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Insertion of Acetylene into the Ru–Si Bond of a Bis(μ-Silylene) Complex. Synthesis and Structure of a 2,5-Disilaruthenacyclopentene Complex

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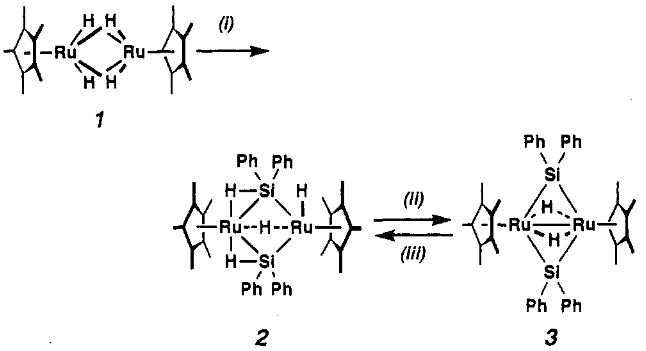
Summary: Treatment of the bis(μ-silylene) complex $[Cp'Ru(\mu\text{-}SiPh_2)(\mu\text{-}H)]_2$ (3) with acetylene yields the μ-2,5-1-disilaruthenacyclopentene complex $Cp'Ru(\mu\text{-}SiPh_2CH{=}CHSiPh_2)(\mu\text{-}H)_2RuCp'$ (4) as a result of the insertion of C_2H_2 into a Ru–Si bond of 3. The reaction of 4 with H_2 results in cleavage of a Si–C bond of the metallacycle to form the μ-vinylsilyl complex $Cp'_2Ru_2(SiPh_2CH{=}CH_2)(\mu\text{-}\eta^2\text{-}HSiPh_2)(\mu\text{-}H)(H)$ (5). The molecular structure of 4 was determined by single-crystal X-ray diffraction.

Transition-metal complexes having both M–H and M–Si bonds have been attracting interest as key intermediates of several catalytic reactions of silanes, such as hydrosilylation[1] or dehydrogenative coupling of primary or secondary silanes.[2] Since the time that a new class of transition-metal complex having a bridging divalent silicon ligand was synthesized in the early 1970s, important advances have been made in the synthetic study of μ-silylene complexes. However, thus far there have been only a few studies of the reactivities of μ-silylene complexes, while the chemistry of the corresponding μ-carbene complexes has been widely investigated.[3] In a previous communication, we reported the synthesis of the bis(μ-silylene) complex $[Cp'Ru(\mu\text{-}SiPh_2)(\mu\text{-}H)]_2$ (3; Cp′ = η^5-C_5Me_5) by pyrolysis of $[Cp'Ru(\mu\text{-}\eta^2\text{-}HSiPh_2)]_2(\mu\text{-}H)(H)$ (2) obtained as a result of "*bimetallic activation*"[4] of diphenylsilane with the diruthenium tetrahydride complex $Cp'Ru(\mu\text{-}H)_4RuCp'$ (1) (Scheme 1).[5] We report here that acetylene inserts into the Ru–Si bond of bis(μ-silylene) complex 3 to generate a novel dinuclear μ-2,5-disilaruthenacyclopentene complex.

Scheme 1[a]



[a] Legend: (*i*) 2.5 equiv of Ph_2SiH_2; (*ii*) refluxing in toluene; (*iii*) 10 atm of H_2 at room temperature.

The reaction of 3 with 1 atm of acetylene in toluene at 80 °C for 6 h results in the exclusive formation of the 2,5-disilaruthenacyclopentene complex $Cp'Ru(\mu\text{-}SiPh_2\text{-}CH{=}CHSiPh_2)(\mu\text{-}H_2)RuCp'$ (4; 85% yield).[6] This reaction proceeded even at room temperature, but the rate was much slower (30% conversion/4 days). The ^1H and ^{13}C NMR spectra of 4 showed characteristic resonances arising from the disilaruthenacyclopentene ligand. A signal due to the methine proton appeared at δ 6.15 with satellite peaks ($^2J_{SiH}$ = 13 Hz) in the ^1H NMR spectrum. The ^{13}C NMR spectrum revealed a signal for the methine carbon as a doublet (J_{CH} = 145.9 Hz) at δ 92.5. Complex 4 is soluble in pentane and diethyl ether and very soluble in toluene and tetrahydrofuran. Purple prismatic single

