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Silabenzene and Disilabenzene Complexes of Ruthenium

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The syntheses of sila- and disilabenzene complexes of “Cp*Ru” (Cp* = C_5Me_5) are described. $Li[C_5H_5SiH(^tBu)]$ reacted with $[Cp^*RuCl]_4$ to give the neutral silacyclohexadienyl complex $Cp^*Ru[\eta^5\text{-}C_5H_5SiH(^tBu)]$ (**2**), characterized by NMR spectroscopy. Reaction of **2** with the Lewis acid $B(C_6F_5)_3$ gave the product of Si−H abstraction, $[Cp^*Ru(\eta^6\text{-}C_5H_5Si^tBu)][BH(C_6F_5)_3]$ (**3**). Complex **3** represents the first example of an isolated silabenzene complex. The characterization of **3** follows from ^1H, ^{13}C, ^{29}Si, ^{19}F, and ^{11}B NMR and IR spectroscopies. Finally, *trans*-1,4-dihydrohexamethyl-1,4-disilacyclohexa-2,5-diene reacted with $Cp'(PMe_3)_2RuCH_2SiMe_3$ (Cp′ = C_5Me_4Et) to give $Cp'(PMe_3)RuH(\eta^2$-hexamethyl-1,4-disilabenzene) (**4**), whose structure (by X-ray crystallography) may be described as a metallodisilanorbornadiene.

Introduction

Silabenzenes have long been of interest as analogues to benzene, the simplest 6π-electron aromatic system of carbon.[1] However, such species have been elusive, although theory predicts significant aromatic character for some silabenzenes, and both sila- and disilabenzene have been observed in low-temperature matrices.[1,2] Pioneering work by the groups of Barton and West in the late 1970s to mid 1980s provided the first evidence for the existence of potentially aromatic sila- and disilabenzene derivatives.[2,3] However, these π-systems are extremely reactive and could only be isolated at room temperature as products of dimerization or through trapping experiments.[2,3] In 1988 Märkl et al. reported the synthesis of 2,6-bis(trimethylsilyl)-1,4-di-*tert*-butylsilabenzene, which was stable only below −100 °C in solution and was stabilized by coordination of a Lewis base to the silicon center.[4] Only recently, Okazaki and co-workers have succeeded in the synthesis of the first stable examples of silabenzenoid compounds, as 2-silanaphthalene and silabenzene derivatives.[5] Both of these compounds take advantage of an extremely bulky substituent at silicon, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt), to provide stability to the silaaromatic systems. Interestingly, these compounds have been characterized both structurally and theoretically as having full delocalization of their π-electrons.[5] 1,4-Disilabenzene itself has been trapped in a frozen argon matrix and characterized spectroscopically, and another member of this series, hexamethyldisilabenzene, has been generated photolytically and trapped with various reagents.[3d,e] Very recently, a 1,4-disila(Dewar-benzene) derivative has also been isolated.[6]

Our work has shown that aromaticity in silacyclopentadienyl (silolyl) anions is promoted by η^5-coordination to transition metal fragments.[7] Thus, it seemed that η^6-silabenzene complexes might be viable synthetic targets and interesting new examples of π-delocalized silaaromatic ligands. Some support for this notion came from a literature report describing observation of the

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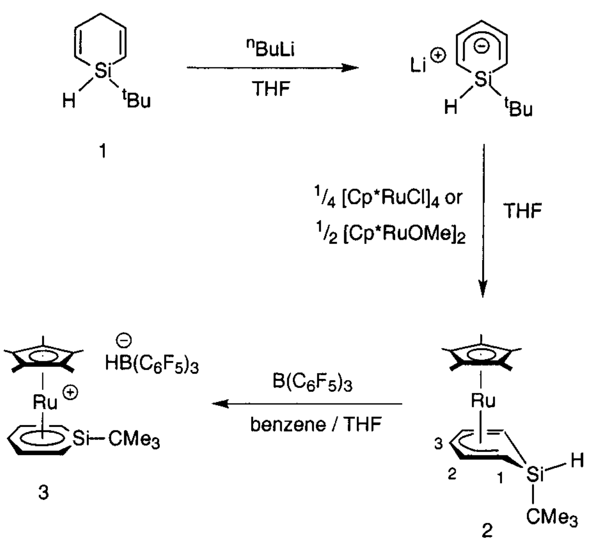
Scheme 1



[η^6-4-cyclohexyl-1-methylsilabenzene]Fe radical cation in the mass spectrum of [η^5-4-cyclohexyl-1,1-dimethylsilacyclohexadienyl]Fe(CO)$_3^+$.[8] Here we report the synthesis and characterization of the first transition metal silabenzene complex and a disilabenzene complex that adopts a metallodisilanorbornadiene structure.

Results and Discussion

A Silabenzene Complex. The ruthenium-based fragment Cp*Ru$^+$ is known to bind strongly to six-electron π-systems, and a number of complexes of the type [Cp*Ru(η^6-arene)]$^+$ are known.[9] Our synthetic strategy therefore targeted the generation of an analogous silabenzene complex, via abstraction of hydride from silicon[10] in an appropriate silacyclohexadiene complex. A similar method for generating an η^6-arene ligand via dealkylation of coordinated η^5-cyclohexadienyl has been reported.[11] Furthermore, it has recently been shown that treatment of the related η^5-cyclohexadienyl complex Cp*Ru[η^5-6-*exo*-methylcyclohexadienyl] with various Lewis acids results in hydride abstraction and formation of [Cp*Ru(η^6-arene)]$^+$ derivatives.[12] For the purpose of preparing a silacyclohexadienyl complex, we prepared the silacyclohexadiene **1** in two steps from C$_5$H$_6$SnBu$_2$ according to literature procedures[13] (Scheme 1).

It was shown previously that **1** can be deprotonated with ^{n}BuLi to give the "nonclassical silabenzene anion" Li[C$_5$H$_5$SiH(^{t}Bu)].[14] Reaction of this anion with either 1/4[Cp*RuCl]$_4$[15] or 1/2[Cp*RuOMe]$_2$[16] (tetrahydrofuran, room temperature) resulted in formation of the ruthenium silacyclohexadienyl complex Cp*Ru[η^5-C$_5$H$_5$SiH-(^{t}Bu)] (**2**), isolated in 45% yield as an orange microcrystalline solid upon crystallization from CH$_3$CN (Scheme 1). This reaction proceeded in nearly quantitative yield by ^{1}H NMR spectroscopy (tetrahydrofuran-d_8); thus the low isolated yield of **2** is due to its high solubility in various solvents (pentane, acetonitrile, diethyl ether, tetrahydrofuran, and hexamethyldisiloxane). Interestingly, only one isomer of **2** is formed in this reaction (by ^{1}H NMR spectroscopy). Presumably, this is the isomer with the *tert*-butyl group *exo* to the metal center, as the *endo* isomer would probably result in unfavorable nonbonding contacts with the Cp* ligand.

