Synthesis and Reactivity of (Pentamethylcyclopentadienyl)ruthenium Complexes of the Stable Neutral Silylene $\overline{\mathrm{Si(^tBuNCH{=}CHN}}\mathrm{^tBu)}$

Jeffrey M. Dysard and T. Don Tilley*

Department of Chemistry, University of California at Berkeley,
Berkeley, California 94720-1460

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The coordination chemistry of the stable silylene $\overline{\mathrm{Si(^tBuNCHCHN}}\mathrm{^tBu)}$ (**1**) in Cp*Ru complexes has been investigated. Silylene **1** reacts with 0.25 equiv of $\mathrm{[Cp^*RuCl]_4}$ to give the 16-electron Ru silylene complex $\mathrm{Cp^*\{\eta^1\text{-}\overline{Si(^tBuNCHCHN}{}^tBu)\}RuCl}$ (**2**). This complex reacts with primary silanes to give the unusual products $\mathrm{[(Cp^*Ru)_2(H)(\mu\text{-}H)(\mu,\eta^2\text{-}HSiRCl)(\mu,\eta^2\text{-}Cl\overline{Si(^tBuNCHCHN}{}^tBu)]}$ (**3**, R = Ph; **4**, R = Hex (*n*-hexyl)). The structures of these products were confirmed by ^{1}H, ^{13}C, and ^{29}Si NMR and IR spectroscopy and, in the case of **4**, by X-ray crystallography. In addition, reaction of **1** with 1 equiv of $\mathrm{[Cp^*Ru(NCMe)_3]OTf}$ gave the product of displacement of one acetonitrile group from Ru, $\mathrm{[Cp^*Ru(\{\eta^1\text{-}\overline{Si(^tBuNCHCHN}{}^tBu)\}(NCMe)_2]OTf}$ (**5**). Heating **5** in THF results in precipitation of a crystalline complex formulated as $\mathrm{[Cp^*Ru\{\eta^5\!:\eta^1\text{-}\overline{Si(^tBuNCHCHN}{}^tBu)\}Cp^*Ru(NCMe)_2](OTf)_2}$ (**6**).

Introduction

The study of compounds containing silicon in a six-π-electron aromatic ring has been an area of intense research over the past decade[1] and has led to an enhanced understanding of the electronic nature and reactivity of these systems.[2] In related work, effort has been devoted to development of the transition-metal coordination chemistry of these species, which can lead to more stable derivatives and new reaction pathways.[3,4]

The initial report by Denk and co-workers in 1994 on the synthesis of the free silylene $\overline{\mathrm{Si(^tBuNCHCHN}}\mathrm{^tBu)}$ (**1**),[5] which features some aromatic character in its six-π-electron ring system, has led to numerous studies on compounds of this type.[6] Coordination of the silicon lone pair of **1** to a transition metal produces silylene complexes with characteristic spectroscopic properties (vide infra).[6e,7] Most of these complexes feature metal centers with carbonyl ligands, although recently the molybdocene complex $\mathrm{Cp_2Mo(\overline{Si(^tBuNCHCHN}{}^tBu)}$ has been reported, as well as complexes of Ni and Pt possessing the related ligand $\mathrm{Si[1,2\text{-}(NCH_2{}^tBu)_2C_6H_4]}$.[6e,7] Other silylene complexes, featuring a range of different metal centers, ligand sets, and substituents at silicon, possess

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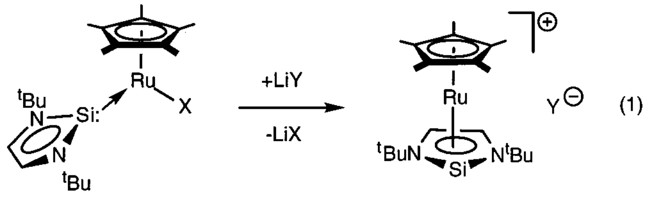
characteristic ^{29}Si NMR shifts at extremely low field, in the range of 250−350 ppm.[8] For example, the complexes $(R_3P)_2Pt{=}SiMes_2$ and $[PhB(CH_2PPh_2)_3](H)_2Ir{=}SiMes_2$ (R = cyclohexyl, ^{i}Pr; Mes = 2,4,6-$Me_3C_6H_2$) exhibit ^{29}Si NMR shifts of 358 and 241.2 ppm, respectively.[8b,c] In contrast, complexes of stable silylenes give rise to ^{29}Si NMR shifts in the range 97.5−146.9 ppm, which is similar to shifts previously observed for base-stabilized silylene complexes of the type $L_nMSiR_2(B)$ (B = two-electron donor).[6e,7,9] This comparison suggests a fundamental difference in the electronic structures of the two types of ligands, and this is further supported by the observation that, whereas silylene complexes prepared by coordination of a stable free silylene to a metal have not been observed to act as silicon-centered Lewis acids, other silylene complexes coordinate Lewis bases.[8i,9] Evidence that **1** acts primarily as a σ-donor toward transition metals is found in the IR stretching frequencies and ^{13}C NMR chemical shifts for the CO ligands in Ni(Si(^{t}BuNCHCHN^{t}Bu)$_2$(CO)$_2$, which are nearly identical with corresponding values reported for the phosphine complex $Ni(Ph_3P)_2(CO)_2$.[7a,10] For comparison, it has been concluded on a theoretical basis that bonds between Ru and Si in complexes of the type $CpL_2Ru{=}SiY_2^+$ possess some π character.[8g,11]

These differences most likely result from the internal stabilization of **1** and related silylenes via donation of electron density into the empty π-type orbital on silicon by the nitrogen lone pairs. In fact, it has been concluded on both an experimental and theoretical basis that the unusual stability of **1** may arise as a result of aromatic resonance of the six π-electrons in the five-membered heterocyclic ring.[12] This description of the electronic structure of **1** suggested that it might act as a six-electron, η^5-donor ligand toward an appropriate transition-metal fragment. This notion is further supported by the fact that the isostructural compound MeB(^{t}BuNCHCHN^{t}Bu) forms a π-complex with $Cr(CO)_3$.[13] To investigate this possibility, we have examined the behavior of **1** in the coordination sphere of unsaturated Cp*Ru fragments.

