Stoichiometric and Catalytic Activation of Allyldimethylsilane. Synthesis of $[RuH_2\{\eta^4\text{-}HSiMe_2(CH{=}CHMe)\}(PCy_3)_2]$

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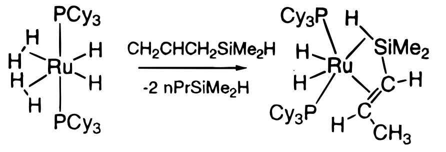
Summary: The bis(dihydrogen)ruthenium complex $RuH_2(H_2)_2(PCy_3)_2$ ***(1)*** *reacts with* $(CH_2{=}CHCH_2)Me_2SiH$ *to produce the title complex* ***4****, a very reactive species stabilized by coordination of a vinylsilane ligand via* $Ru-(\eta^2\text{-}H-Si)$ *and* $Ru-(\eta^2\text{-}C{=}C)$ *bonds.* ***4*** *catalyzes dehydrogenative silylation of* $(CH_2{=}CHCH_2)Me_2SiH$ *and redistribution at silicon under* C_2H_4 *pressure.*

The reactions of silanes with transition metals are attracting steady interest in connection with the wide catalytic applications of many transition-metal-mediated transformations of organosilanes, including hydrosilylation, dehydrogenative silylation, and polysilane production.[1] Silyl hydride complexes are involved in all these catalytic processes, and $M-(\eta^2\text{-}H-Si)$ complexes are considered as key intermediates in the oxidative addition of silanes to a transition-metal center.[2] The bonding pictures in $M-(\eta^2\text{-}H-Si)$ and $M-(\eta^2\text{-}H_2)$ complexes are very similar. Substantial information has been gained on the properties of $M-(\eta^2\text{-}H_2)$ complexes, and their reactivity highly depends on the stretching of the $\eta^2\text{-}H_2$ ligand.[3] However, the $M-(\eta^2\text{-}H-Si)$ systems have been less documented and require more study.

We have recently reported the first catalytic application of the bis(dihydrogen) complex $RuH_2(H_2)_2(PCy_3)_2$ (**1**) and demonstrated that **1** serves as a precursor for an efficient production of vinylsilane.[4,5] The stoichiometric reactivity of **1** toward alkenes and silanes was investigated and has already given useful information for the extension of the scope of this catalytic reaction.[4,6−8] Substitution of one or two dihydrogen ligands can be achieved by addition of mono- or disilanes to **1**, and we have recently reported the synthesis of the first bis(silane) complexes $[RuH_2\{(\eta^2\text{-}HSiMe_2)_2X\}(PCy_3)_2]$ ($X = C_6H_4$, **2**; $X = O$, **3**), where the two H−Si bonds are η^2-coordinated to the metal.[6] Addition of alkenes to **1** leads to π-coordination or hydrogen transfer, depending upon the nature of the alkene.[8] These results prompted us to study the reactivity of **1** toward an allylsilane in order to evaluate the competition between π-coordination of the olefinic group and σ-coordination of the Si−H group. In this communication, we report the reaction of **1** with $(CH_2{=}CHCH_2)Me_2SiH$ leading to a new $Ru-(\eta^2\text{-}H-Si)$ complex on the path of oxidative addition and catalytic studies in the presence of ethylene and allylsilane.

Addition of 3 equiv of $(CH_2{=}CHCH_2)Me_2SiH$ to a suspension of **1** in pentane results in immediate dissolution, and after workup, the new complex $[RuH_2\{\eta^4\text{-}HSiMe_2(CH{=}CHMe)\}(PCy_3)_2]$ **(4)** can be isolated as a white powder in 61% yield. **4** is a ruthenium(II) dihydride complex stabilized by coordination of a vinylsilane ligand via $Ru-(\eta^2\text{-}H-Si)$ and $Ru-(\eta^2\text{-}C{=}C)$ bonds. It results from the substitution of the two dihydrogen ligands of **1** by the allylsilane with concomitant isomerization of the olefinic part (see eq 1). When the reaction is performed in C_6D_6 in an NMR tube, a quantitative reaction is observed, producing **4** and 2 equiv of $PrMe_2SiH$. **4** is fully characterized by elemental analysis, multinuclear NMR spectroscopy, and X-ray determination.[9,10] The ^1H NMR spectrum of **4** shows at 296 K (C_7D_8, 400 MHz) in the hydride region three signals of equal intensity at δ −8.77, −9.46, and −12.46. The last two signals display a triplet of doublets consistent with two inequivalent hydrides ($J_{H-H} = 8.5$ Hz) with coupling to two ^{31}P nuclei ($J_{H-P} = 25$ and 34 Hz). The first one is broad but clearly shows satellites due to coupling with the silicon atom. The coupling constant value J_{Si-H} of 105 Hz is further confirmed by the $^{29}Si\{^{31}P\}$ INEPT ^1H spectrum, showing a doublet at δ −11.3. This J_{Si-H} value falls in the upper limit of the known range (20−140 Hz) of J_{Si-H} values for (η^2-Si−H) bonds[11] and indicates an early stage of activation of the Si−H bond.



