d, $J_{\text{HH}} = 6.99$ Hz, 2 H), 6.15 (s, 2 H, NCHCHN), 3.64 (septet, $J_{\text{HH}} = 6.68$ Hz, 2 H, CHMe_2), 2.84 (septet, $J_{\text{HH}} = 6.86$ Hz, 1 H, CHMe_2), 2.72 (s, 6 H), 2.12 (s, 3 H, SO_2PhCH_3), 2.01 (d, $J_{\text{HH}} = 6.68$ Hz, 6 H, CHMe_2), 1.76 (s, 6 H), 1.49 (d, $J_{\text{HH}} = 6.68$ Hz, 6 H, CHMe_2), 1.25 (d, $J_{\text{HH}} = 6.86$ Hz, 6 H, CHMe_2), 1.09 (s, 15 H, C_5Me_5), -10.47 (s, $J_{\text{SiH}} = 54.0$ Hz, 2 H, RuH). $^{13}\text{C}\{\text{H}\}$ NMR (C_6D_6 , 150.9 MHz): δ 183.4 (NCN), 151.5, 150.9, 148.3, 141.2, 140.7, 140.1, 138.1, 136.4, 129.6, 129.1, 124.3, 120.9, 95.1 (C_5Me_5), 36.2, 35.2, 28.3, 24.7, 24.4, 21.7, 21.4, 20.0, 11.1 (C_5Me_5). ^{29}Si NMR (C_6D_6 , 99.4 MHz): δ 145 ($J_{\text{SiH}} = 54.0$ Hz). Anal. calcd for $\text{C}_{51}\text{H}_{67}\text{N}_3\text{O}_2\text{SSiRu}$: C, 66.92; H, 7.38; N, 4.59; S, 3.50. Found: C, 66.43; H, 7.55; N, 4.62; S, 3.91.

Cp*(IXy)(H)₂RuSi(N₂Flu)Mes (15). A 4 mL benzene solution of 9-diazafluorene (0.019 g, 0.097 mmol) was added to a 10 mL benzene solution of **3** (0.065 g, 0.097 mmol), and the resulting solution was stirred at ambient temperature for an hour. All volatile materials were removed under vacuum, and the resulting solid was washed three times with 5 mL of pentane followed by removal of solvent under vacuum to afford an orange powder. Yield: 0.074 g (88%). ^1H NMR (benzene- d_6 , 600 MHz): δ 9.12 (d, $^3J_{\text{HH}} = 7.61$ Hz, 1 H, fluorenyl aromatic hydrogens), 7.98 (d, $^3J_{\text{HH}} = 7.48$ Hz, 1 H, fluorenyl aromatic hydrogens), 7.80 (d, $^3J_{\text{HH}} = 7.48$ Hz, 1 H, fluorenyl aromatic hydrogens), 7.74 (d, $^3J_{\text{HH}} = 7.31$ Hz, 1 H, fluorenyl aromatic hydrogens), 7.30 (t, $^3J_{\text{HH}} = 7.33$ Hz, 1 H, fluorenyl aromatic hydrogens), 7.24 (t, $^3J_{\text{HH}} = 7.33$ Hz, 1 H, fluorenyl aromatic hydrogens), 7.21 (t, $^3J_{\text{HH}} = 7.33$ Hz, 1 H, fluorenyl aromatic hydrogens), 6.96 (t, $^3J_{\text{HH}} = 7.44$ Hz, 2 H), 6.90 (d, $^3J_{\text{HH}} = 7.13$ Hz, 2 H), 6.86–6.83 (m, 4 H), 2.72 (s, 6 H), 2.64 (s, 6 H), 2.23 (s, 3 H), 1.85 (s, 6 H), 1.26 (s, 15 H, C_5Me_5), -9.84 (s, $J_{\text{SiH}} = 38.2$ Hz, 2 H, RuH). Anal. calcd for $\text{C}_{51}\text{H}_{56}\text{N}_4\text{SiRu}$: C, 71.71; H, 6.61; N, 6.56. Found: C, 71.46; H, 6.92; N, 6.09.

Computational Details. DFT calculations were carried out with PBE0 hybrid functional,²⁴ corrected for dispersion as proposed by Grimme (D3 correction, BJ damping).²⁵ Calculations were performed with the Gaussian 09 suite of programs,²⁶ locally modified to take into account dispersion corrections for energies and their first and second derivatives. Geometry optimizations were performed without any symmetry constraints using the Def2-SVP basis set (BS1)²⁷ for all atoms and quasi-relativistic effective core potentials for Ru.²⁸ The nature of the stationary points as minima or transition states was characterized by analytical Hessian calculations. The connection between transition states, reactants, and products was verified by IRC calculations. Statistical mechanics calculations of thermal and entropic effects were carried out using the rigid rotor/harmonic oscillator approximations at 298 K and 1 atm ($G^{\text{gas,PBE0-D3bj,BS1}}$).

Electronic energies were refined with single point energy calculations using the Def2-TZVPP basis set (BS2)²⁷ for all atoms; solvent effects (benzene) were included by means of SMD²⁹ single point energy calculations. Finally, Gibbs free energies in solution were estimated as

$$G^{\text{benzene,PBE0-D3bj,BS2}} = E^{\text{benzene,PBE0-D3bj,BS2}} + G^{\text{gas,PBE0-D3bj,BS1}} - E^{\text{gas,PBE0-D3bj,BS1}}$$

NBO analyses were performed with NBO 6.0.³⁰

X-ray Crystallography Details. X-ray diffraction data were collected using Bruker AXS three-circle diffractometers coupled to APEX-II CCD detectors with either QUAZAR multilayer mirror- or graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Data collection strategy determination, integration, scaling, and space group determination were performed with Bruker APEX2 software (v. 2011.4 or v. 2014.1). Structures were solved by SHELXS-2013 direct methods³¹ or Superflip V 04/17/13³² and refined with SHELXL-2013, with refinement of F2 on all data by full-matrix least-squares. Molecular structures were visualized with ORTEP 3.2 and rendered with POV-Ray 3.6.

■ ASSOCIATED CONTENT

Supporting Information

Kinetic experiments, influence of the functional on a part of the Gibbs energy profile, various energy results for the reaction profile, selected NBO results, X-ray crystallography details, and crystallographic information files (cif). List of coordinates for all optimized structures as a separate .xyz file. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b05571.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Support for this research was provided by The National Science Foundation under grant no. CHE-1265674. Support for the Molecular Graphics and Computational Facility is provided by the National Science Foundation under grant no. CHE-0840505. H.J.L. thanks Daniel S. Levine and Han-Jung Li for helpful discussions and Micah S. Ziegler for X-ray crystallographic analyses. C.R. and O.E. acknowledge the computational resources of the CTMM group of the Institut Charles Gerhardt. C.L. thanks la Chaire TOTAL of Pôle Balard for an invited Professor position.

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