Results and Discussion

The Cp*Ru$^+$ cation is known to readily form stable complexes with a variety of six-π-electron arenes.[14] We envisioned the synthesis of an η^5-silylene complex via generation of a cationic complex that could achieve an 18-electron count only by η^5-coordination of the silylene, as illustrated in eq 1 (where Y is a noncoordinating anion).



(1)

The reaction of **1** with the dimer $[Cp^*Ru(\mu\text{-OMe})]_2$[15] (benzene-$d_6$, tetrahydrofuran-$d_8$, room temperature) resulted in complex reaction mixtures (by ^{1}H NMR spectroscopy). However, treatment of a dichloromethane solution of $[Cp^*Ru(\mu_3\text{-Cl})]_4$[16] with a pentane solution containing 4 equiv of **1** resulted in a dramatic color change from dark orange to deep blue. Workup of the reaction mixture provided dark blue Cp*{η^1-Si(^{t}Bu-NCHCHN^{t}Bu)}RuCl (**2**) in 71% yield after crystallization from toluene. The ^{1}H NMR spectrum for this compound contains singlets for the Cp* and ^{t}Bu groups (at δ 1.55 and 1.51, respectively), and a singlet at δ 6.95 for the equivalent ring hydrogens of the aromatic silylene ligand. In addition, the ^{29}Si NMR spectrum of **2** exhibits a resonance at δ 112, which is within the range expected for a silylene complex of this type (vide supra).[6e,7] Compound **2** represents a member of the small class of isolable 16-electron complexes of the type Cp*LRuX. An analogous carbene complex was recently reported,[17] and examples containing bulky monodentate phosphine ligands have been known for some time.[18]

Complex **2** is thermally robust, although heating a concentrated toluene solution at 120 °C for several hours resulted in the precipitation of [Cp*Ru(η^6-toluene)]Cl (34% isolated yield, identified by ^{1}H NMR spectroscopy)[19] as well as many unidentified soluble products (by ^{1}H NMR spectroscopy). To compare the reactivity

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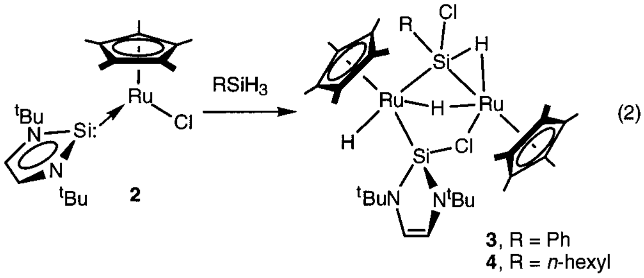
of **2** with that of the analogous phosphine complexes, we examined the reaction with $PhSiH_3$. The phosphine complex Cp*($^iPr_3P$)RuCl reacts rapidly with $PhSiH_3$ via oxidative addition, to give Cp*($^iPr_3P$)Ru(H)(Cl)(SiH_2-Ph).[18a] In contrast, **2** reacted slowly with 1 equiv of $PhSiH_3$ (over 2 h in benzene, room temperature) to give the more complex product [(Cp*Ru)$_2$(H)(μ-H)(μ,η^2-HSiPhCl)(μ,η^2-Cl Si(^{t}BuNCHCHN^{t}Bu)] (**3**) in high yield (88%, eq 2).



Complex **3** was isolated and fully characterized, and assignment of the structure shown in eq 2 is based on ^1H and ^{29}Si NMR spectroscopic data. In the ^1H NMR spectrum, four signals are observed at δ 1.95 and 1.68 and at δ 1.74 and 0.94 for the inequivalent Cp* and ^{t}-BuN groups, respectively. In addition, the presence of two distinct doublets for the inequivalent olefinic protons (δ 5.91 and 5.90; $^3J_{HH}$ = 15 Hz) reveals that the complex lacks a plane of symmetry bisecting the silylene ring. The ^1H NMR spectrum of **3** also exhibits three distinct resonances in the hydride region at room temperature. A doublet at δ −6.80 ($^2J_{HH}$ = 3 Hz) is attributed to the η^2-Si−H proton, as it also possesses ^{29}Si satellites (J_{SiH} = 42 Hz). This value for the Si−H coupling constant falls in the range previously observed for η^2-Si−H interactions (20−140 Hz)[20] and is much less than those of free silanes (~200 Hz).[21] In addition, the IR spectrum for **3** reveals a broad stretch at 1869 cm^{-1}, which is a characteristic feature of η^2-Si−H structures.[20] The ^1H NMR spectrum also exhibits a doublet at δ −13.2 ($^2J_{HH}$ = 3 Hz) and a singlet at δ −12.2 for the other two Ru−H hydrogens. The presence of three distinct resonances for these hydrogens is rather surprising, given that all of the hydride ligands in the related complex [{Cp*Ru(μ,η^2-HSiEt$_2$)}$_2$(μ-H)(H)] are equivalent at room temperature on the NMR time scale.[22] It is noteworthy that heating a sample of **3** to 70 °C in toluene-d_8 did not result in coalescence of the two doublets in the hydride region but did result in the precipitation of a white crystalline powder. On a preparatory scale, **3** was heated in toluene to 75 °C, resulting in precipitation of [Cp*Ru(η^6-toluene)]Cl (42% isolated yield)[19] and formation of many soluble products which could not be identified by ^1H NMR spectroscopy. Interestingly, the reaction of **2** with $PhSiD_3$ confirmed that all three of these hydrides originate from the added silane, as no Ru−H peaks were observed in the ^1H NMR spectrum. However, after 12 h hydride resonances appeared while the Cp* region of the spectrum became complicated, suggesting a process which scrambles the hydride ligands with the hydrogen atoms of the Cp* ligand. Finally, a ^{29}Si INEPT spectrum of **3** revealed a multiplet at δ 143.3 (J_{SiH} = 42 Hz, $^2J_{SiH}$ = 15 Hz) for the η^2-Si−H silicon as well as a doublet at δ 33.4 ($^2J_{SiH}$ = 15 Hz) for the silicon atom in the heterocyclic ring.