Compound **2** was fully characterized, and the structure shown in Scheme 1 is based largely on NMR spectroscopy. The ^{1}H NMR spectrum of **2** exhibits resonances for the ^{t}Bu and Cp* groups at δ 0.85 and 1.69, respectively. The silacyclohexadienyl ring hydrogens resonate as multiplets at δ 1.88 (H1, H5) and 4.65 (H2, H3, and H4). These resonances are very similar to those for the related silacyclohexadiene complex [Fe-(η^5-C$_5$H$_5$SiMe$_2$)$_2$] (δ 2.20, 4.85, and 4.97).[17] In addition, a resonance at δ 4.77 is assigned, based on a ^{1}H, ^{29}Si HMQC experiment, as the silicon-bound hydrogen. The observed $^1J_{\mathrm{SiH}}$ coupling constant (195 Hz) is similar to that for the free silane (191 Hz) but greater than that for Li[C$_5$H$_5$SiH(^{t}Bu)] (150 Hz).[14] The ^{13}C NMR shifts for the coordinated silacyclohexadienyl ring carbons of **2**, δ 33.0 (C1, C5), 82.7 (C3), and 91.8 (C2, C4), are similar to corresponding values reported for [Fe(η^5-C$_5$H$_5$SiMe$_2$)$_2$] (δ 38.87, 78.54, and 94.47) and are also consistent with shifts for the pentadienyl ligand in Cp*Ru(η^5-pentadienyl) (δ 42.5, 82.5, and 91.5).[17,18] It is worth noting that these ^{13}C chemical shifts are quite different from those in Li[C$_5$H$_5$SiH(^{t}Bu)] (δ 81.5 (C1, C5), 142.6 (C2, C4), and 92.4 (C3)).[14] Also, the ^{29}Si NMR spectrum of **2** exhibits a resonance at δ −33.7, which is somewhat upfield relative to the analogous ^{29}Si shift of δ −16.2 for Li-[C$_5$H$_5$SiH(^{t}Bu)].[14] Finally, the IR spectrum for **2** contains a strong stretch for the Si−H bond at 2087 cm^{-1}.

Initial attempts to abstract hydride from **2** employed the trityl reagent [Ph$_3$C][B(C$_6$F$_5$)$_4$], room temperature, and various solvents (benzene, tetrahydrofuran, dichloromethane). However, these reactions gave only mixtures of products containing species that could not be identified. In contrast, **2** reacted cleanly with the highly Lewis acidic borane B(C$_6$F$_5$)$_3$ to give [Cp*Ru(η^6-C$_5$H$_5$-Si^{t}Bu)][BH(C$_6$F$_5$)$_3$] (**3**, Scheme 1).

Interestingly, the course of this reaction is highly dependent on the solvent employed, as there is no reaction in ethereal solvents (tetrahydrofuran, diethyl ether). In benzene-d_6 the reaction produced several

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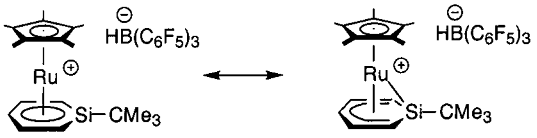
Table 1. Comparison of Ring Carbon ^{13}C NMR Shifts[a]

Compound	C1, C5	C2, C4	C3
Li[$C_5H_5SiH(^tBu)$][14]	81.5	142.6	92.4
Cp*Ru(η^5-pentadienyl)[18]	42.5	91.5	82.5
Cp*Ru[η^5-$C_5H_5SiH(^tBu)$] (**2**)	33.0	91.8	82.7
[Cp*Ru(η^6-$C_5H_5Si^tBu$)][$BH(C_6F_5)_3$] (**3**)	39.8	92.5	83.3
[Cp*Ru(η^6-benzene)]OTf[9]	88.5	88.5	88.5
C_5H_5Si(Tbt)[5c]	122.2	143.4	116.1

[a] Note: C1 and C5 are the carbons *ortho* to silicon in a ring, C2 and C4 are in the *meta* positions, and C3 is *para* to silicon. For Cp*Ru(η^5-pentadienyl), the labels refer to analogous carbon atoms in the pentadienyl ligand.

products (by ^{1}H NMR spectroscopy). However, addition of tetrahydrofuran (0.35 mL of benzene and 0.10 mL of tetrahydrofuran) to this mixture converted these products to **3** (84% yield by ^{1}H NMR spectroscopy). Reaction also took place in a benzene/THF mixture (90:10) to give **3** in 85% yield (by ^{1}H NMR spectroscopy). Notably, removal of solvent gave **3** as an impure tan foam which did not contain THF (by ^{1}H NMR spectroscopy). It would therefore seem that the role of THF in this reaction is to provide a more polar solvent mixture, which aids in formation of the ion pair. In pure tetrahydrofuran, however, formation of a strong adduct with the borane appears to inhibit its reaction with the Si−H bond. Complex **3** could not be isolated in pure form from other Cp*-containing impurities, and thus, characterization is based largely on spectroscopic methods.

The ^{1}H NMR spectrum for **3** is quite revealing, in that resonances for the silabenzene ring protons appear as a doublet (C1, C5, 2.34 ppm, $^3J_{HH} = 10$ Hz), a triplet (C3, 4.24 ppm, $^3J_{HH} = 5$ Hz), and a doublet of doublets (C2, C4, 4.58 ppm, $^3J_{HH} = 5$ Hz, $^3J_{HH} = 10$ Hz). No resonance for an Si−H bond was visible in the spectrum, and its absence is further supported by the lack of J_{HH} coupling constants attributable to this group. The ^{13}C NMR spectrum exhibits new resonances for the silabenzene ring carbons (δ 39.8 (C1, C5), 83.3 (C3), and 92.5 (C2, C4)). Interestingly, these resonances are not perturbed significantly from those in **2** (δ 33.0 (C1, C5), 82.7 (C3), and 91.8 (C2, C4)) and are also similar to shifts for the related carbons in Cp*Ru(η^5-pentadienyl)[18] (δ 42.5 (C1, C5), 82.5 (C3), and 91.5 (C2, C4)). Furthermore, as expected,[9] the ^{13}C shifts for **3** are shifted considerably upfield relative to those for the free silabenzene derivative C_5H_5Si(Tbt)[5c] (δ 122.2 (C1, C5), 116.1 (C3), and 143.4 (C2, C4)). The above comparisons (see Table 1) suggest that the bonding of the silabenzene in **3** may best be described as an η^5,η^1-interaction (resonance form **3b**) with limited delocalization in the silabenzene ligand, but the available data are somewhat ambiguous given that the ^{13}C shift for the coordinated benzene ligand in Cp*Ru(η^6-C_6H_6)$^+$ is similar to those for C2−4 in **3**.



3a **3b**

The proton-coupled ^{29}Si INEPT spectrum of **3** displays a resonance at δ −23.1 which exhibits no $^1J_{SiH}$ coupling. This resonance is shifted only slightly from that in **2** (δ −33.7) and is quite upfield from the corresponding peak in C_5H_5Si(Tbt) (δ 92.1).[5c] The three resonances observed in the ^{19}F NMR spectrum (δ −133.8, −156.0, and −163.4) and the peak in the ^{11}B NMR spectrum (δ 2.16) are consistent with the presence of a borate anion.[19] Although a B−H resonance could not be identified in the ^{1}H NMR spectrum of **3** (presumably due to the quadrupolar boron nucleus), a B−H stretch was observed in the IR spectrum at 2380 cm^{-1}. Finally, the cation in **3** was definitively identified by high-resolution mass spectrometry (FAB).