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This can be compared to the titanium alkyne complex $Cp_2Ti(\eta^2\text{-}^tBuC_2SiMe_2H)$ showing a temperature-dependent Si−H−Ti interaction ($J = 93$ Hz at 193 K and 123 Hz at 303 K).[12] The H−Si band in the IR spectrum of the free allylsilane is found at 2121 cm^{-1} and is shifted to 1945 cm^{-1} in **4**, supporting the Ru−(η^2-H−Si) coordination.

The structure from X-ray determination of a crystal of **4** at 140K confirms the isomerization of the allylsilane.[10] As can be seen in Figure 1, the environment around the ruthenium can be considered as a highly distorted octahedron with the middle of the Si−H and C═C bonds each occupying one site of coordination. The three hydrogen atoms H, H′, H″ were located in a difference Fourier map and their coordinates were refined isotropically. All the Ru−H bonds are equal within experimental error (1.61(7)−1.74(7) Å). The Si−H bond distance (1.59(8) Å) is longer than a covalent Si−H bond in free silanes but shorter than in the bis(silane) complex **2** (1.83(3) and 1.88(3) Å).[6] This is in agreement with the different J_{Si-H} values measured for **4** (105 Hz) and **2** (63 Hz) and suggests reduced Ru (dπ) to Si−H (σ*) back-donation. The Ru−Si bond length is 2.498(2) Å, in the range observed for ruthenium silyl compounds (2.34−2.51 Å).[13] Of particular interest is the Si−C(2) distance, 1.820(6) Å, shorter than normal Si−C(sp^2) bonds (1.85−1.91 Å). This might reflect some partial double-bond character, as previously reported in other ruthenium complexes.[14]