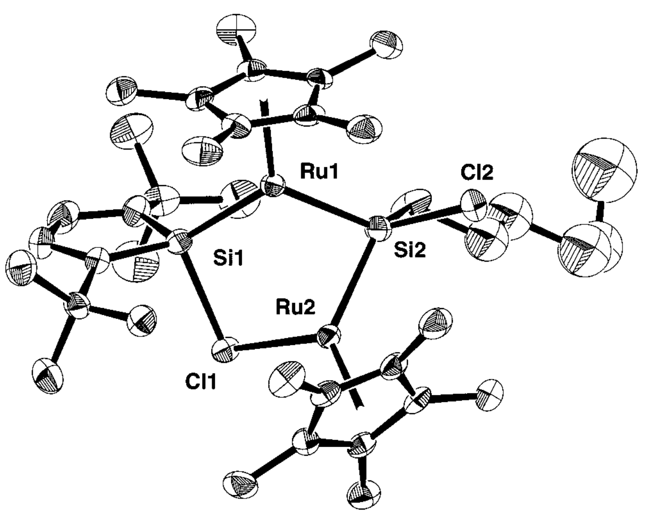


Figure 1. ORTEP diagram of [(Cp*Ru)$_2$(H)(μ-H)(μ,η^2-HSi(Hex)Cl)(μ-(ClSi(tBuNCHCHNtBu)] (**4**).

Although X-ray-quality crystals of **3** could not be obtained, suitable crystals were obtained for the isostructural (by NMR spectroscopy) analogue containing an *n*-hexyl substituent at silicon, ([(Cp*Ru)$_2$(H)(μ-H)(μ,η^2-HSiHexCl)(μ,η^2-Cl Si(^{t}BuNCHCHN^{t}Bu)] (**4**), prepared by the same method used for **3** (eq 2). The crystal structure of **4** contains one molecule of disordered pentane, which was modeled successfully with isotropic, partial-occupancy carbon atoms (see Experimental Section for details). In addition, the hexyl group showed signs of disorder, which was modeled using six isotropic, full-occupancy, carbon atoms. With this disorder, it was not possible to locate the positions of the three hydride ligands. The molecular structure of **4** (Figure 1) is best described as [Cp*RuH] and [Cp*Ru] fragments bridged by μ-H, η^2-H−SiHexCl, and η^2-Cl−Si(^{t}BuNCHCHN^{t}Bu) groups. There is a significant bonding interaction between Cl(1) and Ru(2), as evidenced by the relatively short contact between these two atoms (2.500(2) Å; Table 2). For comparison, the Ru−Cl distances in the 18-electron complexes Cp*(PPh$_3$)$_2$RuCl (2.453(2) Å) and Cp*(PMe$_3$)$_2$RuCl (average 2.44 Å)[23] are only slightly shorter than in **4**. This is further reflected in the Si(1)−Cl(1) distance (2.311(2) Å), which is significantly longer than the Si(2)−Cl(2) distance (2.171(3) Å). This feature of the structure is reminiscent of bimetallic complexes possessing Si(OR)$_3$ silyl ligands bonded in an μ_2,η^2-Si−O manner.[24] The Ru(1)−Ru(2) distance in **4** (3.07 Å) is only slightly longer than that in [{Cp*Ru(μ,η^2-HSiEt$_2$)}$_2$(μ-H)(H)] (2.971(1) Å), which is consistent with the presence of a bridging hydride ligand as shown

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Table 1. Summary of Crystallographic Data

empirical formula	$Ru_2Si_2H_{66}C_{36}N_2Cl_2$
fw	856.15
cryst color, habit	red-orange, block
cryst dimens	0.26 × 0.24 × 0.15 mm
cryst syst	monoclinic
cell determination (2θ range)	7589 (4.0−45.0°)
lattice params	$a = 11.6120(2)$ Å $b = 30.2657(5)$ Å $c = 12.1923(1)$ Å $\beta = 91.996(1)°$ $V = 4282.33(9)$ Å^3
space group	$P2_1/n$ (No. 14)
Z	4
D_{calcd}	1.328 g/cm^3
μ(Mo Kα)	9.11 cm^{-1}
diffractometer	Siemens SMART
radiation	Mo Kα ($\lambda = 0.710\ 69$ Å), graphite monochromated
temp	−137 °C
scan type	ω (0.3° per frame)
no. of rflns measd	total: 19 437 unique: 7407 ($R_{int} = 0.025$)
no. of observns ($I > 3.00\sigma(I)$)	4606
structure soln	direct methods (SIR92)
refinement	full-matrix least squares
residuals: R; R_w	0.037; 0.049
max peak in final diff map	1.39 e/Å^3
min peak in final diff map	−0.93 e/Å^3

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for 4

(a) Bond Distances

Ru(1)−Si(1)	2.328(2)	Ru(1)−Si(2)	2.332(2)
Ru(1)−Cp*[a]	1.8991(5)	Ru(2)−Cp*	1.8434(5)
Ru(2)−Si(2)	2.394(2)	Ru(2)−Cl(1)	2.500(2)
Si(1)−Cl(1)	2.311(2)	Si(2)−Cl(2)	2.171(3)

(b) Bond Angles

Si(1)−Ru(1)−Si(2)	109.61(6)	Ru(1)−Si(2)−Ru(2)	81.06(6)
Si(2)−Ru(2)−Cl(1)	101.09(6)	Ru(1)−Si(1)−Cl(1)	102.66(7)
Ru(2)−Cl(1)−Si(1)	93.92(7)	N(1)−Si(1)−N(2)	91.6(2)

[a] Cp* denotes the centroid of the five-membered ring.

in eq 2.[22] Finally, Si(2) is almost symmetrically bound between the two Ru atoms, as the two Ru−Si bond lengths are very similar (Ru(1)−Si(2) = 2.332(2) Å, Ru(2)−Si(2) = 2.394(2) Å) and nearly identical with the Ru(1)−Si(1) distance of 2.328(2) Å.