A Disilabenzene Complex. Given our success in isolating η^5-silacyclopentadienyl and η^6-silabenzene complexes of the Cp*Ru fragment, we envisioned the stabilization of a 1,4-disilabenzene derivative by coordination (Scheme 2). We have previously described the synthesis of a range of ruthenium silyl complexes via reaction of Cp*$(PMe_3)_2RuCH_2SiMe_3$ at elevated temperatures with various hydrosilanes $HSiX_3$. These reactions proceed with loss of $SiMe_4$ and formation of Cp*$(PMe_3)_2RuSiX_3$ complexes.[20] It was therefore expected that Cp*$(PMe_3)_2RuCH_2SiMe_3$ would react with the previously reported *trans*-1,4-dihydrohexamethyl-1,4-disilacyclohexa-2,5-diene (Scheme 2)[3d,e,21] to give complex **A** upon loss of $SiMe_4$. We hoped that further heating would result in loss of the PMe_3 ligands and coordination of the diene portion of the disilacyclohexadiene ligand to then give complex **B**. This is supported by the fact that heating Cp*$(PMe_3)_2RuSi(CH{=}CH_2)Ph_2$ in toluene results in formation of the silaallyl complex Cp*(PMe_3)Ru(η^3-$Ph_2SiCHCH_2$).[22] Reaction of **B** with Ph_3C^+ or $B(C_6F_5)_3$ was then expected to give the desired η^6-disilabenzene complex **C**.

Heating Cp′$(PMe_3)_2RuCH_2SiMe_3$ (Cp′ = C_5Me_4Et) with *trans*-1,4-dihydrohexamethyl-1,4-disilacyclohexa-2,5-diene in toluene at 90 °C for 12 h did not produce **B**, but instead gave Cp′(PMe_3)RuH(η^2-hexamethyl-1,4-disilabenzene) (**4**), isolated as a white crystalline solid in 86% yield (Scheme 2). The ^{1}H NMR spectrum of **4** exhibits a characteristic hydride peak at δ −12.55 with a $^2J_{PRuH}$ coupling constant (34 Hz) typical for hydride complexes of Cp$(PR_3)_n$Ru and Cp*$(PR_3)_n$Ru ($n = 1$ or 2).[23] In addition, there are two distinct resonances for the inequivalent Si−Me groups at δ 0.63 (s) and 0.75 (d, $^4J_{PH} = 1$ Hz). Finally, two different peaks are observed in the ^{29}Si NMR spectrum of **4** at δ 44.0 (d, $^2J_{PSi} = 22$ Hz) and 31.5 (d, $^2J_{PSi} = 7$ Hz).

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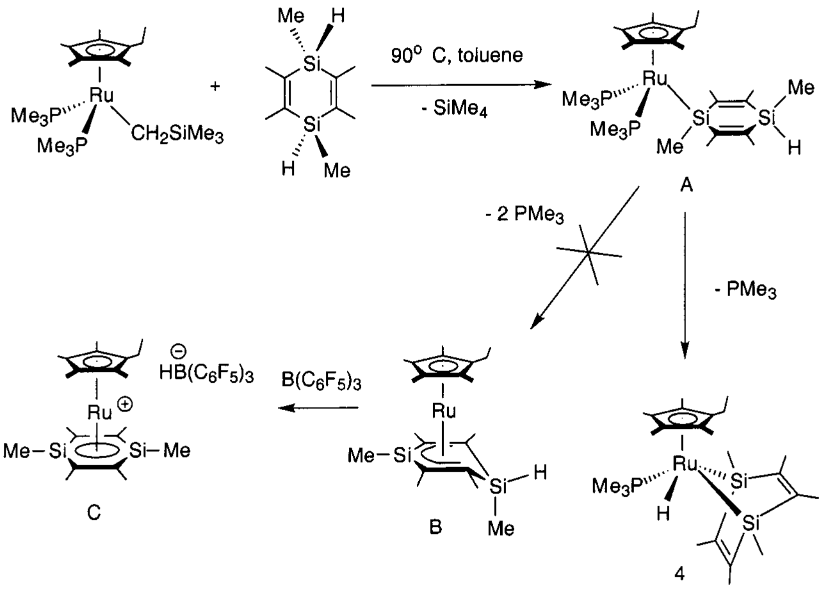
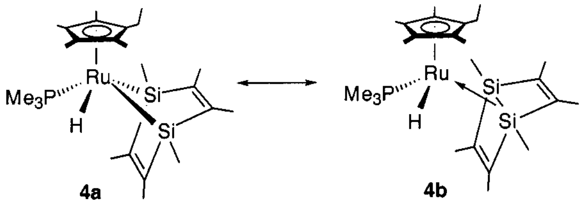
Scheme 2



X-ray quality crystals of **4** were grown by slow cooling of a concentrated toluene solution to −35 °C, and an ORTEP diagram is shown in Figure 1. The PMe_3 group was disordered over two positions and was modeled as two partial occupancy phosphorus and six partial occupancy carbon atoms (see Experimental Section for details). This disorder prevented accurate location of the hydride ligand. Complex **4** adopts a four-legged piano stool geometry with the legs composed of the PMe_3, H, and η^2-hexamethyl-1,4-disilabenzene ligands. Although several complexes of the type $Cp^*(PMe_3)RuH(SiR_3)_2$ have been reported in the literature,[20,24] **4** represents the first crystallographically characterized complex of this type. The Ru−Si distances (2.430(1) and 2.430(2) Å) fall in the high end of the range reported for Ru−Si bonds (2.190−2.465 Å).[22] The Me−Si−Si alignment in **4** is surprisingly linear (178°), and the angle between the Si(1)−C(1)−C(2)−Si(2) and Si(1)−C(3)−C(4)−Si(2) planes (71.66°) is rather acute. Finally, the sum of the angles about Si(1) and Si(2) (321° and 330.9°, respectively) reflects tetrahedral silicon centers.

