Cyclometalated N-Heterocyclic Carbene Complexes of Ruthenium for Access to Electron-Rich Silylene Complexes That Bind the Lewis Acids CuOTf and AgOTf

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Ⓢ *Supporting Information*

ABSTRACT: The synthesis of the cyclometalated complexes Cp*Ru(IXy-H) (**2**) [IXy = 1,3-bis(2,6-dimethylphenyl)-imidazol-2-ylidene; IXy-H = 1-(2-CH$_2$C$_6$H$_3$-6-methyl)-3-(2,6-dimethylphenyl)imidazol-2-ylidene-1-yl (the deprotonated form of IXy); Cp* = η^5-C$_5$Me$_5$] and Cp*Ru(IXy-H)(N$_2$) (**3**) was achieved by dehydrochlorination of Cp*Ru(IXy)Cl (**1**) with KCH$_2$Ph. Complexes **2** and **3** activate primary silanes (RSiH$_3$) to afford the silyl complexes Cp*(IXy-H)(H)RuSiH$_2$R [R = *p*-Tol (**4**), Mes (**5**), Trip (**6**)]. Density functional theory studies indicated that these complexes are close in energy to the corresponding isomeric silylene species Cp*(IXy)(H)Ru=SiHR. Indeed, reactivity studies indicated that various reagents trap the silylene isomer of **6**, Cp*(IXy)(H)Ru=SiHTrip (**6a**).

Thus, benzaldehyde reacts with **6** to give the [2 + 2] cycloaddition product **7**, while 4-bromoacetophenone reacts via C−H bond cleavage and formation of the enolate Cp*(IXy)(H)$_2$RuSiH[OC(=CH$_2$)C$_6$H$_4$Br]Trip (**8**). Addition of the O−H bond of 2,6-dimethylphenol across the Ru=Si bond of **6a** gives Cp*(IXy)(H)$_2$RuSiH(2,6-Me$_2$C$_6$H$_3$O)Trip (**9**). Interestingly, CuOTf and AgOTf also react with **6** to provide unusual Lewis acid-stabilized silylene complexes in which MOTf bridges the Ru−Si bond. The AgOTf complex, which was crystallographically characterized, exhibits a structure similar to that of [Cp*(*i*Pr$_3$P)Ru(μ-H)$_2$SiHMes]$^+$, with a three-center, two-electron Ru−Ag−Si interaction. Natural bond orbital analysis of the MOTf complexes supported this type of bonding and characterized the donor interaction with Ag (or Cu) as involving a delocalized interaction with contributions from the carbene, silylene, and hydride ligands of Ru.
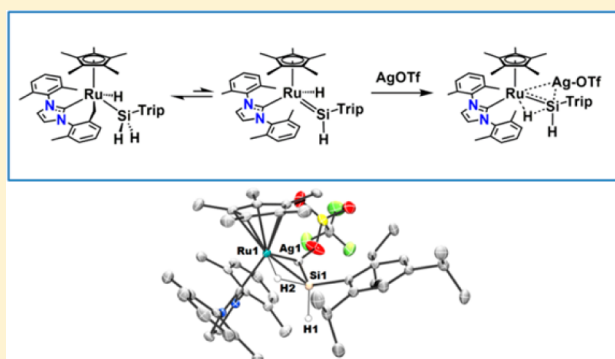
INTRODUCTION

Transition-metal silylene complexes, which formally contain divalent silicon coordinated to the metal center, have attracted considerable attention because of their ability to mediate unusual transformations of organosilanes.[1−4] An important facet to research in this area involves reactivity studies designed to probe the influence of structural variations in these L$_n$MSiRR′ species. Silylene complexes have now been accessible for about 25 years, and there are several reaction pathways that allow access to this class of compounds.[5] One relatively general synthetic method is based on 1,2-migration of an α-substituent (most commonly hydrogen) from the silicon atom of a silyl ligand to a vacant coordination site of the metal center.[5−7] This approach has proven useful, for example, in the synthesis of piano-stool silylene complexes of group 6[8] and 8[9] metals, of the types Cp*L$_2$(H)M=SiR$_2$ (M = Mo, L$_2$ = dmpe; M = W, L = CO; Cp* = η^5-C$_5$Me$_5$) and Cp*L(H)M=SiR$_2$ (M = Ru, L = CO, PMe^{i}Pr$_2$; M = Os, L = P^{i}Pr$_3$). In general, it is

clear that the ancillary ligand L plays a critical role in stabilizing silylene complexes and in determining their steric and electronic properties. For example, attempts to prepare Cp*(^{i}Pr$_3$P)(H)Ru=SiRR′ silylene complexes have not been successful, while a number of corresponding PMe^{i}Pr$_2$ derivatives have been obtained.[9a] Similarly, whereas (^{i}Pr$_3$P)$_2$Pt=SiMes$_2$ is thermally unstable, the analogue (Cy$_3$P)$_2$Pt=SiMes$_2$ can be isolated as a green solid.[10]

N-heterocyclic carbene (NHC) ligands have been heavily utilized in main-group and transition-metal chemistry over the past two decades.[11] Many advances have been made in the development of NHC ligands, which may have diverse electronic and steric properties, and in general these ligands form stable complexes and allow access to coordinatively unsaturated metal centers. Thus, the exceptional donor

properties of NHC ligands could be useful in the synthesis and isolation of reactive complexes possessing unsaturation at the metal or at a ligated main-group element. In this regard, Nolan and co-workers reported comparisons of the binding affinities of phosphine (PCy$_3$ and P^{i}Pr$_3$) and NHC ligands to [Cp*RuCl]$_4$, which demonstrate that NHCs are in general superior donors.[12] Additionally, Ohki et al.[13] reported Cp*Fe-(IMes)(Me) [IMes =1,3-bis(mesityl)imidazol-2-ylidene] and its participation in interesting C−H activation chemistry at elevated temperatures. For these reasons, it was of interest to target new ruthenium−silicon complexes based on a Cp*-(NHC)Ru fragment in order to investigate potentially new reaction pathways for silylene complexes derived therefrom. As reported below, this work began with attempts to prepare Cp*Ru(IXy)(alkyl) [IXy = 1,3-bis(2,6-dimethylphenyl)-imidazol-2-ylidene] complexes as starting materials for the formation of Ru−Si bonds via Si−H activations.[8,9a,b] This led to the formation of Ru(IV) silyl complexes with a metalated NHC ligand, which behave as masked silylene complexes via C−H elimination reactions.[14] These new silylene complexes possess properties distinct from other species of this type in that they favor the binding of Lewis acids (AgOTf, CuOTf) over Lewis bases [N,N-dimethylaminopyridine, PMe$_2$Ph, OPMe$_2$Ph, and tetrahydrofuran (THF)].

RESULTS AND DISCUSSION

**Cyclometalations in Cp*Ru(IXy) Precursor Complexes.** A convenient, general route to neutral, hydrogen-substituted ruthenium silylene complexes of the type Cp*(^{i}Pr$_2$MeP)(H)-Ru=SiHR is based on the addition of a primary silane (RSiH$_3$) to the benzyl complex Cp*(^{i}Pr$_2$MeP)Ru(η^3-CH$_2$Ph), which results in toluene elimination and α-migration to yield the final silylene product (eq 1).[9a] The benzyl complex is readily
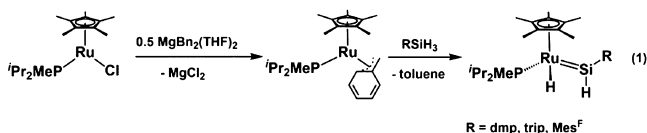
prepared by reaction of dibenzylmagnesium with the chloride complex Cp*(^{i}Pr$_2$MeP)RuCl.[9a] Thus, initial attempts to prepare NHC-supported silylene complexes were based on this strategy, starting from Cp*Ru(IXy)Cl (**1**).

The 16-electron complex **1** was obtained in a straightforward way by reaction of [Cp*RuCl]$_4$ with 4 equiv of IXy in THF, which gave a 93% yield of analytically pure **1** as a purple powder from evaporation of the toluene extract (Scheme 1). In an attempt to obtain a benzyl complex analogous to Cp*(^{i}Pr$_2$MeP)Ru(η^3-CH$_2$Ph), **1** was treated with 1 equiv of KCH$_2$Ph in toluene. However, this reaction instead gave

Scheme 1
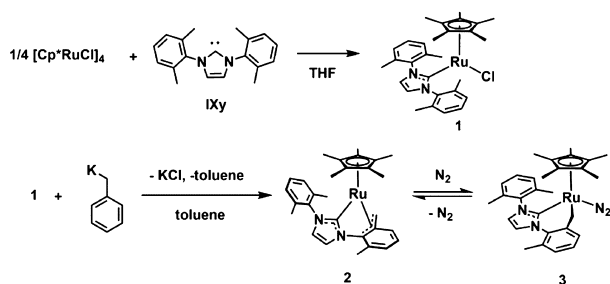
[Cp*Ru(IXy-H)] (**2**) [IXy-H = 1-(2-CH$_2$C$_6$H$_3$-6-methyl)-3-(2,6-dimethylphenyl)imidazol-2-ylidene-1-yl (the deprotonated form of IXy)], which was isolated as dark-brown crystals in 92% yield by removal of solvent under vacuum. The solid-state structure of **2** (Figure 1) is consistent with the chemical
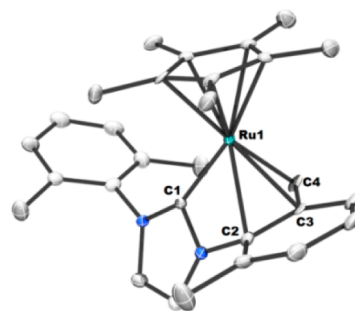

Figure 1. Molecular structure of **2** displaying thermal ellipsoids at the 50% probability level. H atoms have been omitted for clarity.

drawing given in Scheme 1, which features metalation of a C−H bond of the IXy ligand. This results in conversion of IXy into a chelating ligand featuring donation of the carbene carbon atom and a benzylic entity (derived from a xylyl group of IXy) to the ruthenium center. This 18-electron complex therefore possesses a structure related to that of the previously reported η^3-benzyl complex Cp*(^{i}Pr$_2$MeP)Ru(η^3-CH$_2$Ph).[9a] The benzylic C(3)−C(4) and C(2)−C(3) bond lengths are roughly equivalent at 1.44 Å, which is intermediate between accepted values for C−C single and double bonds.