Interestingly, 1.0 equiv of silane is required in this reaction, as demonstrated by the fact that treatment of **2** with 0.5 equiv of silane gives only 0.5 equiv of product (**3** or **4**), leaving 0.5 equiv of **2** unchanged (by ^{1}H NMR, 1,3,5-trimethoxybenzene standard), while the yield of **3** or **4** is nearly quantitative when 1 equiv of silane is employed (by ^{1}H NMR spectroscopy, 94%). No intermediates were detected throughout the course of this reaction (by ^{1}H NMR spectroscopy at room temperature). Also, an insoluble, fine precipitate which forms as a byproduct in this reaction was isolated after extraction of **3** or **4** with pentane (95% yield based on combined molecular weights of $PhSiH_3$ and **1**). The IR spectrum of this powder (from the reaction to form **3**) contains a characteristic Si−H stretch at 2089 cm^{-1}, and the ^{1}H NMR spectrum (dichloromethane-d_2) revealed only very broad resonances in the aryl (δ 7.10−7.30) and alkyl (δ 1.20−1.40; 1.60−2.20) regions. In addition, the elemental analysis of this byproduct did not correspond to the composition expected for a product resulting from the 1:1 combination of $PhSiH_3$ with **1** (the species formally eliminated in the formation of **3**). Thus, we currently have little information regarding the mechanism of formation for **3** and **4**. However, the scenario outlined in Scheme 1 seems reasonable on the basis of known chemistry.

Presumably, the first step in this reaction is the oxidative addition of silane to **2** (to form **A**), as observed in the reaction of $Cp^*(^iPr_3P)RuCl$ with $PhSiH_3$.[18a] This is most likely followed by an equilibrium process which exchanges the Ru−Cl and Si−H substituents. This notion is supported by the analogous reaction of $Cp^*(^iPr_3P)RuCl$ with $MesSiH_3$, which produced $Cp^*(^iPr_3P)RuH_2(SiHClMes)$ as the result of the same reductive elimination/oxidative addition sequence.[25] Apparently, the chlorosilyl species **B** rapidly scavenges a “Cp*RuCl” fragment from earlier in the reaction sequence (e.g., from **A**) to give the final product (Scheme 1). Note that formation of the product requires loss of both **1** (0.5 equiv) and $PhSiH_3$ (0.5 equiv). These species are apparently consumed in the formation of the sparingly soluble byproduct, which could not be fully characterized. In this regard, it is worth noting that **1** and $PhSiH_3$ do not react in a direct way (benzene, over 12 h at room temperature) or in the presence of **3** or **4**.

Attempts to directly convert **2** to a complex incorporating an η^5-silylene ligand have met with little success. For example, **2** did not react with $Li[B(C_6F_5)_4]$ in ethereal or aliphatic hydrocarbons (tetrahydrofuran, 1,2-dimethoxyethane, diethyl ether, pentane, hexanes), even after heating to reflux for several hours. However, reaction did take place in aromatic or halogenated solvents (benzene, fluorobenzene, toluene, dichloromethane) at room temperature, to give complex reaction mixtures (by ^{1}H NMR spectroscopy). Furthermore, **2** did not react with Me_3SiOTf ($OTf = OSO_2CF_3$) (CH_2Cl_2, THF, and benzene solvents at room temperature over 24 h) but did react with AgOTf (CH_2Cl_2, THF, benzene) to give multiple products which did not appear to contain the desired product (by ^{1}H NMR spectroscopy).

An efficient and convenient synthesis of π-complexes of Ru, established by Fagan, involves the reaction of $[Cp^*Ru(NCMe)_3]OTf$ with an arene to give compounds of the type $[Cp^*Ru(\eta^6\text{-arene})]OTf$.[14] Treatment of a dichloromethane solution of $[Cp^*Ru(NCMe)_3]OTf$ with 1 equiv of **1** in pentane resulted in a darkening of the initial orange-yellow reaction mixture. Upon removal of the volatile materials $[Cp^*Ru(\{\eta^1\text{-}\overline{Si(^tBuNCHCHN}{}^tBu)\}(NCMe)_2]OTf$ (**5**) was isolated in 95% yield as an analytically pure yellow-orange powder (eq 3).

Characterization of **5** as an η^1-silylene complex is based on ^{1}H and ^{29}Si NMR spectroscopy. In the ^{1}H NMR spectrum of **5** there are two resonances at δ 1.62 and 1.50 for the Cp* and ^{t}BuN groups, respectively. In addition, there are resonances at δ 6.82 for the olefinic protons of the silylene ligand and at δ 2.44 for the acetonitrile ligands. The ^{29}Si NMR spectrum for **5** contains a singlet at δ 109.5.

In an attempt to prevent η^1-coordination of the silylene to Ru we investigated the reaction of the borane adduct $(C_6F_5)_3B{-}\overline{Si(^tBuNCHCHN}{}^tBu)$[6d] with $[Cp^*Ru(NCMe)_3]OTf$. Unfortunately, as in the case for uncomplexed **1**, this reaction produced only **5** in quantitative yield (^{1}H NMR spectroscopy). Initial attempts to convert