Two resonance forms (**4a** and **4b**) can be invoked to describe the bonding in **4**. At one extreme **4** can be described as a metallodisilanorbornadiene complex possessing a Ru(IV) center bound to two silyl ligands which do not interact (**4a**). The other resonance structure (**4b**) represents a Dewar−disilabenzene complex with a Si−Si bond coordinated to ruthenium. Interestingly, the Si(1)−Si(2) distance (2.621(2) Å) is relatively short compared to the same distance in other crystallographically characterized examples of hexamethyldisilacyclohexadiene derivatives. For example, the corresponding distances in *cis*-bis(1,4-trimethylsilyl)-1,2,3,4,5,6-hexamethyl-1,4-disilacyclohexa-2,5-diene and a 1,4-disilabarralene derivative (1,4-dimethyl-2,3,5,6,7,8-hexaphenyl-1,4-disilabicyclo[2.2.2]octa-2,5,7-triene) are 3.405 and 2.93 Å, respectively.[25] The Si−Si separation in **4** is also short relative to analogous distances in complexes possessing chelating disilyl ligands, such as trihydrido[bis(dimethylsilyl)benzene]bis(triphenylphosphine)iridium (3.150 Å)[26] and (η^4-cyclohexa-1,3-diene)(2-*tert*-butyl-1,1,4,4-tetrafluoro-1,4-disilabutene)$Fe(CO)_2$(2.754(9) Å).[27] Moreover, the Si−Ru−Si angle in **4** (65.24(4)°) is smaller than the corresponding values in the latter two complexes (80.68(4)° and 73.1(3)°, respectively).[26,27]



The somewhat short Si−Si contact in **4** (2.621(2) Å) suggests an interaction between the two silicon centers. For comparison, it has been argued that in the dimers $[(PR_3)_2PtSiR_2]_2$, the short Si−Si separation (2.55−2.65 Å) is consistent with a bonding interaction.[28] However, for related 1,3-cyclodisiloxanes $(R_2SiO)_2$ possessing short Si−Si contacts (2.31−2.39 Å), it has been concluded on a theoretical basis that the bonding is best described as four equivalent, localized Si−O bonds with no appreciable σ-bonding between the silicon atoms.[29] Finally, the length of the Si−Si separation in **4** compared to the

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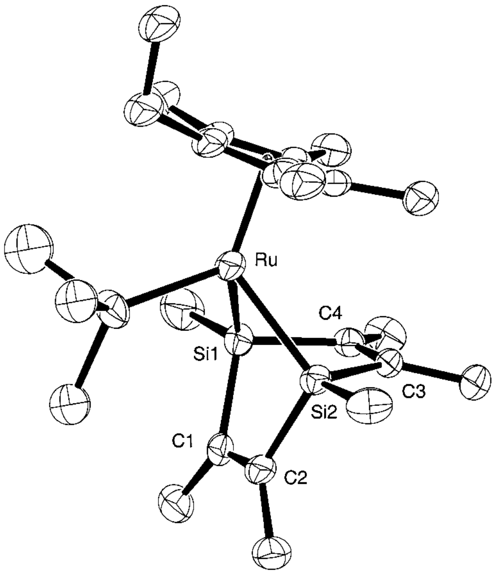

Figure 1. ORTEP diagram of Cp′(PMe$_3$)RuH(η^2-hexamethyl-1,4-disilabenzene) (**4**).

Si−Si bond distance in the known Dewar−disilabenzene derivative 1,4-dimethyl-2,3,5,6-trimethylsilyl-1,4-disila-Dewar-benzene (2.244(2) Å)[6] suggests that there may not be a strong bonding interaction between the two silicon centers in **4**. Given the data described above, it was difficult to describe the bonding in **4**. Thus, a theoretical investigation was undertaken.

The bonding in **4** has been examined within the framework of molecular orbital theory with Kohn−Sham density functional calculations. Calculations were performed on the model system Cp(PH$_3$)RuH(η^2-hexamethyl-1,4-disilabenzene) (**5**), in which the Cp′ and PMe$_3$ ligands in **4** are replaced by Cp and PH$_3$, respectively. In **5**, the six methyl substituents on the disilabenzene fragment remain “intact”, as they are in **4**. The model system has been fully geometry optimized, providing a structure that preserves the important geometric features observed in the X-ray structure of **4**. Most notably, the Si−Si bond is calculated to be 2.67 Å, which agrees well with the X-ray value of 2.62 Å. The two Ru−Si bond distances, which are calculated to be 2.45 Å, also agree well with the X-ray values of 2.43 Å. Other parameters, tabulated in Table 3, also show that **5** is a reasonable model for **4**.

Three molecular orbitals in **5** can be distinguished as exhibiting Si−Ru bonding character. These are the HOMO-5, HOMO, and HOMO-1 orbitals, which are shown in Figure 2a, 2b, and 2c, respectively, as isosurface plots. HOMO-5 (Figure 2a) can be characterized as a σ-type orbital which is bonding between the Ru and each Si atom. Since there is a node between the two Si−Si centers, there is no Si−Si orbital interaction associated with this MO. Thus, the HOMO-5 orbital provides a bonding picture suggestive of resonance structure **4a**. On the other hand, the HOMO and HOMO-1 of **5** (Figure 2b and 2c) can be described as C−C π-bonding orbitals with significant Ru−Si bonding character. Since no orbital nodes exist between the Si−Si atoms, these two orbitals are suggestive of a weak Si−Si bond that is coordinating to the Ru center, as depicted in resonance structure **4b**.

Table 2. Summary of Crystallographic Data

empirical formula	RuSi$_2$PC$_{24}$H$_{45}$
fw	521.83
cryst color, habit	white, platelike
cryst dimens	0.32 × 0.18 × 0.05 mm
cryst syst	triclinic
cell determination (2θ range)	3050 (4.0−45.0°)
lattice params	a = 9.1338(8) Å
	b = 10.3057(9) Å
	c = 15.584(1) Å
	α = 96.093(2)°
	β = 91.242(2)°
	γ = 114.225(1)°
	V = 1326.8(2) Å^3
space group	$P\bar{1}$ (#2)
Z	2
D_{calc}	1.306 g/cm^4
μ(Mo Kα)	7.50 cm^{-1}
diffractometer	Siemens SMART
radiation	Mo Kα (λ = 0.71069 Å)
	graphite monochromated
temperature	−106 °C
scan type	ω (0.3° per frame)
no. of reflns measd	total: 6011
	unique: 4236 (R_{int} =0.014)
no. observations (I>3.00$\sigma(I)$)	3039
structure solution	direct methods (SIR92)
refinement	full-matrix least-squares
residuals: R; R_w	0.035; 0.044
max peak in final diff map	0.74 e/Å^3
min peak in final diff map	-0.49 e/Å^3

Table 3. Comparison of Selected Geometric Parameters Derived from the Experimental X-ray Structure of 4 and the Calculated Model System, 5

parameter[a]	X-ray structure	calculated structure
Si−Si	2.62	2.66
Ru−Si (av)	2.43	2.46
P−Ru	2.28	2.28
Ru−Cp centroid	1.92	1.95
Si−Ru−Si angle	65	65
C(Me)−Si−Si angle (av)	178	177

[a] Distances reported in angstroms, angles reported in degrees.