Interestingly, cooling a saturated pentane solution of **2** at −30 °C under nitrogen afforded X-ray-quality orange crystals of the dinitrogen complex [Cp*Ru(IXy-H)N$_2$] (**3**) [Figure 2;
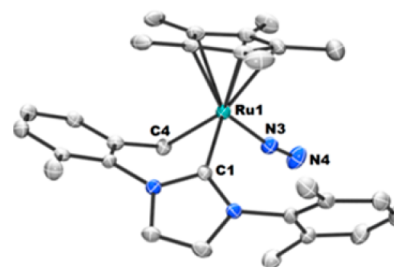

Figure 2. Molecular structure of **3** displaying thermal ellipsoids at the 50% probability level. H atoms have been omitted for clarity.

Ru−N 1.93(4) Å, N−N 1.11(5) Å], which appears to possess a modestly activated N$_2$ ligand.[15] The infrared spectrum of solid **3** revealed a ν(N$_2$) stretching vibration at 2069 cm^{-1}, which is comparable to the corresponding value for the Ru(0) complex Ru(N$_2$)(P(CH$_2$CH$_2$PCy$_2$)$_3$)[15a] and indicates that there is significant π back-bonding from Ru to the N$_2$ ligand.

Upon dissolution of crystalline **3** in a hydrocarbon solvent such as pentane or benzene, visible gas evolution indicated that the labile N$_2$ ligand readily dissociates in solution. The ^{1}H NMR spectrum of a solution prepared by dissolving **3** in benzene-d_6 at 24 °C under an atmosphere of nitrogen exhibited two Cp* resonances at 1.48 and 1.40 ppm in a 1:1.4 ratio, associated with **2** and **3**, respectively. The ruthenium-bound CH$_2$ unit of **3** gives rise to a doublet resonance at 2.58 ppm ($^2J_{HH}$ = 9.9 Hz) for one of the diastereotopic hydrogens, and the additional doublet resonance for this group is obscured by a

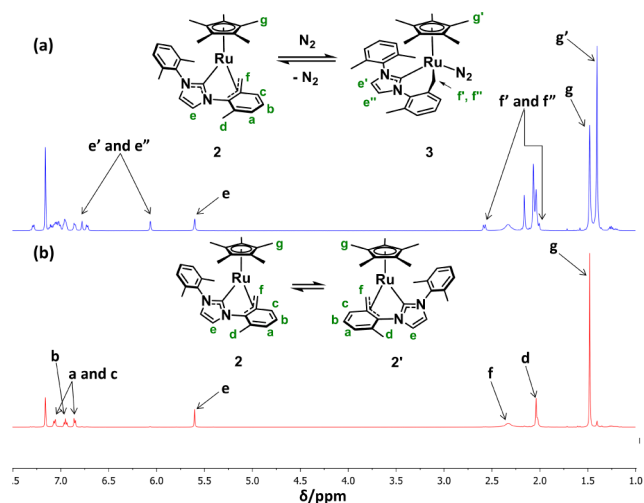resonance for xylyl groups at ~2.0 ppm (Figure 3a). Interestingly, cooling a benzene-d_6 solution of the 2/3 mixture

Figure 3. (a) ^{1}H NMR spectrum of **2/3** in C_6D_6 under N_2 at 24 °C. (b) The resulting spectrum after degassing with three freeze−pump−thaw cycles.

to 7 °C resulted in a change in the integrated ratio of Cp* resonances from 1:1.4 to 1:2.5 in favor of **3**, presumably reflecting the greater N_2 gas solubility and entropic effects on the equilibrium for N_2 binding (Scheme 1) at lower temperature. In addition, degassing the solution under vacuum with three freeze−pump−thaw cycles resulted in nearly complete disappearance of the resonances due to **3** (Figure 3b).

The room-temperature ^{1}H NMR spectrum of the degassed solution of **2** appears to reflect C_s symmetry associated with dynamic behavior of the complex. This spectrum contains three sets of resonances at 7.07 (2H, d), 6.95 (2H, t), and 6.85 (2H, d) ppm assigned to the six ring protons of the xylyl groups (a, b, and c in Figure 3b) and a single resonance at 5.60 ppm for the two protons of the imidazolylidene ring (e in Figure 3b). It should be noted that in contrast to **2**, the imidazolydiene protons of **3** are inequivalent (Figure 3a), suggesting that no comparable dynamic behavior exists for the dinitrogen complex. These results imply that **2** is stereochemically nonrigid and rapidly interconverts between enantiomers **2** and **2′** on the NMR time scale at room temperature (eq 2).
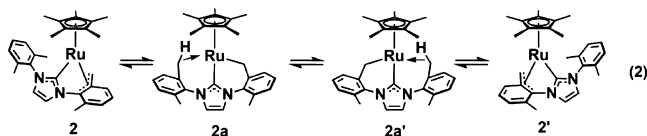

We postulate that the dynamic behavior of **2** may involve the intermediates **2a** and **2a′**, resulting from coordination of a benzylic C−H bond to ruthenium. Intermediates **2a** and **2a′** would interconvert via a C−H activation process and transfer of a hydrogen atom from one carbon atom to another. This hydrogen transfer may be mediated by C−H oxidative addition at ruthenium or by direct transfer of hydrogen between the carbon centers within the coordination sphere of the metal.[16] Cooling a toluene-d_8 solution of **2** to −78 °C did not reveal ^{1}H NMR resonances associated with **2a** or any other intermediates. However, the density functional theory (DFT)-optimized structure of **2a** shows that the pyramidal Ru (out of the

plane defined by the Cp* centroid, $C_{carbene}$, and $C_{metalated}$) has an agostic C−H interaction with a methyl group of the non-cyclometalated xylyl group, giving a formally 18-electron Ru complex (see the Supporting Information). This agostic interaction results in a rather short Ru···H distance of 2.00 Å and an elongated C−H bond length of 1.13 Å (compared with 1.10 Å for the other C−H bonds at the same carbon atom).[17]

Ruthenium(IV) Silyl Hydride Complexes with a Cyclometalated NHC Ligand. The cyclometalated complexes **2** and **3** are potentially useful starting materials for the syntheses of complexes containing ruthenium−element multiple bonds, especially in light of the bond activations described above (e.g., in eq 2). For example, group 14 compounds $RR'EH_2$ (E = Si, Ge, Sn) might be transformed to ylene complexes of the type Cp*(IXy)(H)Ru(=ERR′) by the reaction sequence shown in Scheme 2. This reactivity has considerable precedent[5,9b] and

Scheme 2
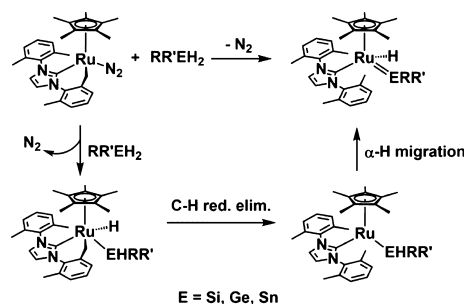
would involve initial E−H oxidative addition followed by C−H reductive elimination and then α-hydrogen migration. With this strategy in mind, complex **3** was treated with the silanes *p*-TolSiH$_3$, MesSiH$_3$, and TripSiH$_3$ (Trip = 2,4,6-triisopropylphenyl). As shown in eq 3, these reactions did not provide the
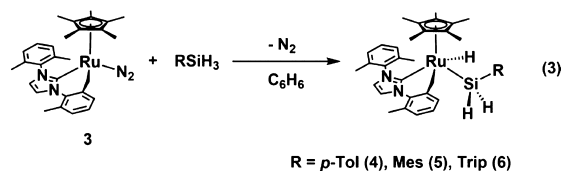
anticipated silylene complexes but instead gave the cyclometalated silyl hydride complexes Cp*(IXy-H)(H)RuSiH$_2$R [R = *p*-Tol (**4**), Mes (**5**), Trip (**6**), respectively]. These isolated complexes are thermally stable, colorless solids that were characterized by elemental analysis and multinuclear NMR spectroscopy. In the ^{1}H NMR spectra, all three compounds exhibit resonances for the inequivalent hydrogens bound to silicon, and two sets of doublets are assigned to the diastereotopic methylene hydrogens of the cyclometalated IXy ligand. The NMR data and selected bond lengths for complexes **4**−**6** are summarized in Table 1. The hydride ligands appear at around −10 ppm in the ^{1}H NMR spectrum, and the small $^2J_{SiH}$ coupling constants (~20 Hz for **4** and **5**; <7 Hz for **6**) indicate a weak or negligible interaction between the hydride and silyl ligands. In addition, the upfield [29]Si resonances for **4**, **5**, and **6** are consistent with the presence of silyl ligands bonded to ruthenium.[18] The solid-state structures of **4** and **6** were determined by X-ray crystallography (Figure 4) and revealed unexceptional Ru−CH$_2$, Ru−H, and Ru−Si bond distances (Table 1).