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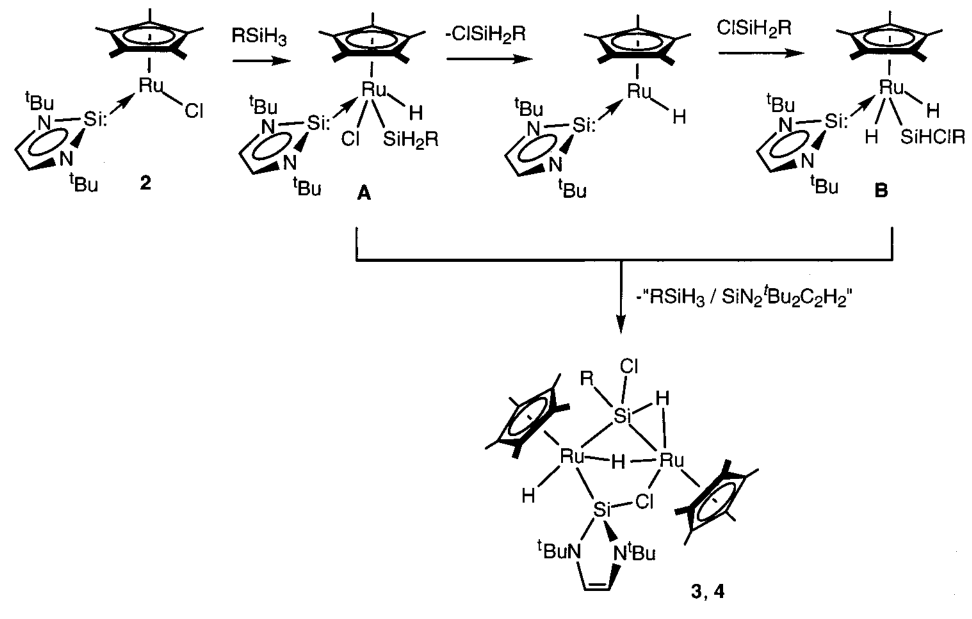
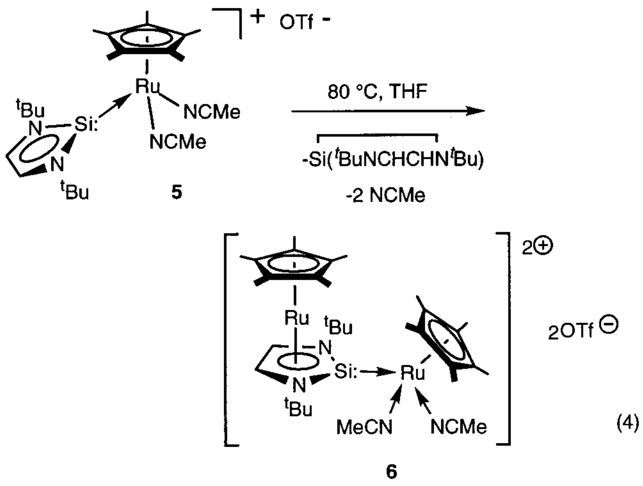
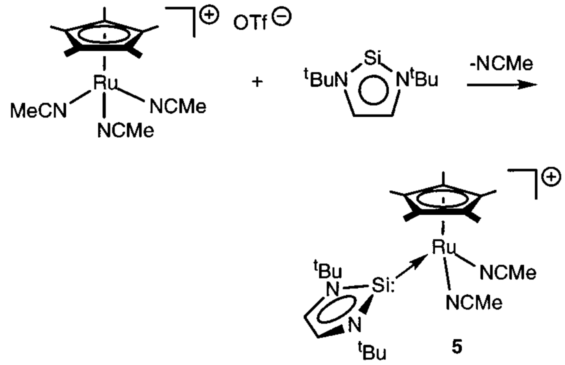
(25) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1992**, 1201.

Scheme 1





(4)



(3)

5 to a product containing an η^5-silylene focused on removal of the two acetonitrile ligands. However, heating dichloromethane or nitromethane solutions of **5** to reflux resulted only in decomposition. In addition, heating solutions of **5** in either benzene or dichloromethane in the presence of a reagent that may remove the acetonitrile (CuI, CuBr, BPh_3, or $B(C_6F_5)_3$) resulted only in complex product mixtures by ^1H NMR spectroscopy. Heating a solid sample of **5** to 150 °C under dynamic vacuum did not result in loss of acetonitrile. However, heating a tetrahydrofuran solution of **5** to 80 °C resulted in loss of acetonitrile and precipitation of a highly crystalline yellow material (**6**; 40% yield), whose NMR spectra are consistent with the structure $\{Cp^*Ru[\eta^5{:}\,\eta^1\text{-}Si(\overline{^tBuNCHCHN^tBu})]Cp^*Ru(NCMe)_2\}(OTf)_2$ (eq 4).

The ^1H NMR spectrum of **6** reveals the presence of a mirror plane of symmetry bisecting the silylene ligand, as one ^tBu resonance (δ 1.43), one peak for the olefinic protons (δ 6.93), and one resonance for both acetonitrile ligands (δ 2.62) are observed. In addition, there are two separate resonances for the Cp* ligands (δ 1.98 and 1.71). Interestingly, the ^{13}C NMR shifts for the ring carbons of the η^5-silylene ligand (89 ppm) resonate considerably upfield of the corresponding shift in **5** (121 ppm), apparently as a result of the coordinated Ru. In addition, there is a significant upfield shift for the ^{29}Si NMR resonance upon formation of **6** (δ 109.1 for **5**; δ 16.9 for **6**). This rather large difference in chemical shift may reflect significant donation of electron density from ruthenium to silicon. X-ray-quality crystals of **6** were grown by vapor diffusion of pentane into a concentrated methylene chloride solution. Although this crystallographic investigation confirmed the connectivity and gross structural features of the complex, including the η^5-coordination of the silylene ligand, refinement of accurate metric parameters was not possible due to severe disorder of the molecule over a rotational axis.