To examine the nature of the Ru−Si bonding in the HOMO and HOMO-1 orbitals, we first studied the Si−Si bonding in the isolated disilabenzene fragment frozen in the geometry that it has in **5**. The HOMO of this “frozen” fragment, shown in Figure 2d, can be characterized as a weak Si−Si σ-bonding orbital.[30] The contribution of this Si−Si bonding orbital to the Ru−Si bonding in **5** can be assessed by constructing molecular orbitals using a basis of orbitals from the free disilabenzene and Cp(PH$_3$)RuH fragments. By using this procedure we can, in the framework of molecular orbital theory, quantify the contribution of this Si−Si σ-bonding orbital to the two Ru−Si bonding orbitals (HOMO and HOMO-1 of **5**). Shown on the left-hand side of Figure 3 are isosurface plots of the HOMO and HOMO-1 orbitals of **5**. On the right-hand side of Figure 3 are isosurface plots of the three fragment orbitals which have coefficients that are the largest in magnitude. The values shown below these fragment orbitals are the molecular orbital eigenvector coefficients. Both the HOMO and HOMO-1 are primarily composed of a Ru d-based

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(30) Full geometry optimization of hexamethyl-1,4-disilabenzene gives a Dewer benzene structure with a Si−Si bond distance of 2.28 Å. This is in good agreement with the Si−Si bond distance of 2.24 Å recently observed by Ando and co-workers for a similar 1,4-disilabezene complex.[6] The Cartesian coordinates of the optimized disilabenzene complex is provided in the Supporting Information.

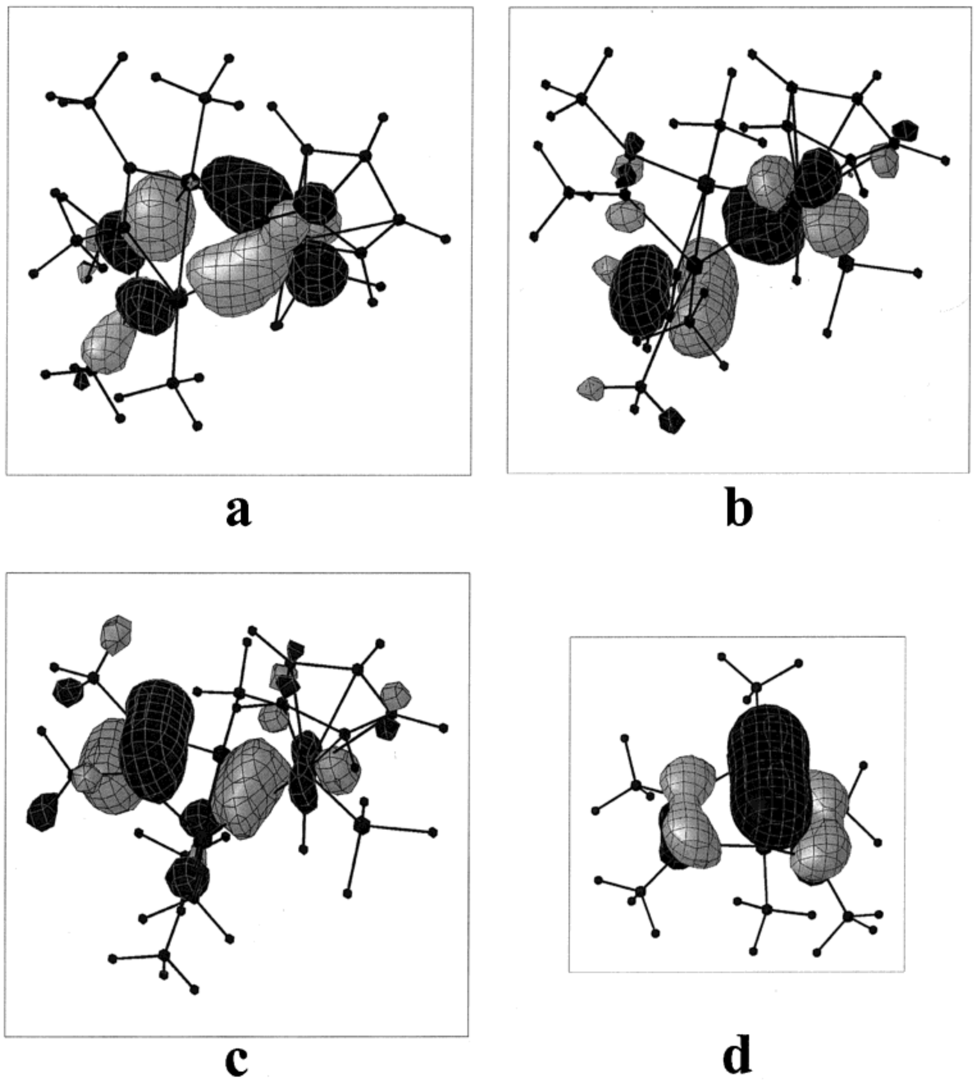


Figure 2. Isosurface plots of the Kohn−Sham molecular orbitals of **5** (a−c) and the isolated disilabenzene fragment (d) fixed in the geometry of **5**. The molecular orbitals presented in a−c can be characterized as Si−Ru bonding orbitals. The molecular orbital of the disilabenzene fragment shown in d is characterized as a Si−Si bonding orbital.

orbital, the Si−Si σ-bonding orbital of the disilabenzene fragment previously shown in Figure 2d, and a C═C π-bonding orbital of the disilabenzene fragment. This analysis reveals that HOMO and HOMO-1 of **5** both have significant contributions from the Si−Si σ-bonding orbital of the disilabenzene fragment and that there is constructive overlap between the Si−Si σ-bonding orbital and the d orbitals of the Ru center. We note that the Si−Si σ-bonding orbital of the disilabenzene fragment does not contribute significantly to any other molecular orbitals in **5**. Thus, it can be said that there is a weak Si−Si σ-type interaction in **5** that contributes to the bonding of the disilabenzene fragment to the Ru center. Consistent with this, a Mayer bond order calculation provided a Si−Si bond order of 0.17 and Ru−Si bond orders of 0.53 and 0.48.

From this analysis we conclude that the bonding in **5** (and by analogy also in **4**) can be described as intermediate between the two extreme resonance forms **4a** and **4b**, such that it is a metallodisilanorbornadiene that possesses a weak Si−Si σ-bond that participates in the bonding to the Ru center.

Interestingly, the formation of **4** implies that a rearrangement occurs in which the *trans* arrangement of the Si−Me bonds is converted to a *cis* geometry. In fact, we had specifically employed the *trans* isomer of hexamethyl-1,4-disilacyclohexadiene in the hope that intramolecular oxidative addition of the second Si−H bond would not interfere with coordination of the diene portion of the molecule. By monitoring the reaction of $Cp'(PMe_3)_2RuCH_2SiMe_3$ with *trans*-1,4-dihydrohexamethyl-1,4-disilacyclohexa-2,5-diene in toluene-d_8 at 90 °C, an intermediate (**A**) was observed to build up after 6 h (9% by ^{1}H NMR spectroscopy). For intermediate **A**, a resonance at δ 4.87 is attributed to the Si−H hydrogen, and a pseudodoublet at δ 1.18 is assigned to the 18 hydrogens of the PMe_3 ligands. In addition, **A** exhibits two resonances at δ 0.61 and 0.49 for the Si−Me groups, and four resonances are observed for the ring methyl groups of the disilacylohexadiene and Cp′ (δ 1.67, 1.72, 1.91, and 1.98) ligands. The ^{31}P NMR spectrum of **A** exhibits a singlet at δ −0.42 for the equivalent PMe_3 ligands.