Table 1. NMR Data (in Benzene-d_6) and Selected Bond Lengths for 4−6

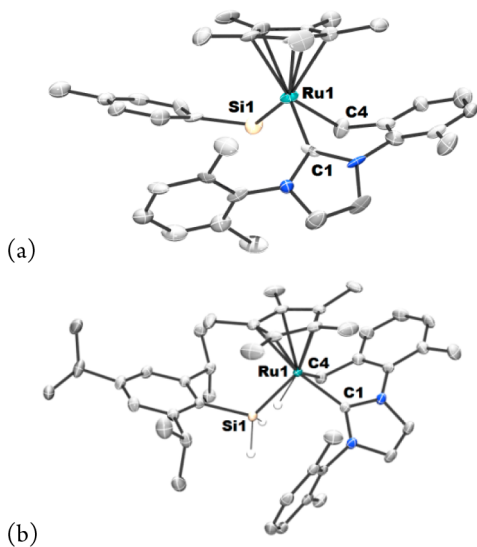| complex	δ^1_H(Si−H) ($^1J_{SiH}$)	δ^1_H(Ru−H) ($^2J_{SiH}$)	δ^{29}_{Si}(Ru−Si)	Ru−CH$_2$ (Å)	Ru−Si (Å)
Cp*(IXy-H)(H)RuSiH$_2$-p-Tol (4)	4.87 (183 Hz), 4.55 (171 Hz)	−10.04 (21.6 Hz)	5.3	2.029(9)	2.351(3)
Cp*(IXy-H)(H)RuSiH$_2$Mes (5)^a	4.58 (175 Hz), 4.52 (176 Hz)	−9.75 (17.4 Hz)	−19.8	−	−
Cp*(IXy-H)(H)RuSiH$_2$Trip (6)	4.42 (259 Hz), 4.23 (269 Hz)	−9.51 (<7 Hz)	−26.2	2.206(3)	2.422(7)

^{a}No crystal structure.

(a)

(b)

Figure 4. Molecular structures of (a) 4 and (b) 6 displaying thermal ellipsoids at the 50% probability level. Selected H atoms have been omitted for clarity.

influenced by the inclusion of the dispersion corrections, and thus, dispersion corrections were not considered further. The Gibbs energy differences between the corresponding silyl hydride and silylene complexes are 12.6 kcal/mol (4/4a), 4.9 kcal/mol (5/5a), and 2.5 kcal/mol (6/6a) (Figure 5). These
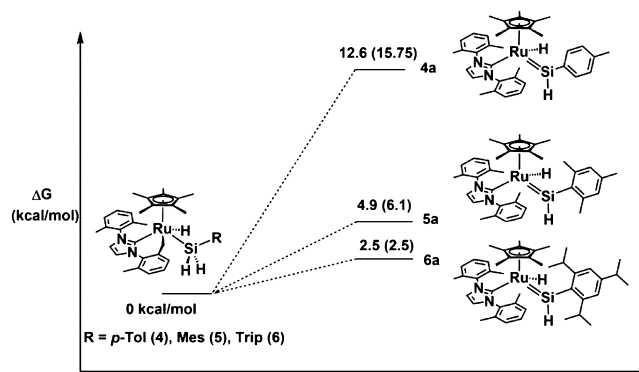

Figure 5. Gibbs energies (kcal/mol) for silylene hydride complexes 4a, 5a, and 6a relative to metalated Ru silyl hydride complexes 4, 5, and 6. Values in parentheses include dispersion corrections.

The distinctly larger $^2J_{SiH}$ coupling constant for 4 versus 6 suggests that the Si−H bond is more strongly activated (and oxidatively added) in 6. On the basis of this information alone, it would seem that the silane might be more readily displaced from 4 in its reaction chemistry. However, complex 4 in benzene-d_6 remained unchanged over 9 days under an atmosphere of ethylene at 24 °C, whereas under the same conditions 6 reacted to eliminate free TripSiH$_3$ and form a new complex. By ^{1}H NMR spectroscopy, the latter was characterized in solution as the ethylene complex Cp*(IXy-H)Ru(η^2-C$_2$H$_4$), which exhibits two sets of doublet resonances at 2.58 ($^1J_{HH}$ = 10.98 Hz) and 2.50 ($^1J_{HH}$ = 10.98 Hz) ppm corresponding to diastereotopic RuCH$_2$ methylene hydrogens and three broad resonances at 1.96 (2H), 1.72 (1H), and 1.16 (1H) ppm attributed to the four hydrogens of the ethylene ligand. Presumably this reactivity of 6 is driven by steric pressure exerted by the bulky Trip group.

DFT Analysis of the Relative Stabilities of the Silyl Hydride and Corresponding Silylene Hydride Complexes. On the basis of spectroscopic data, 4, 5, and 6 are described as Ru(IV) silyl hydride complexes both in solution and in the solid state. Notably, analogous Cp*($^iPr_2$MeP)Ru derivatives adopt the isomeric silylene hydride structures Cp*($^iPr_2$MeP)(H)Ru=SiHR.[9a] This difference may originate in a higher tendency of the IXy ligand to undergo cyclometalation and/or the stronger donor properties of the NHC ligand versus the phosphine ligand, which could stabilize the relatively high oxidation state for ruthenium. To gain more insight into these differences, DFT calculations including Grimme's dispersion corrections were also carried out (see Computational Details). The energies of 4a, 5a, and 6a relative to those of silyl complexes 4, 5, and 6 were not significantly

trends indicate that the Mes- and Trip-substituted silylene complexes are likely to be more readily accessible in the reaction chemistry of 5 and 6. Of course, this assumes a rapid equilibrium between the two types of isomeric structures. With increasing bulk of the aryl group, the lower coordination number of the nonmetalated silylene isomer becomes more preferred. This preference is more pronounced with the bulky Trip substituent.

The optimized structures of 4a, 5a, and 6a are shown in Figure 6. The Ru−Si bond lengths of 2.227 Å (4a), 2.220 Å (5a), and 2.223 Å (6a) are comparable to those of the crystallographically characterized neutral silylene complexes Cp*($^iPr_2$MeP)(H)Ru=SiHTrip [Ru−Si = 2.205(1) Å][9a] and Cp*(CO)(H)Ru=SiH[C(SiMe$_3$)$_3$] [Ru−Si = 2.220(2) Å].[9c] The Ru−Si−H angles in 4a (122.9°), 5a (127.0°), and 6a (124.8°) are similar, and the silicon center is coplanar with its Ru, H, and C$_{ipso}$ substituents (the sums of the angles at Si are 357.0° for 4a, 359.4° for 5a, and 357.4° for 6a), suggesting sp^2 hybridization at Si. Notably, the angle between the least-squares planes of the aryl substituent and that of the silylene ligand (defined by the Ru, H and Si atoms) varies greatly in going from 4a (30.1°) to 5a (80.6°) and 6a (85.2°). This variation may be attributed to steric factors that enforce an angle close to 90° for the more sterically demanding aryl groups in 5a and 6a, and twisting toward a coplanar arrangement of the silylene and aryl group planes might be favored by π conjugation with the Ru−Si π bond.

Reactions of Cp*(IXy-H)(H)RuSiH$_2$(Trip) (6) with Polar Compounds. Treatment of 6 with 1 equiv of benzaldehyde at ambient temperature immediately and quantitatively afforded the benzaldehyde adduct 7, as evidenced by NMR spectroscopy. Unfortunately, attempts to isolate 7 were unsuccessful
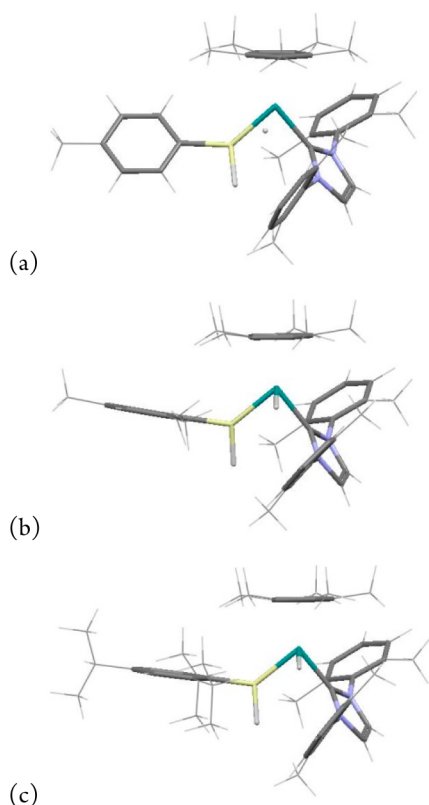
(a)

(b)

(c)

Figure 6. Side views of the optimized structures of (a) **4a**, (b) **5a**, and (c) **6a**.