Concluding Remarks

In this contribution we have described new examples of complexes containing **1** as a neutral two-electron donor, along with preliminary evidence for η^5-ligation of this species to ruthenium. Initial reactivity studies of one of these complexes (**2**) revealed that the silylene ligand is not innocent, as it is easily oxidized to Si(IV) and can participate in several types of reactions. This type of reactivity seems to be common to stable silylenes coordinated to a metal, as Lappert has observed similar chemistry in a related system involving the $Si[1,2\text{-}(NCH_2{}^tBu)_2C_6H_4]$ ligand.[7c]

Experimental Section

All manipulations were performed under an argon atmosphere using standard Schlenk techniques or a nitrogen-filled glovebox. Dry, oxygen-free solvents were employed throughout. Pentane and toluene were distilled from sodium/benzophenone, whereas benzene-d_6 and toluene-d_8 were distilled from Na/K alloy. CH_2Cl_2 and CD_2Cl_2 were dried over CaH_2 and distilled prior to use. The compounds $[Cp^*RuCl]_4$,[16] $[Cp^*Ru(NCMe)_3]$-OTf,[14] $PhSiH_3$,[26] $PhSiD_3$,[26] and Si(^{t}BuNCHCHN^{t}Bu)[5] were prepared according to literature procedures. $HexSiH_3$ was purchased from Gelest Chemical Co. and used as received. NMR spectra were recorded at 300 or 500 MHz (^{1}H) with Bruker AMX-300 and DRX-500 spectrometers, at 125 MHz ($^{13}C\{^1H\}$) with a DRX-500 spectrometer, or at 99 MHz ($^{29}Si\{^1H\}$) with a DRX-500 spectrometer, at ambient temperature unless otherwise noted. Elemental analyses were performed by the 8 laboratory in the College of Chemistry at the University of California, Berkeley. IR samples were prepared as KBr pellets. All IR absorptions are reported in cm^{-1} and were recorded with a Mattson Infinity 60 MI FTIR spectrometer.

Cp*[η^1-Si(^{t}BuNCHCHN^{t}Bu)]RuCl (2). A 150 mL Schlenk tube was charged with $[Cp^*RuCl]_4$ (2.650 g, 2.440 mmol) and 40 mL of CH_2Cl_2 to generate a dark orange solution. A separate 100 mL Schlenk tube was charged with **1** (1.910 g, 9.760 mmol) and 80 mL of pentane to give a clear, colorless solution. This solution was then added to the flask containing $[Cp^*RuCl]_4$ via cannula with immediate generation of a deep purple solution. This reaction mixture was stirred for 30 min before the volatile materials were removed under dynamic vacuum. The remaining purple residue was washed with pentane (3 × 40 mL) and thoroughly dried under dynamic vacuum. Recrystallization from a concentrated toluene solution gave **2** as a deep blue, crystalline solid in 71% yield (3.23 g, 6.90 mmol). ^{1}H NMR (dichloromethane-d_2): δ 6.95 (s, 2 H, Si(^{t}BuNC$_2$*H*$_2$N^{t}Bu)), 1.55 (s, 15 H, C$_5$*Me*$_5$), 1.51 (s, 18 H, N^t*Bu*). $^{13}C\{^1H\}$ NMR (dichloromethane-d_2): δ 122.50 (s, Si(^{t}BuN*C*$_2$H$_2$N^{t}Bu), 82.00 (s, *C*$_5$Me$_5$), 55.53 (s, N*C*Me$_3$), 32.37 (s, NC*Me*$_3$), 11.01 (s, C$_5$*Me*$_5$). $^{29}Si\{^1H\}$ NMR (dichloromethane-d_2): δ 112.7 (s, *Si*(^{t}BuNC$_2$H$_2$N^{t}Bu)). Repeated attempts to obtain combustion analysis data gave variable results that were consistently low in carbon and hydrogen. We assume that this compound does not burn cleanly to CO_2 and H_2O. However, the spectroscopic characterization of **2** and its observed reaction chemistry provide convincing evidence for the proposed formula. IR: 3020 w, 2980 s, 2936 s, 1609 w, 1457 m, 1370 w, 1366 m, 1262 w, 1214 s, 1132s, 1069 m, 1026 s, 1018 w, 815 w, 720 m, 653 s, 512 w, 499 w, 460 w. Mp: 240−244 °C dec.

{(Cp*Ru)$_2$(H)(μ-H)(μ,η^2-HSiPhCl)[μ,η^2-ClSi(^{t}BuNCHCHN^{t}Bu)]} (3). A 100 mL Schlenk tube was charged with **2** (0.220 g, 0.470 mmol) and $PhSiH_3$ (0.051 g, 0.470 mmol). A 50 mL portion of toluene was added to this flask to produce a deep purple solution. This mixture was stirred for 3 h, after which time it had turned deep orange. The volatile materials were removed, and the remaining orange residue was extracted with pentane (3 × 20 mL). The combined extracts were concentrated to 5 mL and cooled to −35 °C to give **3** as red-orange crystals in 88% yield (0.175 g, 0.207 mmol). ^{1}H NMR (benzene-d_6): δ 8.25 (m, 2 H, μ,η^2-HSi*Ph*Cl), 7.32 (m, 3 H, μ,η^2-HSi*Ph*Cl), 5.91 (d, $^3J_{HH}$ = 15 Hz, 1 H, ClSi(^{t}BuNC$_2$*H*$_2$N^{t}Bu)), 5.90 (d, $^3J_{HH}$ = 15 Hz, 1 H, ClSi(^{t}BuNC$_2$*H*$_2$N^{t}Bu)), 1.95 (s, 15 H, C$_5$*Me*$_5$), 1.74 (s, 9 H, N^t*Bu*), 1.68 (s, 15 H, C$_5$*Me*$_5$), 0.94 (s, 9 H, N^t*Bu*), −6.80 (d, $^2J_{HH}$ = 3 Hz, 1 H, μ,η^2-*H*SiPhCl), −12.24 (s, 1 H, Ru−*H*), −13.16 (d, $^2J_{HH}$ = 3 Hz, 1 H, μ-*H*). $^{13}C\{^1H\}$ NMR (toluene-d_8): δ 151.87, 137.41, 133.91, 127.76 (s, μ,η^2-HSi*Ph*Cl), 116.13, 114.63 (s, ClSi(^{t}BuN*C*$_2$H$_2$N^{t}Bu)), 96.08, 90.53 (s, *C*$_5$Me$_5$), 54.17, 53.73 (N*C*Me$_3$), 32.68, 31.67 (s, NC*Me*$_3$), 11.80, 11.16 (s, C$_5$*Me*$_5$). $^{29}Si\{^1H\}$ NMR (benzene-d_6): δ 143.3 (s, μ,η^2-H*Si*PhCl), 33.4 (s, Cl*Si*(^{t}BuNC$_2$H$_2$N^{t}Bu)). Anal. Calcd for $C_{36}H_{58}Cl_2N_2Ru_2Si_2$: C, 50.98; H, 6.89; N, 3.30. Found: C, 51.30; H, 6.90; N, 3.23. IR 2969 s, 2903 s, 2086 m, 1869 br m (μ,η^2-*HSi*PhCl), 1642 m, 1630 w, 1459 s, 1365 s, 1266 s, 1212 s, 1110 s, 1067 s, 1029 s, 996 s, 801 w, 742 m, 718 m, 693 m, 655 s, 579 m, 487 m. Mp: 175−178 °C dec.