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[6] Toluene (25 mL) and $[Cp'Ru(\mu\text{-}SiPh_2)(\mu\text{-}H)]_2$ (0.440 g, 0.524 mmol) were charged in a reaction flask under 1 atm of acetylene. The reaction mixture was stirred for 6 h at 80 °C. The solution was then condensed *in vacuo* and purified by the use of column chromatography on neutral alumina (merck Art. No. 1097) with hexane/toluene. Removal of the solvent under reduced pressure afforded 0.387 g of purple solid (85% yield). Spectroscopic data for 4: ^1H NMR (C_6D_6, 300 MHz) δ 7.48–7.38 (m, 8H, Ph), 7.12–7.00 (m, 12H, Ph), 6.15 (s, $^2J_{SiH}$ = 13.0 Hz, 2H, C*H*), 1.89 (s, 15H, C_5Me_5), 1.01 (s, 15H, C_5Me_5), −14.30 (s, 2H, Ru*H*); ^{13}C NMR (C_6D_6, 126 MHz) δ 148.7 (s, Ph ipso), 142.0 (s, Ph ipso), 137.6 (d, J_{CH} = 156.4 Hz, Ph), 136.0 (d, J_{CH} = 156.4 Hz, Ph), 126.8 (d, J_{CH} = 158.3 Hz, Ph), 126.7 (d, J_{CH} = 157.4 Hz, Ph), 126.6 (d, J_{CH} = 156.4 Hz, Ph), 126.2 (d, J_{CH} = 156.4 Hz, Ph), 95.8 (s, C_5Me_5), 92.5 (d, J_{CH} = 145.9 Hz, *C*H), 85.1 (s, C_5Me_5), 12.2 (q, J_{CH} = 126.8 Hz, C_5Me_5), 9.6 (q, J_{CH} = 127.2 Hz, C_5Me_5); ^{29}Si NMR (C_6D_6, 54 MHz) δ 4.6 (br); IR (KBr) δ (=CH) 2954, 2938 cm^{-1}. Anal. Calcd for $C_{46}H_{54}Ru_2Si_2$: C, 63.86; H, 6.29. Found: C, 63.67; H, 6.16. Spectroscopic data for 4-d_2: ^1H NMR (C_6D_6, 300 MHz) δ 7.48–7.38 (m, 8H, Ph), 7.11–7.10 (m, 12H, Ph), 1.89 (s, 15H, C_5Me_5), 1.01 (s, 15H, C_5Me_5), −14.30 (s, 2H, Ru*H*); IR (KBr) ν(=CD) 2214, 2178 cm^{-1}.

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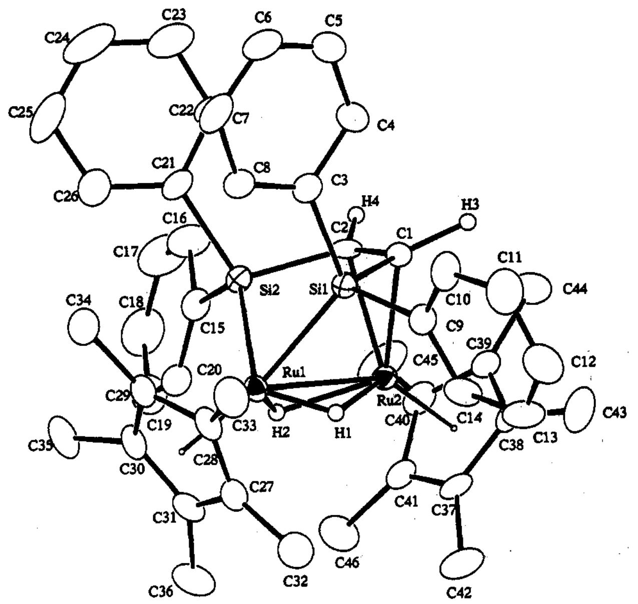