because of its thermal instability. The ^{1}H NMR spectrum of **7** exhibits distinct resonances at −10.63 (Ru−*H*, $^3J_{HH}$ = 4.3 Hz, J_{SiH} = 60.8 Hz), 5.03 (Ru−C*H*), and 7.34 (Si−*H*, $^1J_{SiH}$ = 211 Hz) ppm, and there is one ^{29}Si resonance at −14.5 ppm in the ^{1}H−^{29}Si heteronuclear multiple-bond correlation (HMBC) spectrum. Thus, this complex appears to possess a Ru−H−Si bridging interaction as well as a terminal, unactivated Si−H bond. On the basis of these data, **7** is identified as the product resulting from a [2 + 2] cycloaddition to the silylene complex (Scheme 3). For comparison, Tobita et al.[9c,19] reported that the neutral silylene complex Cp*(CO)(H)Ru=SiH[C(SiMe$_3$)$_3$]

Scheme 3
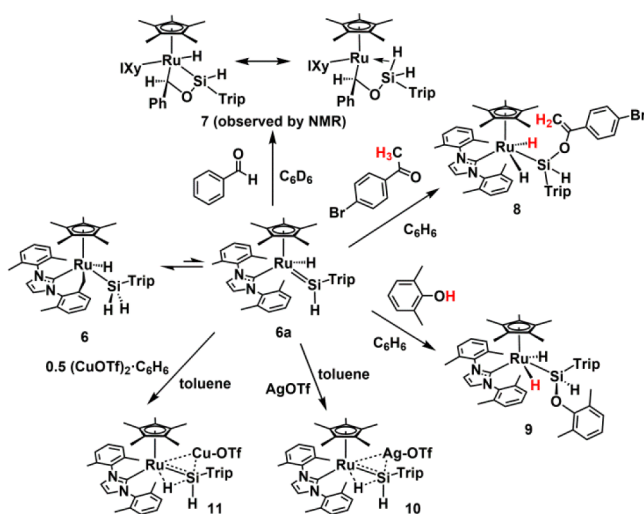
undergoes a similar cycloaddition with benzaldehyde in the first step en route to the final product Cp*(CO)(H)Ru=Si(OCH$_2$Ph)[C(SiMe$_3$)$_3$]. This result suggests that **6** is in equilibrium with the silylene hydride complex **6a** in solution at room temperature (Scheme 3).

The reaction of **6** with 4-bromoacetophenone resulted in formation of Cp*(IXy)(H)$_2$RuSiH[OC(=CH$_2$)C$_6$H$_4$Br]Trip (**8**), which was isolated as a pale-yellow powder in 78% yield (Scheme 3). In its ^{1}H NMR spectrum, complex **8** exhibits one Si−H resonance at 6.45 ppm, two broad signals at 4.66 and 4.45 ppm for the inequivalent hydrogens of a C=CH$_2$ unit, and two upfield signals at −10.48 and −10.94 ppm for the hydride ligands. Crystals of **8** were grown from a saturated pentane solution at −30 °C and characterized by X-ray crystallography (Figure 7). The activation of enolizable ketones
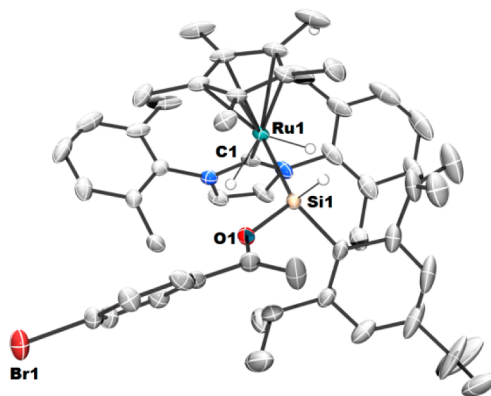

Figure 7. Molecular structure of **8** displaying thermal ellipsoids at the 50% probability level. H atoms have been omitted for clarity.

(such as acetone or acetophenone) by silylene complexes has precedent; for example, silyl enol ethers were isolated as the final products in reactions of the cationic, base-stabilized silylene adduct [Cp*(PMe$_3$)$_2$Ru=SiPh$_2$(NCMe)][BPh$_4$] with acetone or acetophenone.[20] The cationic Ir silylene complex [(PNP)Ir=SiPh$_2$][B(C$_6$F$_5$)$_4$] was also found to activate enolizable ketones to yield silyl enol ether complexes.[21] Additionally, Cp*(CO)(H)Ru=SiH[C(SiMe$_3$)$_3$] reacts with acetophenone to produce the silyl enol ether complex Cp*(CO)(H)$_2$RuSiH[OC(=CH$_2$)Ph]C(SiMe$_3$)$_3$.[19] The latter complex is thought to result from initial coordination of acetophenone to the silylene ligand followed by α-hydrogen transfer to Ru through a six-membered transition state. The formation of **8** again implicates **6a**, the silylene isomer of **6**, as the reactive species in solution since this transformation likely occurs by a mechanism analogous to that reported for Cp*(CO)(H)Ru=SiH[C(SiMe$_3$)$_3$].[19] This was further supported by a deuterium-labeling experiment involving addition of acetophenone-d_3 to **6**, which resulted in the sole formation of Cp*(IXy)(H)(D)RuSiH[OC(=CD$_2$)Ph]Trip (**8**-d_3) as determined by ^{1}H and ^{2}H NMR spectroscopy. Presumably this reaction proceeds by way of coordination of the carbonyl compound to silicon, as shown in Scheme 4.

Treatment of **6** with 2,6-dimethylphenol in benzene-d_6 cleanly afforded Cp*(IXy)(H)$_2$RuSiH(2,6-Me$_2$C$_6$H$_3$O)Trip (**9**) in quantitative yield as determined by ^{1}H NMR spectroscopy (Scheme 3). A labeling experiment utilizing 2,6-Me$_2$C$_6$H$_3$OD in this reaction cleanly gave the monodeuteride Cp*(IXy)(H)(D)RuSiH(2,6-Me$_2$C$_6$H$_3$O)Trip (**9**-d), as indicated by ^{1}H and ^{2}H NMR spectroscopy. No evidence for RuD/

Scheme 4
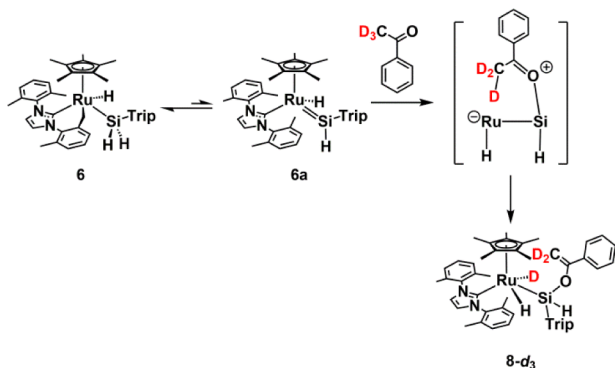
SiH exchange was observed after 6 h in benzene-d_6 solution at 24 °C. These results are consistent with a mechanism related to that shown in Scheme 4 involving coordination of the phenol to silicon followed by H(D) transfer to ruthenium. Kinetics experiments at a reaction temperature of 24 °C in benzene-d_6 solvent employed pseudo-first-order conditions with the phenol in large excess over 3 half-lives (see the Supporting Information). Taken together, the evidence points to a pre-equilibrium involving the interconversion of **6** with **6a** and trapping of **6a** by the phenol (Scheme 3).

As described above, the reactions of **6** with benzaldehyde, acetophenone, and 2,6-dimethylphenol are consistent with a rapid equilibrium between **6** and **6a**, with the latter silylene complex being the more reactive isomer. In an attempt to observe both species as an equilibrium mixture, a toluene-d_8 solution of **6** was cooled to −80 °C. However, the ^{1}H NMR spectrum of the cold solution contained only resonances for the silyl complex **6**. Further evidence for this equilibrium was sought with experiments designed to trap **6a** with a Lewis base, since transition-metal silylene complexes often exhibit Lewis acidic character for the silicon center.[5,9c,21−23] However, the addition of 1 equiv of N,N-dimethylaminopyridine (DMAP), PhMe₂P, or PhMe₂P=O to a benzene-d_6 solution of **6** led to no observed reaction over 3 days. Also, dissolution of **6** in THF-d_8 resulted only in the characteristic ^{1}H NMR resonances for **6**. These results suggest that like [Cp*(PMe₃)(H)Ir(= SiMes₂)]OTf,[24] **6a** may not have a very Lewis acidic silicon center. Surprisingly, however, the Lewis acidic compounds MOTf (M = Cu, Ag) were found to react with **6** to form adducts of the silylene complex **6a** (Scheme 3).