A possible mechanism for the isomerization of **A** is given in Scheme 3. Further heating of this complex could result in loss of a PMe_3 ligand from the Ru center to generate a 16-electron intermediate. This species could then undergo a reversible 1,2-methyl migration

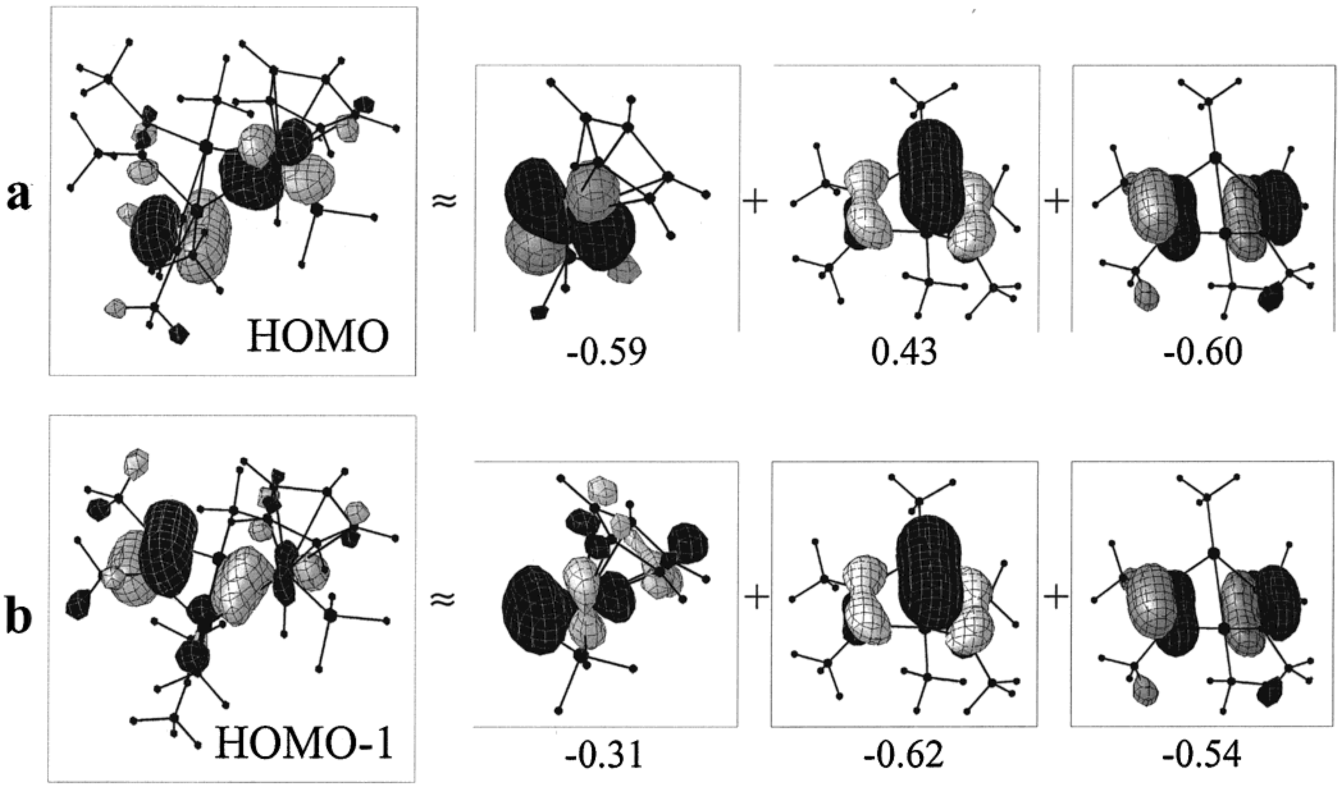
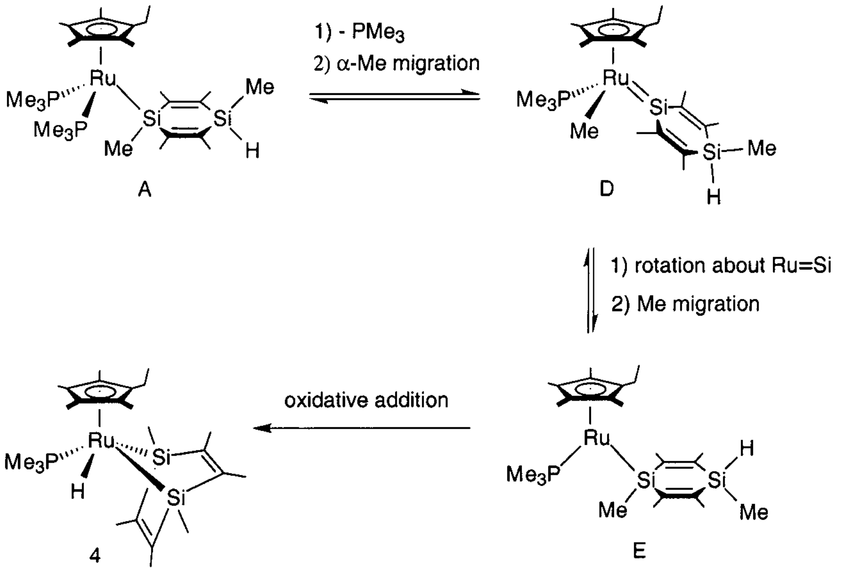


Figure 3. Composition of HOMO and HOMO-1 orbitals of **5** in the basis of the disilabenzene fragment and Cp(PH$_3$)RuH fragment. Isosurface plots of the HOMO and HOMO-1 orbitals of **5** are shown with the three fragment orbitals which have the largest contribution to each. The molecular orbital eigenvector coefficients are shown with each fragment orbital.

Scheme 3



from silicon to Ru, to produce an 18-electron ruthenium silylene complex (**D**, Scheme 3). Rotation about the metal–silicon bond, followed by methyl migration back to silicon, would result in a *cis* arrangement of the Si–Me groups, and oxidative addition of the remaining Si–H bond could produce **4**. There is little precedent for 1,2-methyl migrations of this sort, but an example has been reported for a related Ir system.[31] Furthermore, it is reasonable to expect that rotation about the Ru–Si double bond would be facile given that hindered rotation has not been observed for related species[32] and that calculations suggest that CpL$_2$Ru=SiR$_2$$^+$ silylene complexes possess mainly dative Si–Ru σ-bonds with little Ru–Si π-back-bonding.[33] Finally, it is worth

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mentioning that rotation about a Ru$-$Si double bond has been invoked to explain the fluxional behavior observed in alkoxy-bridged bis(silylene)ruthenium complexes.[34]

Complex **4** is quite thermally stable, as heating a concentrated toluene-d_8 solution to 120 °C for several days resulted in no detectable change. In addition, **4** did not react with $[Ph_3C][B(C_6F_5)_4]$ or $B(C_6F_5)_3$ at room temperature (benzene, toluene, tetrahydrofuran, dichloromethane) or upon heating to 100 °C in toluene. Finally, **4** did not react with BPh_3 (as a phosphine sponge) in toluene or cyclohexane, even upon heating to reflux for 24 h.

