# Stable Silacyclopentadienyl Complexes of Ruthenium: ($\eta^5$-$C_5Me_5$)Ru[$\eta^5$-$Me_4C_4SiSi(SiMe_3)_3$] and X-ray Structure of Its Protonated Form

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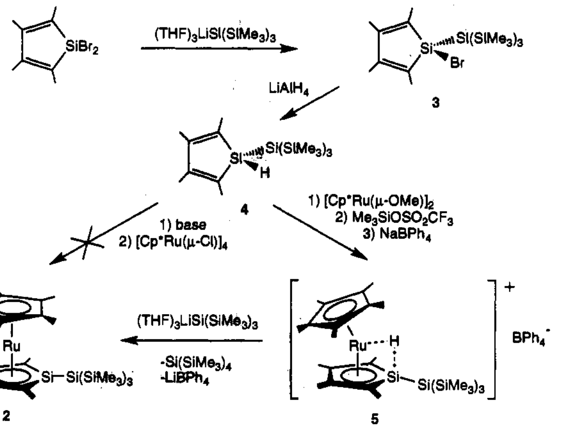
Despite considerable effort, stable silaaromatic compounds have not yet been isolated and fully characterized.[1] However, development of novel $\pi$-systems incorporating multiple bonds to silicon has seemed feasible, particularly since the first reports of stable compounds with Si=C[2a] and Si=Si[2b] double bonds. Theoretical calculations indicate that silabenzene is nearly as aromatic as benzene,[3] whereas the silacyclopentadienide anion is only about 25% as aromatic as $C_5H_5$ [4a] and has a ground state with pyramidal silicon.[4b] Nonetheless, $\eta^5$-silacyclopentadienyl complexes have been vigorously pursued as potentially accessible silaaromatic derivatives, since transition-metal fragments are known to stabilize many reactive species by coordination.[5] The $[Ph_4C_4Si^tBu]^-$ silacyclopentadienide anion has recently been generated in solution, and analysis of NMR parameters for this species suggests some delocalization of the negative charge.[6] We have recently reported the first stable $\eta^5$-germacyclopentadienyl complex, Cp*Ru[$\eta^5$-$Me_4C_4GeSi(SiMe_3)_3$] (**1**, Cp* = $\eta^5$-$C_5Me_5$), prepared via addition of a germacyclopentadienide anion to $[Cp^*Ru(\mu\text{-}Cl)]_4$.[7] Here we report the first transition-metal $\eta^5$-silacyclopentadienyl complexes, which have required a different synthetic approach.

The silole used in this study, $Me_4C_4Si(H)Si(SiMe_3)_3$ (**4**),[8] was synthesized in two steps from the dibromide $Me_4C_4SiBr_2$[9] (Scheme 1). Initial attempts to synthesize Cp*Ru[$\eta^5$-$Me_4C_4SiSi(SiMe_3)_3$] (**2**) were based on the method used to prepare **1**. However, we have so far been unable to generate $[Me_4C_4SiSi(SiMe_3)_3]^-$ cleanly in solution. Compound **4** does not react with $KN(SiMe_3)_2$, $(THF)_3LiSi(SiMe_3)_3$, or KH/18-crown-6, and reactions with KPh, $KCH_2Ph$, and $KCH_2Ph$/18-crown-6 give only complex mixtures (by NMR spectroscopy).

A silacyclopentadienyl ligand was introduced directly via oxidative addition of **4** to $Cp^*Ru^+$, generated in situ by reaction of $[Cp^*Ru(\mu\text{-}OMe)]_2$ with $Me_3SiOSO_2CF_3$ in dichloromethane.[10] After addition of $NaBPh_4$ to the reaction mixture, {Cp*Ru(H)[$\eta^5$-$Me_4C_4SiSi(SiMe_3)_3$]}[$BPh_4$] (**5**) was isolated as amber needles.

**Scheme 1**



The NMR spectra for **5**,[8] including a singlet at $\delta$ – 8.82 assigned to the hydride ligand on ruthenium, are consistent with the structure in Scheme 1.