Reactions of 6 with MOTf (M = Ag, Cu). Reaction of **6** with an equimolar amount of AgOTf in benzene-d_6 resulted in a deep-violet solution and the formation of the new complex **10**. Analysis of the reaction mixture with a [1]H−^{29}Si HMBC NMR experiment revealed the presence of a downfield [29]Si resonance at 182.2 ppm correlated to a downfield ^{1}H NMR resonance at 7.99 ppm. The latter resonance is associated with a strong $^1J_{SiH}$ coupling constant of 176.0 Hz. Taken together, these results indicate the presence of a hydridosilylene (= SiHR) ligand.[9] Complex **10** was isolated as violet crystals from toluene/pentane, and analysis of a THF solution of **10** by positive-ion-mode electrospray ionization mass spectrometry revealed the presence of the {Cp*(IXy)(H)Ru[SiHTrip]Ag}[+] cation (m/z 853.3). In benzene-d_6, **10** has a half-life of ca. 12 h, and after 1 day an insoluble black precipitate (presumably silver metal) forms. The structure of **10** was confirmed by a single-crystal X-ray diffraction experiment, which revealed the presence of a SiHTrip unit bridging Cp*(IXy)(H)Ru and

AgOTf fragments (Figure 8), resulting in Ru−Si and Ru−Ag bond distances of 2.264(1) and 2.6813(8) Å, respectively. The
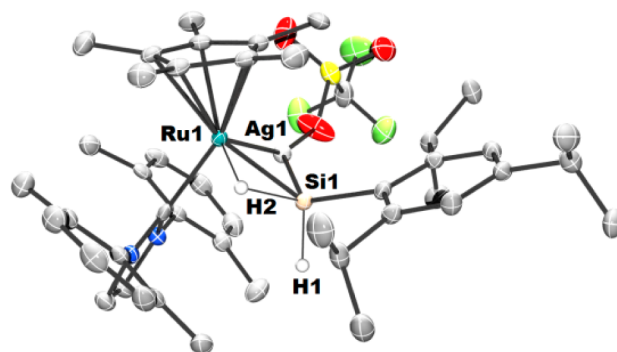

Figure 8. Molecular structure of **10** displaying thermal ellipsoids at the 50% probability level. H atoms have been omitted for clarity.

Ag−Si distance of 2.562(1) Å is slightly longer than that found in the only other structurally characterized silver−silicon-bonded compound, Ag{Si(SiMe₃)[C(Xyl)=NSiMe₃]₂Li}₂(μ-I) [2.482(1) Å],[25] and is roughly equal to the sum of covalent radii of silicon and silver (2.56 Å).[26] Furthermore, the hydride ligand, which was located and refined, adopts a position that bridges the Ru and Si centers (J_{SiH} = 36.6 Hz). The Ru−Si bond length in **10** is only slightly longer than the corresponding distance calculated for **6a** (2.217 Å), consistent with significant sharing of electron density between the Ru, Si, and Ag atoms.

The molecular structure of **10** may be described as a distorted four-legged piano stool, reminiscent of the structurally characterized cationic silylene complex [Cp*(iPr₃P)Ru(μ-H)₂SiHMes][+],[27] which features two hydride ligands in close contact with the silicon center. Formally, the latter silylene complex may be viewed as being derived from protonation of the neutral silylene complex Cp*(iPr₃P)(H)Ru=SiHMes, which does not possess a significant Si···H interaction.[9a] Thus, the addition of a proton results in greater electrophilicity at silicon and strong interactions of the silicon with both hydrides, such that the Ru(μ-H)₂Si moiety is nearly planar.[27] This geometry presumably allows for participation of the formally empty 3p orbital on silicon in bonding to the hydride ligands. Similarly, complex **10** possesses hydride and AgOTf groups that bridge the Ru−Si bond, resulting in a nearly planar Ru(μ-H)(μ-Ag)Si arrangement.[28] The H···Si distance in **10** is longer than the corresponding distance in [Cp*(iPr₃P)Ru(μ-H)₂SiHMes][+],[27] consistent with the smaller J_{SiH} value for **10** (36.6 vs 62.3 Hz). The weaker H···Si interaction in **10** appears to reflect lower silicenium character at silicon, consistent with replacement of a proton with *neutral* AgOTf. Interestingly, **10** may also be viewed as a π complex in which a Ru=Si π bond is coordinated to the silver center (vide infra). Notably, a related adduct, (PNP)Ir=C(H)O^tBu(AgOTf), has been reported by Whited.[29] In this structure, AgOTf appears to interact with the π electron density of the formal Ir=C double bond, as indicated by the 86.5° angle between the IrAgC plane and the carbene IrC(O^tBu)H least-squares plane and an elongation of the Ir−C bond from 1.884 Å in the parent carbene to 1.917 Å in the AgOTf adduct.

Treatment of **6** with 0.5 equiv of (CuOTf)₂·C₆H₆ in benzene-d_6 also resulted in a color change to violet, and both ^{1}H and ^{29}Si NMR spectra indicate a structure similar to **10**. The

resulting copper–ruthenium complex **11** was isolated from toluene/pentane as a violet solid in 71% yield.

Given the similarity of **10** and **11** to the cationic complex [Cp*(^{i}Pr$_3$P)Ru(μ-H)$_2$SiHMes]$^+$, it was of interest to explore their reactivities toward alkenes. It should be noted that the terminal Si–H bond of [Cp*(^{i}Pr$_3$P)Ru(μ-H)$_2$SiHMes]$^+$ adds rapidly to alkenes at −80 °C, whereas the neutral (deprotonated) analogue Cp*(^{i}Pr$_3$P)(H)Ru=SiHMes is unreactive toward alkenes.[9a,b,27] However, treatment of **10** or **11** with either 1-hexene or *tert*-butylethylene in benzene-d_6 did not lead to an observable reaction at 50 °C over 24 h. Presumably this difference reflects lower silicenium character for **10** and **11**, as mentioned above.[9a,b,27]

Complexes **10** and **11** are striking in that they represent the binding of Lewis acids to the silylene ligand of **6a**. This appears to conflict with a major chemical property previously identified for transition-metal silylene complexes, namely, that they act as Lewis acids and bind a variety of Lewis bases at silicon.[5,9c,21−23] This unusual property of **6a** may derive from strong electron donation from the NHC ligand. Whereas **6a** does not bind to THF, DMAP, PhMe$_2$P, or PhMe$_2$P=O, in preference to formation of metalated **6**, it does seem to transiently bind to oxygen-centered substrates as described above (e.g., Scheme 4). Thus, **6a** may be regarded as displaying amphiphilic properties, binding both Lewis acids and Lewis bases in a manner reminiscent of free silylenes.[10,30]

Analysis of the Bonding in 10 and 11. Scheme 5 provides selected representations of the bonding in the Ru(μ-

Scheme 5
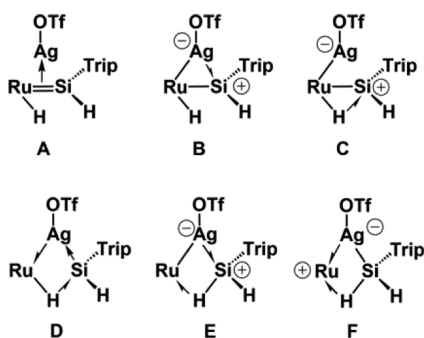
H)(μ-AgOTf)Si portion of complex **10** (structures **A-F**). Structures **A−C** retain Ru−Si bonding, and **A** may be regarded as a π complex in which Ru=Si π-bond electron density is donated to the silver atom. In terms of the classifications for three-center, two-electron interactions developed by Green, Green and Parkin,[31] the Ru−Ag−Si bonding in **A** may be viewed as an [XZX] interaction, with the bridging Ag atom playing the role of a Z-type ligand. Structures **B** and **C** represent valence-bond structures that feature a metal−silicon single bond complemented by RuAgSi (**B**) and RuHSi (**C**) three-center, two-electron bonds. In these structures, the half-arrow describes donation from a bonding electron pair to an acceptor atom.[32] For **B** and **C**, the silicon center possesses silicenium character and is stabilized by donation from the Ru→Ag and Ru−H bonds, respectively. These structures emphasize similarities to the bonding picture developed for [Cp*(^{i}Pr$_3$P)Ru(μ-H)$_2$SiHMes]$^+$, in which a silicenium fragment is stabilized by donation from two Ru−H bonds into a 3p orbital of silicon.[27]

The nature of the bonding in **10** and **11** was probed by natural bond order (NBO) analysis[33] and quantum theory of atoms in molecules (QTAIM)[34] calculations using DFT-optimized structures. The Wiberg bond indices (WBIs), which function as nominal bond orders, for **10** and **11** are 0.66 and 0.62, respectively (see the Supporting Information). These values are higher than the value of 0.51 calculated for silyl complex **6** with a formal Ru−Si single bond but lower than the value of 0.99 calculated for silylene complex **6a**. The negative NBO charges of the MOTf fragments (M = Ag, Cu) in **10** and **11** indicate that the entire ruthenium complex Cp*(IXy)(H)Ru=SiHTrip behaves as an electron donor to MOTf. Thus, this ruthenium silylene complex (**6a**) is stabilized by a Lewis acid.
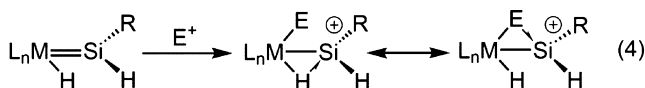
The second-order NBO analysis for **10** and **11** suggests that these compounds are best represented by valence-bond structures **A** and **C**, and no evidence for a structure in which M (M = Ag, Cu) plays the role of an electron donor was found to have a significant weight. On the other hand, the NBO analysis points to the M centers playing the role of an acceptor, with donation being shared almost equally by the occupied Ru−Si, Ru−H, and Ru−C bonding orbitals along with some contribution from a Ru lone pair. This emphasizes the role of the NHC ligand in enhancing the electron-donating power of the entire hydrido silylene complex. Thus, in this complex the interaction of the Ru−silylene group with M is not limited to donation from the formal Ru−Si double bond but also involves delocalization onto other ligands bonded to Ru (in particular Ru−H). The QTAIM analysis is consistent with the NBO analysis in pointing to the dominant role of **A** and **C**. Small negative values of $\nabla^2\rho_b$ for the Ru−Si bonds in **10** and **11** suggest a covalent interaction, while the positive values of $\nabla^2\rho_b$ for the Ru−M and Si−M bonds are consistent with donor−acceptor interactions (see the Supporting Information).