{(Cp*Ru)$_2$(H)(μ-H)(μ,η^2-HSi(Hex)Cl)[μ,η^2-ClSi(^{t}BuNCHCHN^{t}Bu)]} (4). A 100 mL Schlenk tube was charged with **2** (0.152 g, 0.325 mmol) and $HexSiH_3$ (0.038 g, 0.325 mmol). A 50 mL portion of toluene was added to this flask to produce a deep purple solution. This mixture was stirred for 6 h, after which time it had turned deep orange. The volatile materials were removed, and the remaining orange residue was extracted with pentane (3 × 20 mL). The combined extracts were concentrated to 5 mL and cooled to −35 °C to give **4** as red-orange crystals in 85% yield (0.118 g, 0.138 mmol). ^{1}H NMR (benzene-d_6): δ 6.03 (d, $^3J_{HH}$ = 10 Hz, 1 H, ClSi(^{t}BuNC$_2$*H*$_2$N^{t}Bu)), 6.02 (d, $^3J_{HH}$ = 10 Hz, 1 H, ClSi(^{t}BuNC$_2$*H*$_2$N^{t}Bu)), 2.35 (m, 2 H, μ,η^2-HSi(*Hex*)Cl), 1.92 (s, 15 H, C$_5$*Me*$_5$), 1.74 (s, 9 H, N^t*Bu*), 1.67 (s, 15 H, C$_5$*Me*$_5$), 1.54−1.41 (m, 8 H, μ,η^2-HSi(*Hex*)Cl), 1.38 (s, 9 H, N^t*Bu*), 0.96 (t, J_{HH} = 7 Hz, 3 H, μ,η^2-HSi(*Hex*)Cl), −7.17 (d, $^2J_{HH}$ = 3 Hz, ^{29}Si satellites J_{SiH} = 40 Hz, 1 H, μ,η^2-*H*Si(Hex)Cl), −12.92 (s, 1 H, Ru-*H*), −13.21 (d, $^2J_{HH}$ = 3 Hz, 1 H, μ-*H*). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 116.82, 115.41 (s, ClSi(^{t}BuN*C*$_2$H$_2$N^{t}Bu)), 96.31, 91.00 (s, *C*$_5$Me$_5$), 54.75, 54.18 (N*C*Me$_3$), 33.25, 32.90 (s, NC*Me*$_3$), 36.27, 34.17, 32.88, 28.46, 23.74, 14.97 (s, μ,η^2-HSi(*Hex*)Cl), 12.24, 11.75 (s, C$_5$*Me*$_5$). $^{29}Si\{^1H\}$ NMR (benzene-d_6): δ 154.6 (s, μ,η^2-H*Si*(Hex)Cl), 33.1 (s, Cl*Si*(^{t}BuNC$_2$H$_2$N^{t}Bu)). Anal. Calcd for $C_{36}H_{66}Cl_2N_2Ru_2Si_2$: C, 50.50; H, 7.77; N, 3.27. Found: C, 50.69; H, 7.77; N, 3.19. IR: 2960 s, 2907 s, 2086 m, 1841 br m (μ,η^2-*HSi*(Hex)Cl), 1641 m, 1465 s, 1391 w, 1375 s, 1265 w, 1216 s, 1110 s, 1068 s, 1028 s, 996 s, 719 w, 649 m, 487 w, 446 w. Mp: 120−122 °C dec.

{Cp*Ru[η^1-Si(^{t}BuNCHCHN^{t}Bu)](NCMe)$_2$}OTf (5). A 250 mL Schlenk tube was charged with $[Cp^*Ru(NCMe)_3]OTf$ (2.770 g, 5.450 mmol) and 30 mL of CH_2Cl_2 to generate a deep yellow-orange solution. **1** (1.070 g, 5.450 mmol) and 150 mL of pentane were placed in a separate 200 mL Schlenk tube, and the contents of this flask were added via cannula to the flask containing $[Cp^*Ru(NCMe)_3]OTf$ to give an orange solution. The resulting reaction solution was stirred for 30 min, after which time the volatile materials were removed under dynamic vacuum. Thorough drying of the remaining residue gave **5** as a dark yellow powder in 95% yield (3.28 g, 0.518 mmol). ^{1}H NMR (dichloromethane-d_2): δ 6.82 (s, 2 H, Si(^{t}BuNC$_2$*H*$_2$N^{t}Bu)), 2.44 (s, 6 H, NC*Me*), 1.62 (s, 15 H, C$_5$*Me*$_5$), 1.50 (s, 18 H, N^t*Bu*). $^{13}C\{^1H\}$ NMR (dichloromethane-d_2): δ 126.05 (s, N*C*Me) 121.04 (s, Si(^{t}BuN*C*$_2$H$_2$N^{t}Bu), 87.42 (s, *C*$_5$Me$_5$), 55.81 (s, N*C*Me$_3$), 32.90 (s, NC*Me*$_3$), 10.59 (s, C$_5$*Me*$_5$), 4.74 (s, NC*Me*). $^{29}Si\{^1H\}$ NMR (dichloromethane-d_2): δ 109.1 (s, *Si*(^{t}BuNC$_2$H$_2$N^{t}Bu)). Anal. Calcd for $C_{25}H_{41}F_3N_4O_3RuSSi$: C, 45.23; H, 6.23; N, 8.44. Found: C, 44.78; H, 6.38; N, 7.93. IR: 3354 br s, 2975 s, 2968 s, 2010 m, 1920 m, 1638 m, 1459 m, 1367 m, 1282 s, 1247 s, 1224 sh, 1159 s, 1030 s, 938 w, 756 w, 638 s, 517 w. Mp: 145−148 °C dec.