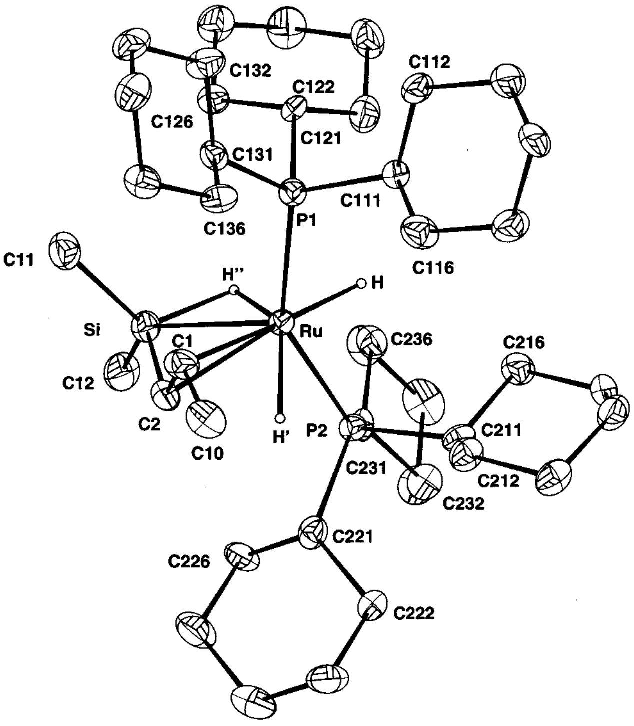

Figure 1. CAMERON view of $RuH_2\{(\eta^4\text{-}HSiMe_2(CH{=}CHMe)\}(PCy_3)_2$ **(4)**. Selected bond lengths (Å): Ru−P(1), 2.354(2); Ru−P(2), 2.322(1); Ru−Si, 2.498(2); Si−H″, 1.59(8); Ru−H, 1.61(7); Ru−H′, 1.64(9); Ru−H″, 1.74(7); Si−C(2), 1.820(6); C(1)−C(2), 1.394(9); Ru−C(1), 2.316(6); Ru−C(2), 2.269(6). Selected bond angles (deg): P(1)−Ru−P(2), 145.30(6); P(1)−Ru−H, 75(3); P(2)−Ru−H, 74(3); P(1)−Ru−H′, 145(3); P(2)−Ru−H′, 49(3); P(1)−Ru−H″, 94(3); P(2)−Ru−H″, 96(3); H−Ru−H′, 120(4); Ru−H″−Si, 97(4); P(1)−Ru−Si, 105.72(6); P(2)−Ru−Si, 103.47(6); Ru−C(2)−C(1), 74.2(4); Ru−C(1)−C(2), 70.5(4).

The silane ligand in **4** is only weakly bound and is readily displaced by bubbling H_2, CO, or C_2H_4, leading to the formation of **1**, $RuH_2(CO)_2(PCy_3)_2$,[15] or $[RuH\{(\eta^3\text{-}C_6H_8)PCy_2\}(C_2H_4)(PCy_3)]$ (**5**),[8,16] respectively. Furthermore, ^1H and ^{31}P NMR monitoring of a C_6D_6 solution of **4** shows total conversion within 15 h to a mixture of $RuH_3\{(\eta^3\text{-}C_6H_8)PCy_2\}(PCy_3)$ (**6**)[16] and the new dihydrido silyl complex $RuH_2[SiMe_2(C_3H_7)]\{(\eta^3\text{-}C_6H_8)PCy_2\}(PCy_3)$ (**7**) in a 2:3 ratio.[17] This reaction occurs with extensive H−D exchange, as already reported in the case of **6**.[8] Thus, the stepwise activation of silane leads first to **4**, prior to oxidative addition producing **7** with concomitant hydrogen transfer from one cyclohexyl ring to the C═C bond of the silyl group. **4** is therefore a reactive intermediate resulting from the trapping of an unsaturated ruthenium dihydride fragment by the bidentate vinylsilane ligand. The high value of the J_{Si-H} coupling constant and the short Si−H distance demonstrate the weak activation of the Si−H bond in the present case. Further investigations of this process (theoretical and kinetic studies) are currently underway (in particular

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(9) Complex **4**: $(CH_2{=}CHCH_2)Me_2SiH$ (190 μL; 1.34 mmol) was added to a solution of **1** (297 mg; 0.45 mmol) in pentane (12 mL). Immediate dissolution was observed with formation of a green-brown solution. The mixture was stirred for 20 min. The solution was concentrated to 5 mL, and a white solid precipitated. The product was filtered out, washed twice with ether (2 mL) at −20 °C, and dried under vacuum (yield 61%). Anal. Calcd for $RuC_{41}H_{80}P_2Si$: C, 64.44; H, 10.44; Found: C, 64.59; H, 10.53. ^1H NMR (400 MHz, C_7D_8, 296 K): δ −12.46 (dt, 1H, $J_{H-P} = 34$ Hz, $J_{H-H} = 8.5$ Hz, Ru−H), −9.46 (dt, 1H, $J_{H-P} = 25$ Hz, $J_{H-H} = 8.5$ Hz, Ru−H), −7.74 (s, 1H, $J_{Si-H} = 105$ Hz, Ru−H−Si), 0.52 (s, 12H, Si−CH_3), 1.29−2.32 (m, 66H, PCy_3), 2.40 (d, 3H, $J_{H-H} = 5.3$ Hz, C−CH_3), 3.15 (dt, 1H, $J_{H-H} = 12$ Hz and $J_{H-P} = 4$ Hz, $SiMe_2CH$), 3.81 (m, 1H, CHMe). ^1H NMR (250 MHz, C_7D_8, 253 K): T_1 (min) = 173 ms (Ru−H−Si), 118 ms (Ru−H). $^{29}Si\{^{31}P\}$ INEPT ^1H nonrefocalized (79.5 MHz, C_6D_6, 293 K): δ −11.3 (d, $J_{Si-H} = 106$ Hz). $^{31}P\{^1H\}$ NMR (161.99 MHz, C_7D_8, 253 K): δ 69.12 and 63.66 ($J_{P1-P2} = 206$ Hz). INVHMQC GE $^1H-^{13}C\{^{31}P\}$ (253 K, C_7D_8): δ 48.2 (d, $J_{C-H} = 150$ Hz, SiCHCHMe), 64.4 (d, $J_{C-H} = 154$ Hz, C═CHMe), 26.5 (q, $J_{C-H} = 126$ Hz, C-CH_3), 1.09 (q, $J_{C-H} = 119$ Hz, SiCH_3), −1.08 (q, $J_{C5-H} = 119$ Hz, SiCH_3). IR (Nujol mull): 1945 cm^{-1} (ν(Ru−H−Si)). The only change observed in the ^1H NMR spectra when the temperature is lowered is the decoalescence of the broad signal at δ 0.52, resulting in the observation, at 253 K, of two signals at δ 0.87 and 0.48 of equal intensity corresponding to the two inequivalent methyl groups bound to the silicon (the exchange process is characterized by a $\Delta G^{\ddagger}$ value of ca. 55 kJ/mol).