Structures **D−F** are additional valence-bond structures that describe three-center, two-electron bonding involving the bridging hydride and AgOTf groups but without Ru−Si bonding. Such structures are analogous to those used to describe the bonding in η^3-silane complexes of the type [PhB(CH$_2$PPh$_2$)$_3$](H)Ru(η^3-H$_2$SiRR′).[35] In **D** and **E**, the silicon centers formally possess electron-deficient silylene (**D**) and silicenium (**E**) characters and are stabilized by donation from the Ru−H and Ru→Ag bonds, respectively. Structure **F** may be described as possessing a silyl anion complex of AgOTf as a ligand. In this case, coordination of (TfO)AgSiH$_2$(Trip) involves donation to ruthenium from two bonding orbitals associated with silicon (Si−H and Si→Ag) and is therefore highly related to the situation observed for η^3-silane complexes of ruthenium.[35,36]

■ CONCLUDING REMARKS

The results described above highlight the substantial variations in chemical properties that can accompany simple changes in supporting ligands for silylene complexes. The IXy N-heterocyclic carbene ligand of the Cp*(IXy)Ru fragment gives rise to metalated silyl hydride complexes that readily isomerize to reactive silylene complexes. Thus, this system involving rapid isomerization of cyclometalated Cp*(IXy-H)(H)Ru(SiH$_2$Trip) (**6**) to the more reactive isomer Cp*-(IXy)(H)Ru=SiHTrip (**6a**) illustrates convenient access to reactive silylene complexes that may be difficult to isolate in pure form. The latter silylene complex has been shown to participate in C−H, O−H, and C=O bond activations.

Most notably, **6a** adds the electrophiles CuOTf and AgOTf to produce "silylene adducts" of the type Cp*(IXy)Ru(μ-H)(μ-MOTf)SiHTrip (**10** and **11**). Such adducts are related to cationic silylene complexes such as $[Cp*(^iPr_3P)Ru(\mu$-H)$_2$SiHMes]$^+$,[27] which possess two three-center, two-electron RuHSi interactions and an activated terminal Si−H bond that directly adds to olefins.[27] In the latter case, the bridge bonding and reactive Si−H bond result from addition of a proton to Cp*($^iPr_3P$)(H)Ru=SiHMes. Interestingly, addition of AgOTf to **6a** also results in the formation of two three-center, two-electron interactions (RuAgSi and RuHSi), but the resulting terminal Si−H bond does not add to 1-hexene (vide supra). This may be understood in terms of the neutrality of the added electrophile, which does not impart enough cationic character to the silicon center (AgOTf vs H$^+$). However, these results point to the possible formation of a large class of reactive metal silylene complexes of the type $[L_nM(\mu$-H)(μ-E)SiHR]$^{n+}$ activated by addition of an electrophile (E) to a silylene complex (eq 4). This class of compounds could exhibit a wide range of electronic and chemical properties, depending on the natures of E and L_nM.

$$L_nM=Si\overset{R}{\underset{H}{\cdots}} \quad \overset{E^+}{\longrightarrow} \quad L_nM-Si\overset{\oplus R}{\underset{H}{\cdots}}E \quad \longleftrightarrow \quad L_nM-Si\overset{\oplus R}{\underset{H}{\cdots}}E \qquad (4)$$

■ EXPERIMENTAL SECTION

General Procedures. All experiments were conducted under nitrogen using standard Schlenk techniques or in a N$_2$-filled drybox. Non-deuterated solvents were distilled under N$_2$ from appropriate drying agents and stored in PTFE-valved flasks. Benzene-d_6 was dried by vacuum distillation from Na/K alloy. The compounds [Cp*RuCl]$_4$,[37] IXy,[38] and KBn[39] were prepared according to literature procedures. 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 protonated solvent for ^{1}H NMR spectra. ^{13}C{^{1}H} NMR spectra were calibrated internally with the resonance for the solvent relative to tetramethylsilane. For ^{13}C{^{1}H} 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 ^{1}H−^{29}Si HMBC experiments unless specified otherwise. All spectra were recorded at room temperature unless otherwise noted. Complex multiplets are noted as "m" and broad resonances as "br".

Syntheses. *Cp*Ru(IXy)Cl (1).* A Schlenk flask was charged with 50 mL of THF and a mixture of IXy (2.00 g, 7.2 mmol) and [Cp*RuCl]$_4$ (1.96g, 1.8 mmol). Upon stirring for 2 h at ambient temperature, all volatile materials were removed under vacuum. The remaining solid was extracted with 100 mL of toluene, and the resulting dark-purple solution was filtered through Celite and then evaporated under vacuum to give an analytically pure purple solid. Yield: 3.69 g (93%). ^{1}H NMR (C$_6$D$_6$, 600 MHz): δ 7.01 (t, J_{HH} = 8.0 Hz, 4H), 6.93 (br, 4H), 6.14 (s, 2H), 2.29 (br, 12H, xylyl Me), 1.22 (s, 15H, C$_5$Me$_5$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 150.9 MHz): δ 199.9 (NCN), 139.4, 137.9, 134.9, 128.8, 128.3, 127.9, 122.6, 72.8 (C$_5$Me$_5$), 19.7, 18.7, 10.5 (C$_5$Me$_5$). Anal. Calcd for C$_{29}$H$_{35}$N$_2$RuCl: C, 63.55; H, 6.44; N, 5.11. Found: C, 63.40; H, 6.17; N, 5.02.

*Cp*Ru(IXy-H) (2) and Cp*Ru(IXy-H)(N$_2$) (3).* In a drybox, a 6 mL toluene solution of **1** (0.189 g, 0.34 mmol) and KCH$_2$Ph (0.045 g, 0.34 mmol) was stirred at ambient temperature for 3 h. After removal of all volatile materials under vacuum, the solid was extracted with 30 mL of pentane. The filtrate was dried under vacuum to afford **2** as an analytically pure brown solid. Yield: 0.1623 g (92%). Anal. Calcd for C$_{29}$H$_{34}$N$_2$Ru: C, 68.07; H, 6.70; N, 5.47. Found: C, 68.18; H, 6.90; N,

5.49. Cooling a saturated pentane solution of **2** under N$_2$ at −30 °C afforded yellow crystals of **3**. The crystals were crushed under vacuum (causing the formation of **2**), and thus, a yield cannot be reported. ν(N$_2$) = 2069 cm^{-1}. The ^{1}H NMR spectrum of **2** (without **3**) was obtained by subjecting a benzene-d_6 solution of **2** to three freeze−pump−thaw cycles. ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 7.07 (d, J_{HH} = 7.5 Hz, 2H, xylyl H), 6.95 (t, J_{HH} = 7.5 Hz, 2H, xylyl H), 6.85 (d, J_{HH} = 7.5 Hz, 2H, xylyl H), 5.60 (s, 2H, imidazolylidene H), 2.33 (br, 4H, xylyl Me), 2.04 (s, 6H, xylyl Me), 1.48 (s, 15H, C$_5$Me$_5$).

Cp(IXy-H)(H)RuSiH$_2$-p-Tol (4).* In a drybox, a 6 mL benzene solution of **3** (0.081 g, 0.15 mmol) and H$_3$Si-p-Tol (0.022 g, 0.18 mmol) was stirred at ambient temperature for 3 h. All volatile materials were removed under vacuum, and the solid was washed with 5 mL of pentane three times and then dried under vacuum to afford a white powder. Yield: 0.084 g (83%). ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 7.40 (d, J_{HH} = 7.6 Hz, 2H), 7.23 (t, J_{HH} = 7.6 Hz, 1H), 7.19 (d, J_{HH} = 7.6 Hz, 1H), 7.11 (d, J_{HH} = 7.4 Hz, 3H), 6.92 (m, 2H), 6.74 (d, J_{HH} = 7.6 Hz, 1H), 6.65 (d, J_{HH} = 2.2 Hz, 1H), 5.97 (d, J_{HH} = 2.2 Hz, 1H), 4.87 (t, J_{SiH} = 179 Hz, J_{HH} = 5.0 Hz, 1H), 4.55 (t, J_{SiH} = 165 Hz, J_{HH} = 5.0 Hz, 1H), 2.39 (d, J_{HH} = 11.3 Hz, 1H, CH$_2$), 2.30 (s, 3H, CH$_3$), 2.12 (s, 3H, CH$_3$), 2.11 (s, 3H, CH$_3$), 1.93 (s, 3H, CH$_3$), 1.56 (d, J_{HH} = 11.3 Hz, 1H, CH$_2$), 1.32 (s, 15H, C$_5$Me$_5$), −10.04 (t, J_{SiH} = 23.6 Hz, J_{HH} = 5.0 Hz, 1H, RuH). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.8 MHz): δ 196.5 (NCN), 150.2, 140.9, 139.3, 138.9, 137.6, 136.4, 136.1, 135.2, 129.6, 128.5, 128.2, 127.9, 127.5, 125.8, 125.6, 124.0, 121.5, 120.9, 93.3 (C$_5$Me$_5$), 21.2, 19.1, 18.7, 18.4, 12.8, 8.9 (C$_5$Me$_5$). ^{29}Si NMR (C$_6$D$_6$, 99.4 MHz): δ 5.3. Anal. Calcd for C$_{36}$H$_{44}$N$_2$SiRu: C, 68.21; H, 7.00; N, 4.42. Found: C, 68.34; H, 7.05; N, 4.33.