Concluding Remarks

In this contribution we have described the first examples of transition metal complexes containing silabenzene and disilabenzene ligands. Abstraction of a hydride from silicon is a viable route to complexes of this type, and we have utilized this method in generating 1-*tert*-butylsilabenzene in the coordination sphere of Cp*Ru. In addition, hexamethyl-1,4-disilabenzene has been coordinated to Ru in an η^2 fashion. Binding of the disilabenzene in this manner seems to involve an interesting rearrangement, which may occur via a silylene intermediate. It is of course yet to be seen whether a less saturated metal center might bind this fragment in an η^6 manner. η^6-Coordination to a transition metal fragment lends further support to the notion that silabenzene derivatives are at least to some degree aromatic. These studies demonstrate that coordination of silabenzenes to a transition metal fragment is a useful way to stabilize these reactive species, and we are currently exploring routes to complexes of various silabenzenes in the hope of gaining a better understanding of their coordination chemistry.

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, toluene, benzene, and diethyl ether were distilled from sodium/benzophenone, whereas benzene-d_6 and toluene-d_8 were distilled from Na/K alloy. The compounds $[Cp^*RuCl]_4$,[15] $C_5H_5SiH^tBu$,[13] $B(C_6F_5)_3$,[35] $Cp'(PMe_3)_2RuCH_2SiMe_3$,[20] and *trans*-1,4-disilahexamethylcyclohexadiene[3d,e,21] were prepared according to literature procedures. NMR spectra were recorded at 300 or 500 MHz (^1H) with Bruker AMX-300 and DRX-500 spectrometers and at 125 MHz ($^{13}C\{^1H\}$), 202 MHz ($^{31}P\{^1H\}$), or 99 MHz ($^{29}Si\{^1H\}$) with the DRX-500 spectrometer, at ambient temperature unless otherwise noted. Elemental analyses were performed by the microanalytical laboratory in the College of Chemistry at the University of California, Berkeley. IR samples of solid materials were prepared as KBr pellets. All IR absorptions are reported in units of cm^{-1} and were recorded with a Mattson Infinity 60 MI FTIR spectrometer.

$Cp^*Ru[\eta^5$-$C_5H_5SiH(^tBu)]$ (2). A 100 mL Schlenk tube was charged with $C_5H_5SiH^tBu$ (0.425 g, 2.79 mmol) and 50 mL of THF. ^{n}BuLi (1.00 mL, 2.80 mmol) was added to this flask via syringe, and the resulting reaction mixture was stirred for 30 min to give a dark orange solution. This solution was then added to a 250 mL round-bottom Schlenk flask containing $[Cp^*RuCl]_4$ (0.758 g, 0.69 mmol) in 100 mL of THF. This reaction mixture was stirred for 30 min before the volatile materials were removed under dynamic vacuum. The remaining dark orange residue was extracted into acetonitrile (3 × 20 mL). The combined extracts were concentrated to 20 mL and cooled to -78 °C to give **2** as a dark orange powder in 45% yield (0.487 g, 1.26 mmol). ^1H NMR (benzene-d_6): δ 4.77 (br s, 1 H, Si*H*), 4.65 (m, 3 H, $C_5H_5SiH^tBu$), 1.88 (m, 2 H, $C_5H_5SiH^tBu$), 1.69 (s, 15 H, C_5Me_5), 0.85 (s, 9 H, Si^tBu). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 91.80 (s, $C_5H_5SiH^tBu$) 88.85 (s, C_5Me_5), 82.74 (s, $C_5H_5SiH^tBu$), 32.97 (s, $C_5H_5SiH^tBu$), 29.80 (s, $SiCMe_3$), 25.21 (s, $SiCMe_3$), 11.37 (s, C_5Me_5). $^{29}Si\{^1H\}$ (benzene-d_6): δ -33.7 (s, $C_5H_5SiH^tBu$). Anal. Calcd for $C_{19}H_{30}RuSi$: C, 58.88; H, 7.80. Found: C, 59.24; H, 7.60. IR: 2916 s, 2845 s, 2087 s (Si$-$H), 1465 m, 1456 m, 1380 m, 1310 m, 1027 w, 835 s, 800 m, 579 m. Mp: 82$-$85 °C.

$[Cp^*Ru(\eta^6$-$C_5H_5Si^tBu)][BH(C_6F_5)_3]$ (3). Compound **2** (0.165 g, 0.43 mmol) and $B(C_6F_5)_3$ (0.218 g, 0.43 mmol) were placed together in a Schlenk tube. Benzene (30 mL) and THF (3 mL) were then added to the flask, producing a light tan solution. This solution was stirred for 30 min, after which time the volatile materials were removed under dynamic vacuum. The remaining residue was isolated, giving **3** (0.380 g) as a slightly contaminated tan foam. This reaction was performed on an NMR-tube reaction scale and checked by ^1H NMR spectroscopy, giving **3** in 84% yield (vs a 1,3,5-trimethoxybenzene standard). ^1H NMR (benzene-d_6): δ 4.58 (dd, $^3J_{HH} = 5$ Hz, $^3J_{HH} = 10$ Hz, 2 H, $C_5H_5Si^tBu$), 4.24 (t, 1 H, $^3J_{HH} = 5$ Hz, $C_5H_5Si^tBu$), 2.34 (d, 2 H, $^3J_{HH} = 10$ Hz, $C_5H_5Si^tBu$), 1.63 (s, 15 H, C_5Me_5), 1.33 (s, 9 H, Si^tBu). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 92.45 (s, $C_5H_5Si^tBu$) 88.48 (s, C_5Me_5), 83.27 (s, $C_5H_5Si^tBu$), 39.82 (s, $C_5H_5Si^tBu$), 30.35 (s, $SiCMe_3$), 29.85 (s, $SiCMe_3$), 11.34 (s, C_5Me_5). $^{29}Si\{^1H\}$ (benzene-d_6): δ -23.1 (s, $C_5H_5Si^tBu$). ^{11}B (160.5 MHz, benzene-d_6, 25 °C): δ 2.16 (br s, $HB(C_6F_5)_3$). ^{19}F (376.5 MHz, benzene-d_6, 25 °C): δ -133.8 (d, *o*-F, $^3J_{FF} = 22$ Hz), -156.0 (t, *p*-F, $^3J_{FF} = 21$ Hz), -163.4 (dd, *m*-F, $^3J_{FF} = 22$ Hz, $^3J_{FF} = 21$ Hz). IR: 2380 s (B$-$H). HRMS (FAB) calcd for $C_{19}H_{29}RuSi$: 387.1082. Found: 387.1098.