The cation in **5** (Figure 1)[11] has the general appearance of a protonated metallocene. The Ru–ring centroid distances are identical within experimental error (1.84 Å), and the centroid–Ru–centroid angle is 164.2(3)°. The five-membered $C_4Si$ ring of the silacyclopentadienyl ligand is planar, and the summation of angles at Si(1) (355.1°, ignoring the SiH group) reflects considerable $sp^2$ character for that atom. An additional indication of delocalization in the silacyclopentadienyl ring is the small difference between the SiC–CCC and SiCC–CC bond lengths, 0.07 (2) Å. Analogous parameters in related compounds vary from ca. 0, for example in **1** (0.01 (1) Å),[7] to 0.16 (1) Å for the germole diene $C_4Me_4Ge(H)Si(SiMe_3)_3$.[12] The 19.0° angle between the Si(1)–Si(2) bond and the $C_4Si$ least-squares plane (the degree to which the silyl group bends away from the Ru center) is somewhat greater than the analogous angle in complex **1** (12.9°), perhaps because of the observed Si···H interaction. The hydride ligand, which was located and refined, is nearer to the silacyclopentadienyl ring, as revealed by the inequivalent ring centroid–Ru–H angles of 113 (3) and 82 (3)°, and the Si(1)–H(1a) distance of 1.70 (7) Å. The Ru···H···Si interaction is similar

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[8] Selected data. **3**: $^1H$ NMR (benzene-$d_6$): $\delta$ 0.32 (s, 27 H, $SiMe_3$), 1.61, 1.98 (s, 12 H, $Me_4C_4Si$). **4**: Anal. Calcd for $C_{17}H_{40}Si_5$: C, 53.0; H, 10.5. Found: C, 52.9; H, 10.6. $^1H$ NMR (benzene-$d_6$): $\delta$ 0.30 (s, 27 H, $SiMe_3$), 1.75, 2.04 (s, 12 H, $Me_4C_4Si$), 4.79 (s, 1 H, SiH). $^{13}C\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 2.86 (s, $SiMe_3$), 14.78, 15.69 (s, *Me*$_4C_4Si$), 129.53, 150.94 (s, $Me_4$*C*$_4$Si). $^{29}Si\{^1H\}$ NMR (dichloromethane-$d_2$, DEPT): $\delta$ –138.64 (s, *Si*$(SiMe_3)_3$), –32.68 (s, $C_4SiH$), –8.90 (s, Si(*Si*$Me_3)_3$). IR (Nujol, cm$^{-1}$): $\nu$(SiH) 2080. **5**: Anal. Calcd for $C_{51}H_{74}BRuSi_5$: C, 65.1; H, 8.05. Found: C, 64.2; H, 8.06. $^1H$ NMR (dichloromethane-$d_2$): $\delta$ –8.82 (s, 1 H, RuH), 0.41 (s, 27 H, $SiMe_3$), 1.36, 2.03 (s, 12 H, $Me_4C_4Si$), 1.82 (s, 15 H, Cp*), 6.90 (t, 4 H, para CH), 7.06 (t, 8 H, meta CH), 7.35 (m, 8 H, ortho Ph). $^{13}C\{^1H\}$ NMR (dichloromethane-$d_2$): $\delta$ 2.74 (s, $SiMe_3$), 10.25 (s, Cp*), 11.61, 14.58 (s, *Me*$_4C_4Si$), 74.36, 108.83 (s, $Me_4$*C*$_4$Si), 95.97 (s, Cp*), 122.00, 125.85, 136.34, 164.40 (Ph). $^{29}Si\{^1H\}$ NMR (dichloromethane-$d_2$, DEPT): $\delta$ –144.40 (s, *Si*$(SiMe_3)_3$), –27.10 (s, $C_4SiH$), –6.85 (s, Si(*Si*$Me_3)_3$). **2**: $^1H$ NMR (benzene-$d_6$) $\delta$ 0.32 (s, 27 H, $SiMe_3$), 1.63, 1.81 (s, 12 H, $Me_4C_4Si$), 1.79 (s, 15 H, $C_5Me_5$); $^{13}C\{^1H\}$ NMR (benzene-$d_6$) $\delta$ 2.84 (s, $SiMe_3$), 11.20 ($C_5$*Me*$_5$), 12.50, 15.75 (s, *Me*$_4C_4Si$), 73.09, 88.53 (s, $Me_4$*C*$_4$Si), 86.02 (*C*$_5Me_5$); $^{29}Si\{^1H\}$ NMR (benzene-$d_6$, DEPT) $\delta$ –124.04 (s, *Si*$(SiMe_3)_3$), –7.35 (s, $C_4Si$), 1.00 (s, Si(*Si*$Me_3)_3$); HRMS (FAB) calcd for $C_{27}H_{55}Si_5Ru$ 621.2194, found 621.2200.