Cp(IXy-H)(H)RuSiH$_2$Mes (5).* In a drybox, a 6 mL benzene solution of **3** (0.098 g, 0.18 mmol) and MesSiH$_3$ (0.033 g, 0.22 mmol) was stirred at ambient temperature for 3 h. All volatile materials were removed under vacuum, and the solid was washed with 5 mL of pentane three times and then dried under vacuum to afford a white powder. Yield: 0.092 g (72%). ^{1}H NMR (C$_6$D$_6$, 600 MHz): δ 7.24 (d, J_{HH} = 7.2 Hz, 1H), 7.11 (t, J_{HH} = 7.2 Hz, 1H), 6.97 (d, J_{HH} = 7.2 Hz, 1H), 6.91 (t, J_{HH} = 7.2 Hz, 2H), 6.88 (s, 2H), 6.74 (d, J_{HH} = 7.2 Hz, 1H), 6.61 (d, J_{HH} = 2.4 Hz, 1H), 5.86 (d, J_{HH} = 2.4 Hz, 1H), 4.57 (d, J_{SiH} = 175 Hz, J_{HH} = 5.4 Hz, 1H), 4.51 (dd, J_{SiH} = 176 Hz, J_{HH} = 5.4 Hz, J_{HH} = 1.8 Hz, 1H), 2.82 (d, J_{HH} = 11.4 Hz, 1H, CH$_2$), 2.42 (s, 6H, Mes Me), 2.29 (s, 3H, CH$_3$), 2.15 (s, 3H, CH$_3$), 2.08 (s, 3H, CH$_3$), 2.05 (d, J_{HH} = 11.4 Hz, 1H, CH$_2$), 1.55 (s, 3H, CH$_3$), 1.32 (s, 15H, C$_5$Me$_5$), −9.75 (s, 1H, RuH). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 150.9 MHz): δ 194.1 (NCN), 144.6, 135.8, 134.6, 129.6, 128.6, 128.2, 127.2, 126.0, 125.4, 124.9, 123.3, 121.0, 93.9 (C$_5$Me$_5$), 24.2, 20.9, 19.5, 18.9, 18.2, 11.8, 9.1 (C$_5$Me$_5$). ^{29}Si NMR (C$_6$D$_6$, 99.4 MHz): δ −19.8. Anal. Calcd for C$_{38}$H$_{48}$N$_2$SiRu: C, 68.95; H, 7.31; N, 4.23. Found: C, 68.65; H, 7.30; N, 4.20.

Cp(IXy-H)(H)RuSiH$_2$Trip (6).* In a drybox, a 6 mL benzene solution of **3** (0.145 g, 0.27 mmol) and TripSiH$_3$ (0.094 g, 0.41 mmol) was stirred at ambient temperature for 3 h. All volatile materials were removed under vacuum, and the solid was washed with 5 mL of pentane three times and then dried under vacuum to afford a white powder. Yield: 0.137 g (68%). ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 7.23 (d, J_{HH} = 6.49 Hz, 1H), 7.19 (s, 2H), 7.13 (m, 1H), 7.01 (m, 2H), 6.89 (t, J_{HH} = 7.10 Hz, 1H), 6.73 (d, J_{HH} = 7.72 Hz, 1H), 6.60 (s, 1H), 5.89 (s, 1H), 4.42 (br, J_{SiH} = 259 Hz, 1H, SiH), 4.23 (br, J_{SiH} = 269 Hz, 1H, SiH), 3.22 (m, 2H, CHMe$_2$), 2.94−2.90 (m, 2H, 1 for CHMe$_2$ and 1 for CH$_2$), 2.20 (d, J_{HH} = 11.9 Hz, 1H, CH$_2$), 2.16 (s, 3H, xylyl Me), 2.07 (s, 3H, xylyl Me), 1.91 (s, 3H, xylyl Me), 1.47 (d, 6H, CHMe$_2$), 1.44 (d, 6H, CHMe$_2$), 1.34 (d, 6H, CHMe$_2$), 1.28 (s, 15H, C$_5$Me$_5$), −9.51 (s, 1H, RuH). ^{13}C NMR (C$_6$D$_6$, 125.8 MHz): δ 194.9 (NCN), 155.9, 150.4, 148.7, 140.8, 140.4, 138.8, 136.3, 135.7, 129.9, 129.5, 128.7, 127.6, 126.9, 126.2, 125.5, 123.0, 121.8, 120.4, 95.4 (C$_5$Me$_5$), 34.0, 26.4, 26.3, 24.5, 20.3, 19.9, 19.7, 14.9, 10.2 (C$_5$Me$_5$). ^{29}Si NMR (C$_6$D$_6$, 99.4 MHz): δ −26.2. Anal. Calcd for C$_{44}$H$_{60}$N$_2$SiRu: C, 70.83; H, 8.11; N, 3.75. Found: C, 70.61; H, 8.34; N, 4.06.

Cp(IXy)(H)Ru[CHPhOSiHTrip] (7).* A 0.7 mL benzene-d_6 solution of **6** (0.030 g, 0.041 mmol) and benzaldehyde (0.004 g, 0.041 mmol) was added to a J. Young NMR tube at ambient temperature within 5 min. Attempts to isolate **7** failed due to its thermal instability. ^{1}H

NMR (C$_6$D$_6$, 500 MHz): δ 8.11 (br, 1H), 7.34 (d, J_{SiH} = 211.3 Hz, J_{HH} = 5.2 Hz, 1H, SiH), 7.33 (s, 1H), 7.10−6.96 (m, 7H), 6.93 (t, J_{HH} = 7.2 Hz, 1H), 6.88 (s, 1H), 6.63 (d, J_{HH} = 7.2 Hz, 1H), 6.32 (d, J_{HH} = 7.3 Hz, 1H), 5.88 (s, 1H), 5.78 (s, 1H), 5.03 (br, 1H, CHPh), 4.72 (septet, J_{HH} = 6.8 Hz, 1H, CHMe$_2$), 2.99 (septet, J_{HH} = 6.7 Hz, 1H, CHMe$_2$), 2.89 (septet, J_{HH} = 6.3 Hz, 1H, CHMe$_2$), 2.26 (s, 3H, xylyl Me), 2.17 (s, 3H, xylyl Me), 2.04 (s, 3H, xylyl Me), 1.76 (s, 3H, xylyl Me), 1.53 (d, J_{HH} = 6.7 Hz, 6H, CHMe_2), 1.44 (d, J_{HH} = 6.7 Hz, 6H, CHMe_2), 1.36 (d, J_{HH} = 6.7 Hz, 3H, CHMe_2), 1.30 (s, 15H, C$_5$$Me_5$), 1.08 (d, J_{HH} = 6.7 Hz, 3H, CHMe_2), −10.63 (d, J_{HH} = 4.0 Hz, J_{SiH} = 60.8 Hz, 1H, RuH). ^{29}Si NMR (C$_6$D$_6$, 99.4 MHz): δ −14.5.

Cp*(IXy)(H)$_2$RuSiH[OC(═CH$_2$)C$_6$H$_4$Br]Trip (8). A 4 mL benzene solution of **6** (0.036 g, 0.048 mmol) and 4-bromoacetophenone (0.010 g, 0.049 mmol) was stirred at ambient temperature for 24 h. After removal of all volatile materials under vacuum, the resulting solid was dissolved in 3 mL of pentane, and pale-yellow crystals were obtained upon cooling to −30 °C. Yield: 0.025 g (55%). ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 7.66 (br, 2H), 7.53 (br, 2H), 7.24 (s, 1H), 7.05 (br, 1H), 7.02 (t, J_{HH} = 7.5 Hz, 1H), 6.92 (d, J_{HH} = 7.5 Hz, 1H), 6.87 (d, J_{HH} = 7.5 Hz, 1H), 6.45 (s, J_{SiH} = 213.0 Hz, 1H, SiH), 5.95 (s, 1H), 5.88 (s, 1H), 4.66 (s, 1H, CH_2), 4.45 (br, 1H, CH_2), 3.92 (br, 1H, CHMe$_2$), 3.50 (br, 1H, CHMe$_2$), 2.90 (septet, J_{HH} = 6.34 Hz, 1H, CHMe$_2$), 2.71 (br, 3H, xylyl Me), 1.94 (s, 3H, xylyl Me), 1.83 (s, 3H, xylyl Me), 1.60 (d, J_{HH} = 6.34 Hz, 3H, CHMe_2), 1.53 (s, 15H, C$_5$$Me_5$), 1.46 (d, J_{HH} = 6.34 Hz, 3H, CHMe_2), 1.35 (br, 6H, CHMe_2), 1.21 (br, 3H, xylyl Me), 1.13 (br, 6H, CHMe_2), −10.48 (br, 1H, RuH), −10.94 (br, 1H, RuH). ^{13}C NMR (C$_6$D$_6$, 125.8 MHz): δ 193.2 (NCN), 159.3 (OCCH$_2$), 148.7, 141.7, 135.1, 139.1, 133.6, 132.8, 131.9, 131.2, 131.1, 131.0, 129.6, 129.3, 128.9, 128.6, 127.6, 123.7, 122.4, 121.5, 121.3, 118.6, 100.4, 94.8 (C$_5$Me$_5$), 87.3 (OCCH$_2$), 34.8, 32.8, 27.7, 25.6, 24.6, 24.5, 23.4, 20.8, 20.3, 19.8, 17.6, 10.5 (C$_5$$Me_5$). ^{29}Si NMR (C$_6D_6$, 99.4 MHz): δ 37.9. Anal. Calcd for C$_{52}$H$_{67}$N$_2$OBrSiRu: C, 66.08; H, 7.15; N, 2.96. Found: C, 66.44; H, 7.63; N, 2.77.