$Cp'(PMe_3)RuH(\eta^2$-1,4-$Si_2C_4Me_6)$ (4). $Cp'(PMe_3)_2RuCH_2SiMe_3$ (0.357 g, 0.73 mmol) and *trans*-1,4-dihydrohexamethyl-1,4-disilacyclohexa-2,5-diene (0.143 g, 0.73 mmol) were placed in a 200 mL sealable reaction vessel. To this reaction flask was added 75 mL of toluene. The flask was placed in an oil bath, and the solution was heated to 90 °C for 12 h. During this time the initial deep yellow solution turned colorless. After this time the volatile materials were removed under dynamic vacuum. The remaining white residue was dissolved in toluene (10 mL), and the resulting solution was cooled to -35 °C, giving **4** as white blocklike crystals in 86% yield (0.327 g, 0.63 mmol). ^1H NMR (benzene-d_6): δ 2.08 (q, 2 H, $^3J_{HH} = 7$ Hz, $C_5Me_4CH_2CH_3$), 2.09, 2.02, 1.91, 1.90 (s, 12 H, SiC_4Me_4Si), 1.62, 1.61, 1.57, 1.57 (s, 12 H, C_5Me_4Et), 0.98 (d, 9 H, $^2J_{PH} = 9$ Hz, PMe_3), 0.84 (t, 3 H, $^3J_{HH} = 7$ Hz, $C_5Me_4CH_2CH_3$), 0.75 (d, 3 H, $^4J_{PH} = 1$ Hz, Si*Me*), 0.63 (s, 3 H, Si*Me*), -12.6 (d, 1 H, $^2J_{PH} = 34$ Hz, Ru-*H*). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 166.79, 165.60, 164.60, 164.12 (s, SiC_4Me_4Si), 100.75 (d, 1 C, $^2J_{PC} = 2$ Hz, C_5Me_4Et), 95.80, 95.30, 94.71, 94.41 (d, 4 C, $^2J_{PC} = 2$ Hz, C_5Me_4Et), 25.01 (d, $J_{PC} = 31$ Hz, PMe_3), 20.39, 18.54, 18.43, 16.95, 16.81, 15.61, 11.68, 11.67, 11.54, 11.47 (s, 10 C, SiC_4Me_4Si and C_5Me_4Et), -0.43 (s, Si*Me*), -3.10 (d, $^3J_{PC} = 1$ Hz, Si*Me*). $^{29}Si\{^1H\}$ (benzene-d_6): δ 44.0 (d, $^2J_{PSi} = 22$ Hz, silicon atom trans to PMe_3), 31.5 (d, $^2J_{PSi} = 7$ Hz, silicon atom cis to PMe_3). $^{31}P\{^1H\}$ NMR (benzene-d_6): δ 6.00 (s, PMe_3) Anal. Calcd for $C_{24}H_{45}PRuSi_2$: C, 55.24; H, 8.69. Found: C, 55.30; H, 8.72. IR: 2890 s, 1949 s (Ru$-$H), 1451 s, 1364 m, 1297 m, 1277 m, 1240 m, 1162 w, 1024 w, 948 s, 848 w, 768 s, 710 m, 667 m. Mp: 143$-$146 °C.

$Cp'(PMe_3)_2Ru(MeSiC_4Me_4SiHMe)$. This complex was identified in the reaction solution (toluene-d_8) of $Cp'(PMe_3)_2RuCH_2SiMe_3$ and *trans*-1,4-dihydrohexamethyl-1,4-disilacyclohexa-2,5-diene (9% by ^1H NMR spectroscopy). ^1H NMR (benzene-

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d_6): δ 4.87 (s, 1 H, SiH), 2.15 (q, 2 H, $^3J_{HH} = 7$ Hz, $C_5Me_4CH_2CH_3$), 1.98, 1.91 (s, 12 H, SiC_4Me_4Si), 1.72, 1.67 (s, 12 H, C_5Me_4Et), 1.18 (d, 18 H, $^2J_{PH} = 9$ Hz, PMe_3), 1.85 (t, 3 H, $^3J_{HH} = 7$ Hz, $C_5Me_4CH_2CH_3$), 0.61 (s, 3 H, SiMe), 0.49 (d, 3 H, $^4J_{PH} = 1$ Hz, SiMe). $^{31}P\{^1H\}$ NMR (benzene-d_6): δ −0.42 (s).

X-ray Crystallography. White, platelike crystals were obtained from a concentrated toluene solution at −35 °C. A crystal of dimensions 0.32 × 0.18 × 0.05 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). An absorption correction was performed using SADABS ($T_{max} = 0.9766$, $T_{min} = 0.8770$). The 6011 integrated reflections were averaged in point group −1 to give 4236 unique reflections ($R_{int} = 0.014$), but only 3039 reflections were considered observed ($I > 3.00\sigma(I)$). No decay correction was necessary. The space group was determined to be $P\bar{1}$. 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. The PMe_3 group bound to Ru was disordered over two positions. This disorder was modeled using two different, partial occupancy, PMe_3 groups. Both P atoms were modeled with anisotropic displacement parameters, and all the carbons (C(22)−C(27)) were refined isotropically. The occupancy of P(2) was constrained to be equal to the difference of one and the occupancy of P(1), as were carbons 25, 26, and 27. Carbons 22, 23, and 24 were constrained to have the same occupancy as P(1). The occupancy factor was refined to 58% for P(1) and carbons 22, 23, and 24 and to 42% for P(2) and carbons 25, 26, and 27. The number of variable parameters was 260, giving a data/parameter ratio of 11.69. The maximum and minimum peaks on the final difference Fourier map were 0.74 and −0.49 e/Å^3, respectively. $R = 0.035$, $R_w = 0.044$, GOF = 1.53. The crystallographic data are summarized in Table 2.

Computational Details. All Kohn−Sham density functional theory calculations were performed with the ADF2000.01 quantum chemistry package.[36] The gradient-corrected exchange functional of Becke[37] and the correlation functional of Perdew[38,39] were utilized in conjunction with the LDA parametrization of Vosko, Wilk, and Nusair[40] for the calculation of both the energy and gradients. An uncontracted triple-ζ basis of Slater-type orbitals was employed for the 4s, 4p, 4d, 5s, and 5p valence shells of the Ru center and is designated as the IV basis in ADF. For the main group elements, a double-ζ basis of Slater-type orbitals was employed for the ns and np valence shells that were augmented with polarization functions and are designated the III basis in ADF. Inner shells were treated with the frozen core approximation. A spin-restricted formalism was used for all calculations, and no symmetry constraints were used during geometry optimizations. In ADF, the system is built-up from fragments that can be either atomic fragments or molecular fragments. The molecular orbital coefficients provided correspond to the symmetrized fragment orbitals in ADF. The molecular orbital eigenvector coefficients in this basis provide a direct interpretation of the molecular orbitals in terms of frontier orbital theory. Isosurface plots were created by the ADFPLT program version 1.0 of J. Autschbach. For all plots shown an isosurface value of ±0.06 au was utilized. Mayer bond order calculations were performed with a minimal single-ζ basis set.[41]

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Supporting Information Available: Tables of crystal, data collection, and refinement parameters, bond distances and angles, and anisotropic displacement parameters for **4**. The Cartesian coordinates of the optimized geometry of the model complex **5** and hexamethyl-1,4-disilabenzene. This material is available free of charge via the Internet at http://pubs.acs.org.

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