(10) Crystal data for **4**: colorless crystal, triclinic, $P\bar{1}$, $a = 10.119(2)$ Å, $b = 12.086(2)$ Å, $c = 19.086(3)$ Å, $\alpha = 86.14(2)°$, $\beta = 85.08(2)°$, $\gamma = 67.87(2)°$, $Z = 2$, $R = 0.052$, GOF = 0.9.

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(16) Reaction of **1** with ethylene affords the π-coordinated complex $[RuH\{(\eta^3\text{-}C_6H_8)PCy_2\}(C_2H_4)(PCy_3)]$ (**5**), whereas with alkenes bearing σ-donor substituents, hydrogenation to the corresponding alkane is achieved and 6−10 hydrogen atoms from **1** can be transferred leading to $[RuH_3\{(\eta^3\text{-}C_6H_8)PCy_2\}(PCy_3)]$ (**6**) or $[RuH\{(\eta^3\text{-}C_6H_8)PCy_2\}\{(\eta^2\text{-}C_6H_9)\text{-}PCy_2\}]$.[8]

(17) Complex **7**: ^1H NMR (200 MHz, C_6D_6) δ −12.38 (dd, 1H, $J_{H-P} = 27$ and 57 Hz, Ru−H), −9.43 (t, 1H, $J_{H-P} = 17$ Hz, Ru−H), 1.05−2.37 (m, 66H, PCy_3), 3.02 (br, 1H, η^3-$C_6H_8{}^{1-3}$), 3.94 (br, 1H, η^3-$C_6H_8{}^{3-1}$), 5.10 (br, 1H, η^3-$C_6H_8{}^2$); ^{31}P NMR (81.015 MHz, C_6D_6) δ 80.8 and 67.9 ($J_{P-P} = 19$ Hz). **7** was characterized by comparison with complexes of the same type. See in particular in ref 4 the spectroscopic data for $RuH_2(SiEt_3)\{(\eta^3\text{-}C_6H_8)PCy_2\}(PCy_3)$ (a catalyst for the dehydrogenative silylation).

Table 1. Reaction of C_2H_4 with $(CH_2{=}CHCH_2)Me_2SiH$ Catalyzed by 1, 4, or 5

entry no.	catalyst	time (min)	amt (%)[a]				
			8	**9**	**10**	**11**	**12**
1	**1**	20[b]	28	10	36	5	8
		60	1	10	36	27	12
2	**4**	20[b]	16	10	37	12	10
		60	1	10	37	25	12
3	**5**	70[b,c]	28	5	37	8	11

[a] Legend: $(CH_2{=}CHCH_2)Me_2Si(CH{=}CH_2)$ (**8**); $(CH_3CH{=}CH)Me_2Si(CH{=}CH_2)$ (**9**); $(CH_2{=}CHCH_2)Me_2SiEt$ (**10**); $Me_2Si(CH{=}CH_2)_2$ (**11**); $Me_2Si(CH{=}CH_2)Et$ (**12**). [b] Time after which $(CH_2{=}CHCH_2)Me_2SiH$ is totally consumed. [c] No more reaction after 70 min.