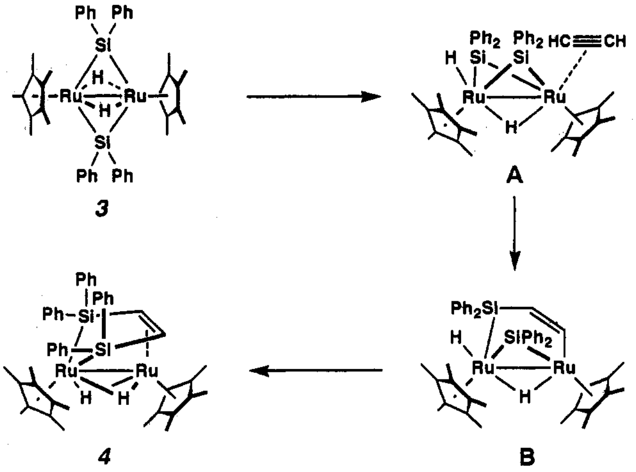
Figure 1. ORTEP drawing of $Cp'Ru(\mu\text{-}SiPh_2CH{=}CHSiPh_2)(\mu\text{-}H)_2RuCp'$ (4). Selected bond distances (Å) and angles (deg): Ru(1)–Ru(2) = 2.759(1), Ru(1)–Si(1) = 2.410(2), Ru(1)–Si(2) = 2.421 (2), Ru(2)–C(1) = 2.270(7), Ru(2)–C(2) = 2.243(7), Si(1)–C(1) = 1.891(7), Si(2)–C(2) = 1.895(7), C(1)–C(2) = 1.406(9); Si(1)–Ru(1)–Si(2) = 75.83(7), Ru(1)–Si(1)–C(1) = 102.0(2), C(3)–Si(1)–C(9) = 100.7(3), Ru(1)–Si(2)–C(2) = 101.1(2), C(15)–Si(2)–C(21) = 99.4(3), Si(1)–C(1)–C(2) = 119.5(5), Si(2)–C(2)–C(1) = 116.8(5). Only bridging and methylene H atoms are shown for clarity.

crystals of 4 suitable for X-ray diffraction studies were obtained from toluene/pentane (1:1) at −20 °C. The results of the single-crystal X-ray structure determination of 4 are displayed in Figure 1 along with the numbering scheme.[7] Figure 1 clearly establishes the disilametallacyclic structure of 4 formed as a result of the insertion of one acetylene molecule into the Ru–Si bond of μ-silylene complex 3.

The interatomic distance between the ruthenium atoms is 2.759(1) Å. The two ruthenium atoms are bridged by a $\mu\text{-}\eta^2{:}\eta^2\text{-}[SiPh_2CH]_2$ fragment. The four atoms of the metallacyclopentene framework (Si(1), C(1), C(2), and Si(2)) are close to coplanar, and the torsional angle between the Si_2C_2 plane and that defined by Ru(1), Si(1), and Si(2) atoms is *ca.* 51°. The values of 2.410(2) and 2.421(2) Å for Ru(1)–Si(1) and Ru(1)–Si(2) distances, respectively, indicate that the ends of the bridging $[SiPh_2CH]_2$ fragment, Si(1) and Si(2), are σ-bonded to Ru(1).[5,8] On the other hand, the significantly longer Ru(2)–Si(1) and Ru(2)–Si(2) separations of 3.036(2) and 2.932(2) Å, respectively, show the absence of the bonding interactions between them. The silicon atoms are 2.969(3) Å apart and thus are nonbonded. The Ru(2)–C(1) and Ru(2)–C(2) distances of 2.270(7) and 2.243(7) Å are consistent with Ru–C π bonds. The C(1)–C(2) distance of 1.406(9) Å represents a double carbon–carbon bond.

The mechanism shown in Scheme 2, which involves *trans*-to-*cis* isomerization of the μ-silylene ligands, possibly accounts for the formation of disilaruthenacycle complex 4. In the early stages of the reaction, μ-silylene ligands in 3 isomerize to generate a *cis*-bis(μ-silylene) species which can coordinate an acetylene molecule to yield intermediate **A**. The insertion of the acetylene into the Ru–Si bond to form intermediate **B** is supported on the basis of earlier results.[8i–l,9,10] An experiment using acetylene-d_2 was attempted in order to verify the insertion step. When the reaction of 3 with 15 equiv of C_2D_2 in benzene-d_6 at 80 °C was monitored by means of NMR spectroscopy, the quantitative formation of the 3,4-dideuterio-2,5-disilaruthenacyclopent-3-ene complex 4-d_2 was observed.[6] Finally, reductive coupling between two bridging ligands in **B** would give the disilaruthenacycle 4. To our knowledge, this is the first example of an acetylene insertion into a metal–silicon bond of a transition-metal complex which has both metal–silicon and metal–hydride bonds. Our results stand in remarkable contrast to those for a d^0 zirconium complex; olefins and alkynes inserted into the Zr–H bond of $Cp_2Zr(PMe_3)(H)SiPh_3$ rather than into the Zr–Si bond.[11]