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[11] Crystal data for {Cp*Ru(H)[$\eta^5$-$Me_4C_4SiSi(SiMe_3)_3$]}[$BPh_4$] (**5**): $C_{51}H_{75}BRuSi$, orthorhombic, *Pnma*, $a$ = 22.223 (5) Å, $b$ = 15.387 (4) Å, $c$ = 16.024 (4) Å, $V$ = 5465 (2) Å$^3$, $Z$ = 4, $T$ = 296 K, $D_{calc}$ = 1.143 g cm$^{-3}$, $R(F)$ = 4.76% for 4150 independent reflections ($4° \leq 2\theta \leq 48°$). All non-hydrogen atoms were refined anisotropically except for one of the symmetry-unique phenyl rings of the $BPh_4$ counterion. This phenyl ring is disordered over two sites in an approximate 50/50 occupancy ratio. Hydrogen atoms were idealized except for H(1a), which was found and refined.

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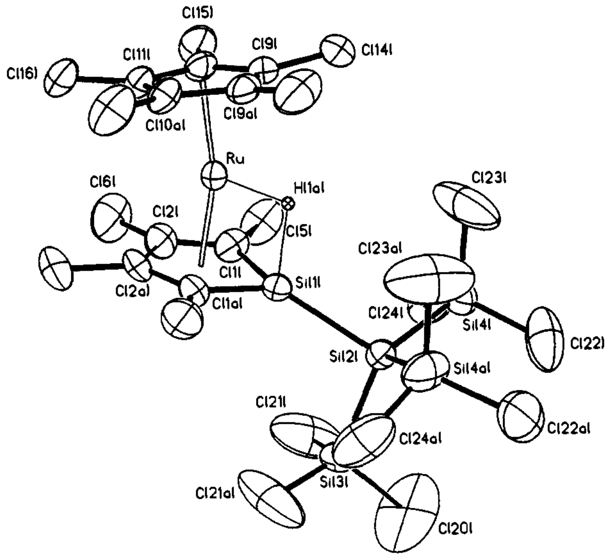

**Figure 1.** ORTEP view of the cation in **5**. Important bond distances (Å) and angles (deg): Ru–CNT(1) 1.842 (6), Ru–Si(1) 2.441 (3), Ru–C(1) 2.252 (7), Ru–C(1a) 2.252 (7), Ru–C(2) 2.222 (7), Ru–C(2a) 2.222 (7), Si(1)–C(1) 1.830 (7), Si(1)–C(1a) 1.830 (7), C(1)–C(2) 1.391 (10), C(2)–C(2a) 1.462 (15), Si(1)–Si(2) 2.326 (4), Ru–CNT(2) 1.837 (7), Ru–H(1a) 1.48 (7), Si(1)–H(1a) 1.70 (7); CNT(1)–Ru–CNT(2) 164.7 (3), Ru–H(1a)–Si(1) 100 (4), Ru–H(1a)–CNT(1) 82 (3), Ru–H(1a)–CNT(2) 113 (3). CNT(1) is the centroid of the ring containing Si(1); CNT(2) is the centroid of the Cp* ring.