Cp*(IXy)(H)$_2$RuSiH(2,6-Me$_2$C$_6$H$_3$O)Trip (9). A 4 mL benzene solution of **6** (0.026 g, 0.035 mmol) and 2,6-dimethylphenol (0.004 g, 0.035 mmol) was stirred for 24 h at ambient temperature. After the removal of all volatile materials under vacuum, the resulting solid was dissolved in 3 mL of pentane, and pale-purple crystals were obtained upon cooling to −30 °C. Yield: 0.022 g (72%). ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 7.21 (s, 1H), 7.14−7.06 (m, br, 3H), 7.05−6.97 (m, br, 2H), 6.97−6.91 (m, br, 2H), 6.90−6.84 (m, 2H), 6.82 (t, J_{HH} = 6.41 Hz, 1H), 6.43 (s, br, 1H, SiH), 5.98 (s, 1H), 5.86 (s, 1H), 4.11 (s, 1H, CHMe$_2$), 3.41 (s, 1H, CHMe$_2$), 2.93 (s, 1H, CHMe$_2$), 2.74 (s, 3H, xylyl Me), 2.64 (s, 3H, xylyl Me), 2.20 (s, 3H, xylyl Me), 1.96 (s, 3H, xylyl Me), 1.91 (s, 3H, xylyl Me), 1.59−1.44 (m, 21H, C$_5$$Me_5$ and CHMe_2), 1.42−1.31 (m, 12H, CHMe_2), 1.10 (s, 3H, xylyl Me), −10.47 (s, 1H, RuH), −11.05 (s, 1H, RuH). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.8 MHz): δ 188.9 (NCN), 147.8, 141.4, 141.3, 137.4, 137.1, 135.0, 134.3, 129.3, 129.2, 128.1, 128.0, 127.2, 127.1, 123.2, 122.4, 121.4, 120.7, 119.3, 94.4 (C$_5$Me$_5$), 34.3, 34.0, 33.4, 29.6, 26.0, 25.6, 24.6, 24.1, 24.0, 23.7, 22.3, 19.4, 19.3, 17.7, 13.8, 10.19 (C$_5$$Me_5$). ^{29}Si NMR (C$_6D_6$, 99.4 MHz): δ −19.0. Anal. Calcd for C$_{52}$H$_{70}$N$_2$OSiRu: C, 71.93; H, 8.13; N, 3.23. Found: C, 71.61; H, 8.08; N, 2.86.

Cp*(IXy)Ru(μ-H)(μ-AgOTf)SiHTrip (10). A 3 mL toluene solution of **6** (0.018 g, 0.024 mmol) was added to a 2 mL toluene solution of AgOTf (0.006 g, 0.024 mmol). After 30 min of stirring at ambient temperature, all volatile materials were removed under vacuum, and the resulting solid was washed twice with 3 mL of pentane to afford a purple solid in 77% yield (0.019 g). ^{1}H NMR (CD$_2$Cl$_2$, 600 MHz): δ 7.99 (d, J_{SiH} = 175 Hz, J_{HH} = 4.8 Hz, 1H, SiH), 7.52 (br, 1H), 7.36 (br, 3H), 7.26 (m, 2H), 7.10 (s, 2H), 6.98 (s, 2H), 3.64 (br, 2H, CHMe$_2$), 2.84 (septet, J_{HH} = 6.82 Hz, 1H, CHMe$_2$), 2.31 (br, 6H, xylyl Me), 2.23 (br, 3H, xylyl Me), 2.12 (br, 3H, xylyl Me), 1.44 (s, 15H, C$_5$$Me_5$), 1.28 (d, J_{HH} = 6.46 Hz, 6H, CHMe_2), 1.21 (d, J_{HH} = 6.82 Hz, 6H, CHMe_2), 1.12 (d, J_{HH} = 6.46 Hz, 6H, CHMe_2), −11.30 (d, J_{SiH} = 36.6 Hz, J_{HH} = 11.3 Hz, 1H, RuH). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 125.8 MHz): δ 187.4 (NCN), 152.9, 150.4, 137.8, 134.8, 134.7, 128.9, 128.1, 125.1, 120.5, 91.1 (C$_5$Me$_5$), 34.2, 34.1, 23.6, 21.1, 19.2, 11.5 (C$_5$$Me_5$). ^{29}Si NMR (CD$_2Cl_2$, 99.4 MHz): δ 182.2. Anal. Calcd for

C$_{45}$H$_{60}$N$_2$F$_3$O$_3$AgSSiRu: C, 53.88; H, 6.03; N, 2.79. Found: C, 54.37; H, 6.27; N, 2.61.

Cp*(IXy)Ru(μ-H)(μ-CuOTf)SiHTrip (11). A 3 mL toluene solution of **6** (0.018 g, 0.024 mmol) was added to a 2 mL toluene solution of (CuOTf)$_2$·C$_6$H$_6$ (0.006 g, 0.024 mmol). After 30 min of stirring at ambient temperature, all volatile materials were removed under vacuum, and the resulting solid was washed twice with 3 mL of pentane to afford a purple solid in 71% yield (0.017 g). ^{1}H NMR (CD$_2$Cl$_2$, 600 MHz): δ 7.80 (s, J_{SiH} = 174 Hz, 1H, SiH), 7.36 (br, 2H), 7.30−7.22 (m, 4H), 7.02 (s, 2H), 6.98 (s, 2H), 3.59 (br, 2H, CHMe$_2$), 2.84 (septet, J_{HH} = 6.80 Hz, 1H, CHMe$_2$), 2.26 (br, 9H, xylyl Me), 1.86 (br, 3H, xylyl Me), 1.42 (s, 15H, C$_5$$Me_5$), 1.26 (d, J_{HH} = 6.42 Hz, 6H, CHMe_2), 1.21 (d, J_{HH} = 6.84 Hz, 6H, CHMe_2), 1.11 (d, J_{HH} = 6.42 Hz, 6H, CHMe_2), −11.49 (s, J_{SiH} = 44 Hz, 1H, RuH). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 150.9 MHz): δ 187.8 (NCN), 153.7, 150.9, 135.9, 135.5, 130.4, 129.5, 129.3, 128.8, 125.7, 123.2, 122.5, 121.0, 91.4 (C$_5$Me$_5$), 34.9, 34.8, 24.3, 21.7, 20.1, 19.9, 18.2, 17.6, 12.5, 12.4, 11.7 (C$_5$$Me_5$). ^{29}Si NMR (CD$_2Cl_2$, 99.4 MHz): δ 176.0. Anal. Calcd for C$_{45}$H$_{60}$N$_2$F$_3$O$_3$CuSSiRu: C, 56.37; H, 6.31; N, 2.92. Found: C, 56.10; H, 6.21; N, 2.76.

Computational Details. Calculations using Gaussian 09 suite of programs[40] were performed at the Molecular Graphics and Computing Facility of the College of Chemistry, University of California, Berkeley. The geometry optimizations were carried out using the TPSS functional.[41] Ru was represented with the effective core potential from the Stuttgart group and the associated optimal basis sets.[42] All other atoms were represented by the 6-31G(d,p) basis set. To include the dispersion corrections for a better evaluation of the relative energies of **4**−**6** and **4a**−**6a**, geometry optimizations were carried out using the Grimme empirical correction (D3) with the damping function proposed by Becke and Johnson.[43] The NBO analysis was carried out using NBO 6[33] as implemented in the local computers of the CTMM group at Université Montpellier 2. The nature of the extrema as minima was confirmed by analytical frequency calculations. Statistical mechanics calculations of thermal and entropic effects were carried out using the rigid rotor/harmonic oscillator approximation at room temperature and 1 atm. The Gibbs energies were calculated at 298.15 K and 1 atm. The topological analysis of the electron densities of complexes **10** and **11** was carried out with the AIMALL[44] program on the computers of UC Berkeley.

X-ray Crystallography Details. X-ray diffraction data were collected using Bruker AXS three-circle diffractometers coupled to a CCD detector with either QUAZAR multilayer mirror- or graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least-squares with SHELXL-97. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included into the model at their geometrically calculated positions and refined using a riding model, except for hydrogen atoms connected to ruthenium or silicon, which were located from the electron difference map.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Kinetic experiments, the optimized structure of **2a**, complete ref 40, selected NBO and QTAIM results, X-ray crystallography details, crystallographic information files (CIF), and a list of coordinates for all optimized structures as a separate .xyz file. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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