Scheme 2



It has been proposed recently with regard to the mechanism of hydrosilylation that unsaturated hydrocarbons preferably insert into the metal–silicon bond rather than the metal–hydride bond.[12,13] Formation of 4

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[7] Crystal data for $Cp'Ru(\mu\text{-}SiPh_2CH{=}CHSiPh_2)(\mu\text{-}H)_2RuCp'$ (4): $C_{46}H_{54}Ru_2Si_2$, monoclinic, $P2_1/c$, $a = 18.625(5)$ Å, $b = 12.290(2)$ Å, $c = 19.657(4)$ Å, $\beta = 114.50(2)°$, $V = 4094(1)$ Å^3, $Z = 4$. Of 7841 reflections collected (Mo Kα, 2θ(max) = 50.0°, 296 K), 7597 were independent and 4246 were observed. $R = 0.042$ and $R_w = 0.035$. Both bridging and methylene H atoms were completely located by sequential difference Fourier synthesis but were not refined.

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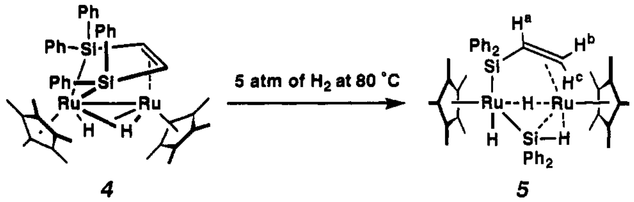
strongly supports the "*silylmetalation path*" for hydrosilylation of olefins or acetylenes.

Complex 4 is stable in C_6D_6 below *ca.* 70 °C but decomposes to generate bis(μ-silylene) complex 3 in low yield along with several unidentified compounds upon heating at 110 °C in a sealed NMR tube. These results suggest that the reaction illustrated in Scheme 2 is reversible. On the other hand, pyrolysis of 4 under pressurized H_2 (5 atm) proceeds smoothly to lead to the exclusive formation of hydrogenated product 5. Treatment of 4 with 5 atm of H_2 in toluene at 80 °C for 2 h affords the μ-vinylsilyl complex $Cp'_2Ru_2(SiPh_2CH{=}CH_2)(\mu\text{-}\eta^2\text{-}HSiPh_2)(\mu\text{-}H)(H)$ (5) in 86% isolated yield (Scheme 3).[14]

A notable feature of the ^1H NMR spectrum of 5 is the upfield shift of the signals of the vinylic protons. Such an upfield shift of the signals due to the coordinated olefinic protons also is observed in the ^1H NMR spectrum of $Cp'Ru(\mu\text{-}CH{=}CH_2)_2(CH_2{=}CH_2)RuCp'$ ($\delta_{CH_2=CH_2}$ 1.86 and 1.58).[4] The ^{29}Si NMR spectrum shows two signals at δ 121.9 (d, J_{SiH} = 47.5 Hz) and 18.5 (s) for the bridging diphenylsilyl group, which is bonded *via* a two-electron three-center (2e-3c) interaction, and the diphenylvinylsilyl ligand, respectively. On the basis of the coupling constant between Si and hydride the bridging silicon forms a 2e-3c bond among Ru, H, and Si.[15] The existence of a 2e-3c bond was also confirmed by IR spectroscopy (ν(Ru-H-Si) = 1750 cm^{-1}).[16]

Scheme 3



The formation of μ-vinylsilyl complex 5 can be rationalized in terms of the hydrogenolysis of intermediate **B**, formed thermally *via* the cleavage of the Si–C bond of the metallacycle of 4. These results strongly suggest the validity of the reaction mechanism shown in Scheme 2.