to Mn···H···Si arrangements observed in Cp(CO)(L)Mn($\eta^2$-H-SiR$_3$) complexes, for which Si–H bond lengths are typically about 1.8 Å.[13] The $J_{SiH}$ coupling constant of 41 Hz for **5** is on the low end of the 40–70 Hz range observed for $J_{HMnSi}$ values in the manganese $\eta^2$-hydrosilane complexes.[13] The Ru–H(1a) distance of 1.48 (7) Å and the Ru–Si(1) distance fo 2.441 (3) Å, represent normal single bond lengths.[14,15]

The deprotonation of **5** was investigated as a straightforward route to the desired $\eta^5$-silacyclopentadienyl ruthenocene **2**. With some bases, such as Li$^n$Bu, LiCH$_2$SiMe$_3$, LiCH(SiMe$_3$)$_2$, and LiPh, reactions occurred to give numerous products which did not include **2** (by $^1$H NMR spectroscopy). Both KN(SiMe$_3$)$_2$ and KO$^t$Bu do not react with **5**, but KCH$_2$Ph deprotonates **5** to some extent to provide a relatively low yield of **2** (by $^1$H NMR spectroscopy). The best results are obtained with (THF)$_3$LiSi(SiMe$_3$)$_3$,[16] which deprotonates **5** in benzene-$d_6$ to give **2** (50%) and Si(SiMe$_3$)$_4$[17] (80–90%) as the only soluble products (by $^1$H NMR spectroscopy using Cp$_2$Fe as internal standard; Scheme 1). The mechanism of this reaction is unclear at this time, but the results are consistent with Gilman's early observation that LiSi(SiMe$_3$)$_3$ deprotonates fluorene to produce Si(SiMe$_3$)$_4$ as the major silicon-containing product. The latter species apparently arises from a secondary reaction of (THF)$_3$LiSi(SiMe$_3$)$_3$ with the direct product of deprotonation, HSi(SiMe$_3$)$_3$.[18] On a preparative scale, the reaction of **5** with (THF)$_3$LiSi(SiMe$_3$)$_3$ provided mixtures of **2** and Si(SiMe$_3$)$_4$ which could not be separated by fractional crystallization from pentane or dichloromethane/acetonitrile. Removal of solvent provides a mixture of **2** and Si(SiMe$_3$)$_4$ containing minor impurities. Compound **2** is air sensitive, but thermally stable under nitrogen in solution for at least several days. The $^1$H and $^{13}$C{$^1$H} NMR spectra of **2** closely resemble those reported for **1**.[7] Evidence for aromatic character in the silacyclopentadienyl ring is found in the $^{13}$C NMR shifts of δ 73.09 and 88.53 (for comparison, the Cp* ring carbon shift is at δ 86.02), which differ less than the analogous shifts for **5** (δ 74.36 and 108.83). Also consistent with increased sp$^2$ character for the ring silicon in **2** is the downfield progression of $^{29}$Si NMR shifts in going from **4** (δ −32.68, $J_{SiH}$ = 181 Hz) to **5** (δ −27.14, $J_{SiH}$ = 41 Hz) to **2** (δ −7.35). Finally, **2** was definitively identified by an exact mass peak in the high-resolution (FAB) mass spectrum.[8]

In conclusion, these results demonstrate that $\eta^5$-silacyclopentadienyl complexes can be obtained as reasonably stable compounds. Furthermore, the physical evidence suggests some delocalization of electron density in the SiC$_4$ ring of **5**, and considerably more for the related ring in **2**. We are continuing efforts to gain more structural and chemical information for $\eta^5$-silacyclopentadienyl complexes.

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**Supplementary Material Available:** Experimental procedures and characterization data for complexes and tables of crystal, data collection, and refinement parameters, bond distances and angles, anisotropic displacement parameters, and hydrogen atom coordinates (14 pages); listing of observed and calculated structure factors (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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