to discriminate between the intermediacy of a species with either a free olefin or a free Si−H bond, or loss of the vinylsilane ligand and further reaction with a reactive unsaturated ruthenium fragment). Interestingly, a somewhat related tautomeric equilibrium between an η^2-SiH_4 group and a hydridosilylmolybdenum complex has been previously reported by Kubas et al.[18]

In a previous paper, we have demonstrated the selective synthesis of triethylvinylsilane when using the system **1**/$HSiEt_3$/C_2H_4.[4] In the case of the allylsilane, the catalytic reaction is much more complex and the selectivity is somewhat unusual, as can be seen in Table 1. The reaction was carried out under 20 bar of C_2H_4 at 20 °C using a mixture of **1** and $(CH_2{=}CHCH_2)SiMe_2H$ in a 1:100 ratio in THF solution. All the silicon products have been characterized by GC-MS analysis. Total conversion of the allylsilane was observed within 20 min (entry 1). $(CH_2{=}CHCH_2)Me_2Si(CH{=}CH_2)$ (**8**) and $(CH_2{=}CHCH_2)Me_2SiEt$ (**10**) are the major products resulting from dehydrogenative silylation and hydrosilylation, respectively. Interestingly, after total conversion of the starting allylsilane, further reaction is observed and redistribution at silicon is catalyzed, leading mainly after 60 min to the conversion of **8** into $Me_2Si(CH{=}CH_2)_2$ (**11**). Propene evolution was detected by GC-MS analysis, in agreement with the mass balance. It should be noted that when H_2 is bubbled into the reaction mixture at the end of a run, total hydrogenation to the corresponding saturated silanes $SiMe_2EtPr$ and $SiMe_2Et_2$ is obtained. The same catalytic behavior is observed when **1** is replaced by **4** (entry 2). We also investigated the use of $[RuH\{(\eta^3\text{-}C_6H_8)PCy_2\}(C_2H_4)(PCy_3)]$ (**5**) as a catalyst, since **5** is the catalyst resting state in the synthesis of triethylvinylsilane.[4] In this case, the reaction rate decreases and no further redistribution is observed (entry 3). In this catalytic process, allylsilane coordination competes successfully with ethylene coordination and the need for two sites of coordination during the catalysis implies the participation of **4** or of a related unsaturated complex and not of **5**, the catalyst for ethylene dehydrogenative silylation. A chelate complex through the allyl and vinyl moieties can thus be generated, allowing further transformation of **8** into **11** through a sequence implying (i) retrosilylation and (ii) dehydrogenative silylation of the dimethylvinylsilane formed by process i. The absence of any transformation of **9** or **10** is in agreement with this proposal. It should be pointed out that C/C exchanges on monosilanes are rare.[19,20]

In summary, we have described the synthesis of the new complex $[RuH_2\{\eta^4\text{-}HSiMe_2(CH{=}CHMe)\}(PCy_3)_2]$ **(4)**, in which the weak Ru−(η^2-H−Si) interaction allows us to stop the dehydrogenation process normally observed when **1** is exposed to olefins. Thermolysis of **4** leads to the dihydrido silyl complex **7**, which formally represents the final stage in the oxidative addition of the starting silane. These two modes of coordination (σ-H−Si in **4** and hydrido silyl in **7**) can be considered as key steps in catalytic transformations of silanes, but more experiments are needed to understand the mechanism of the present catalytic reaction, in particular with respect to the redistribution at silicon. Further investigations into the reactivity of **4** are currently underway.

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Supporting Information Available: Tables giving X-ray diffraction data for **4** and a figure giving the NMR spectrum of **4** in the hydride region (C_6D_6, 293 K, 400 MHz) (12 pages). Ordering information is given on any current masthead page.

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(20) Our results are different from the metathesis of vinylsilanes reported by Marciniec, since they required the presence of an allyl and a vinyl moiety in the same compound to allow chelate coordination. The isomerized $(CH_3CH{=}CH)Me_2Si(CH{=}CH_2)$ (**9**) is stable under our catalytic conditions. See: (a) Marciniec, B. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; Verlag: Frankfurt, Germany, 1996; Vol. 1, p 487. (b) Marciniec, B.; Pietraszuk, C.; Foltynowicz, Z. *J. Organomet. Chem.* **1994**, *474*, 83. (c) Marciniec, B. *New J. Chem.* **1997**, *21*, 815.