We are currently focusing on defining the chemical properties of 4 and 5 and the reactivities of μ-silylene complex 3 with other unsaturated hydrocarbons.

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Supplementary Material Available: Text giving details of the data collection and reduction and the structure solution and refinment and tables of the crystal data and the data collection and reinement parameters, positional parameters, anisotropic thermal parameters, bond lengths and angles, and special contacts (14 pages). Ordering information is given on any current masthead page.

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[14] Toluene (10 mL) and $Cp'Ru(\mu\text{-}SiPh_2CH{=}CHSiPh_2)(\mu\text{-}H)_2RuCp'$ (76.0 mg, 0.088 mmol) were charged in an autoclave with 5 atm of hydrogen. The reaction vessel was heated at 90 °C with vigorous stirring for 40 min, and the solution turned from purple to red. After removal of solvent *in vacuo*, the residue was dissolved in 3 mL of pentane and purified by the use of column chromatography on neutral alumina (Merck Art. No. 1097) with hexane/toluene. Removal of solvent under reduced pressure afforded 65.8 mg of orange solid (86% yield). Spectroscopic data for 5: ^1H NMR (C_6D_6, 500 MHz) δ 8.2–7.0 (m, 20H, Ph), 1.89 (1H, d, J_{HH} = 11.2 Hz, H^b), 1.83 (1H, dd, J_{HH} = 14.4, 2.4 Hz, H^c), 1.64 (15H, s, $C_5\mathit{Me}_5$), 1.44 (1H, dd, J_{HH} = 14.4, 11.2 Hz, H^a), 1.36 (15H, s, $C_5\mathit{Me}_5$), –10.16 (1H, br, J_{SiH} = 47.5 Hz), –14.59 (1H, s, Ru*H*), –18.41 (1H, s, Ru*H*Ru); ^{13}C NMR (C_6D_6, 126 MHz) δ 147.6 (s, Ph ipso), 146.9 (s, Ph ipso), 146.7 (s, Ph ipso), 146.2 (s, Ph ipso), 138.02 (Ph), 138.00 (Ph), 137.4 (Ph), 135.9 (Ph), 128.3 (Ph), 128.1 (Ph), 127.7 (Ph), 127.6 (Ph), 127.1 (Ph), 126.9 (Ph), 126.8 (Ph), 126.4 (Ph), 94.5 (s, C_5Me_5), 92.7 (s, C_5Me_5), 55.7 (dd, J_{CH} = 154.5, 158.3 Hz, $SiCH{=}\mathit{CH}_2$), 48.3 (d, J_{CH} = 140.2 Hz, $Si\mathit{CH}{=}CH_2$), 11.8 (q, J_{CH} = 126.5 Hz, $C_5\mathit{Me}_5$), 10.9 (q, J_{CH} = 127.5 Hz, $C_5\mathit{Me}_5$); ^{29}Si NMR (C_6D_6, INEPT, 54 MHz) δ 121.9 (d, J_{SiH} = 47.5 Hz, $\mu\text{-}\eta^2\text{-}H\mathit{SiPh}_2$), 18.5 (s, $\mathit{Si}Ph_2\text{-}CH{=}CH_2$); IR (KBr) ν(RuH) 2082 cm^{-1}, ν(RuHSi) 1750 cm^{-1}. Anal. Calcd for $C_{46}H_{56}Ru_2Si_2$: C, 63.71; H, 6.51. Found: C, 63.23; H, 6.18. A 2D-HH-COSY experiment shows a cross-peak between the signal at δ -10.16 and the signal for the vinyl group. Irradiation at δ -10.16 changes the shape of the signal at δ 1.81 from a doublet of doublets to a doublet. White it was proved that the β-proton coupled with the hydride, geminal coupling with the other β-proton could not be observed.

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[16] We have already assigned this broad absorption around 1750 cm^{-1} to the stretching of the η^2-Si–H bond on the basis of the differential spectrum between bis(μ-silyl) complex 2 and $[Cp'Ru(\mu\text{-}\eta^2\text{-}DSiPh_2)]_2(\mu\text{-}D)(D)$ (2-d_4): Takao, T.; Suzuki, H.; Tanaka, M. Manuscript in preparation.