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(26) Benkeser, R. A.; Landesman, H.; Foster, D. J. *J. Am. Chem. Soc.* **1952**, *74*, 648.

{Cp*Ru[η^5,η^1-$\overline{\mathrm{Si}(^t\mathrm{BuNCHCHN}}{}^t\mathrm{Bu})$]Cp*Ru(NCMe)$_2$}(OTf)$_2$ (6). 5 (4.500 g, 7.100 mmol) and 100 mL of THF were placed in a 200 mL reaction flask equipped with a Teflon stopcock. This flask was then placed in an oil bath, and the solution was heated to 85 °C for 2 h. During this time a microcrystalline yellow material precipitated from solution. The flask was then removed from the oil bath and slowly cooled to room temperature. The yellow precipitate was isolated by filtration. This material was then dried under dynamic vacuum to afford **6** as a crystalline yellow powder in 40% yield (1.45 g, 1.42 mmol). ^{1}H NMR (methylene chloride-d_2): δ 6.93 (s, 2 H, $\overline{\mathrm{Si}(^t\mathrm{BuNC}_2\mathit{H}_2\mathrm{N}}{}^t\mathrm{Bu})$), 2.62 (s, 6 H, NC*Me*), 1.98 (s, 15 H, $\mathrm{C}_5\mathit{Me}_5$), 1.71 (s, 15 H, $\mathrm{C}_5\mathit{Me}_5$), 1.43 (s, 18 H, $\mathrm{N}^t\mathit{Bu}$). ^{13}C{^{1}H} NMR (methylene chloride-d_2): δ 128.50 (s, N*C*Me), 94.56 ($\mathit{C}_5\mathrm{Me}_5$), 90.79 (s, $\mathit{C}_5\mathrm{Me}_5$), 89.90 (s, $\overline{\mathrm{Si}(^t\mathrm{BuN}\mathit{C}_2\mathrm{H}_2\mathrm{N}}{}^t\mathrm{Bu})$), 61.44 (s, N*C*Me$_3$), 31.52 (s, NC*Me*$_3$), 12.48 (s, $\mathrm{C}_5\mathit{Me}_5$), 10.99 (s, $\mathrm{C}_5\mathit{Me}_5$), 5.04 (s, NC*Me*). ^{29}Si{^{1}H} NMR (methylene chloride-d_2): δ 16.9 (s, $\overline{\mathit{Si}(^t\mathrm{BuNC}_2\mathrm{H}_2\mathrm{N}}{}^t\mathrm{Bu})$). Anal. Calcd for $\mathrm{C}_{36}\mathrm{H}_{56}\mathrm{F}_6\mathrm{N}_4\mathrm{O}_6\mathrm{Ru}_2\mathrm{S}_2\mathrm{Si}$: C, 41.21; H, 5.38; N, 5.34. Found: C, 41.39; H, 5.70; N, 5.08. IR: 3416 br s, 2980 s, 2926 s, 2220 m, 1930 m, 1631 m, 1462 m 1375 m, 1274 s, 1268 s, 1157 s, 1030 s, 946 w, 755 w, 638 s, 557 w, 517 w. Mp: 130−133 °C dec.

X-ray Crystallography. Orange, blocklike crystals of **4** were obtained from a concentrated pentane solution at −35 °C. A crystal of dimensions 0.26 × 0.24 × 0.15 mm was mounted on a glass fiber using Paratone N hydrocarbon oil. Data were collected using a Siemens SMART diffractometer with a CCD area detector. A preliminary orientation matrix and unit cell parameters were determined by collecting 60 10 s frames, followed by spot integration and least-squares refinement. A hemisphere of data was collected using ω scans of 0.3°. Frame data were integrated (*xy* spot spread 1.60°; *z* spot spread 0.60°) using the program SAINT (SAX area-detector integration program; V4.024; Siemens Industrial Automation, Inc., Madison, WI, 1995). The data were corrected for Lorentz and polarization effects. An absorption correction was performed using SADABS ($T_{\mathrm{max}} = 0.8444$, $T_{\mathrm{min}} = 0.7459$). The 19 437 integrated reflections were averaged in point group 2/*m* to give 7407 unique reflections ($R_{\mathrm{int}} = 0.025$), but only 4606 reflections were considered observed ($I > 3.00\sigma(I)$). No decay correction was necessary. Inspection of the systematic absences uniquely defined the space group as $P2_1/n$. The structure was solved using direct methods (SIR92) and refined by full-matrix least-squares methods using teXsan software. The non-hydrogen atoms that showed no disorder were refined anisotropically. C(31)−C(36) are the carbon atoms which correspnd to the *n*-hexyl chain bound to Si(2). These carbon atoms showed signs of probable disorder but were modeled using full-occupancy isotropic carbon atoms. There was also a molecule of disordered pentane present, which was modeled as two full-occupancy, isotropic carbons (C(39) and C(40)), one half-occupancy isotropic carbon C(41), and two 20% occupancy isotropic carbon atoms (C(37) and C(38)). The number of variable parameters was 392, giving a data/parameter ratio of 11.75. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.39 and −0.93 e/Å^3. $R = 0.037$, $R_{\mathrm{w}} = 0.049$, and GOF = 1.75. The crystallographic data are summarized in Table 1.

Acknowledgment is made to the National Science Foundation for their generous support of this work. We thank Dr. Fred Hollander for assistance with the X-ray structure determination.

Supporting Information Available: Tables of crystal, data collection, and refinement parameters, bond distances and angles, and anisotropic displacement parameters for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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