

## REACTION OF ALLYLSILANES WITH DIETHYLENE- ( $\eta^5$ -INDENYL)RHODIUM(I)

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### Summary

Allyltrimethylsilane is catalytically isomerized to propenyltrimethylsilane when heated with diethylene( $\eta^5$ -indenyl)rhodium(I). Diallyldimethylsilane reacts stoichiometrically to form  $[(\eta^2\text{-CH}_2=\text{CHCH}_2)(\eta^2\text{-CH}_3\text{CH}=\text{CH})\text{SiMe}_2(\eta^5\text{-indenyl})\text{-rhodium(I)}]$  (**1**) in 74% yield.  $^1\text{H}$  and  $^{13}\text{C}$  NMR data are reported for **1**.

### Introduction

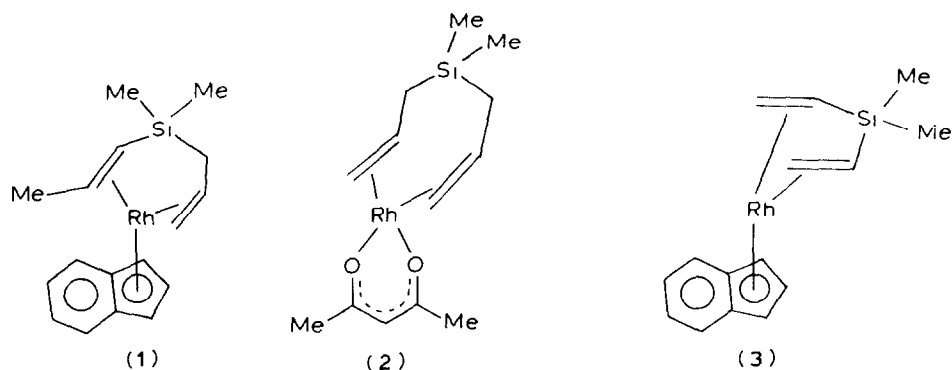
Recently it was reported that allyltrimethylsilane reacts with acetylacetonatodiethylenerrhodium(I) to give the 16-electron complex, acetylacetonatobis( $\eta^2$ -allyltrimethylsilane)rhodium(I) in quantitative yield [1]. As expected diallyldimethylsilane also forms an acetylacetonato complex in which the ligand is both chelating and unaltered. We now report that both allyltrimethyl- and diallyldimethylsilane rearrange to propenyl silanes when treated with the 18-electron complex, diethylene( $\eta^5$ -indenyl)rhodium(I).

### Results and discussion

The reaction of diallyldimethylsilane with diethylene( $\eta^5$ -indenyl)rhodium(I) forms **1** (74%) in which one of the allyl groups of the silane has been rearranged to a *trans*-propenyl group. The reaction is not catalytic and excess ligand can be recovered unchanged.

Compound **1** is an orange solid (m.p. 53°C) which is stable for hours in air under ambient conditions and indefinitely under nitrogen at 0°C. It is very soluble in most organic solvents.

The 200 MHz  $^1\text{H}$  NMR of **1** is consistent with the proposed structure although it is not amenable to complete analysis because of overlapping signals (see Table 1). Those signals which can be analyzed were assigned using spin decoupling techniques and by comparison of the spectrum of **1** to those of **2**, which can be analyzed completely and in which both of the allyl groups remain unrearranged, and **3** which



is also readily analyzed. Table 1 lists chemical shifts, coupling constants and proton numbering schemes for these three compounds. H(1), which resonates at highest field, is assigned as the "inner" proton [2] of the allyl group of **1** and is shown to be coupled to H(2) and H(3) by decoupling experiments. The chemical shift assignments for the propenyl portion of the molecule, also verified by decoupling experiments, are comparable to those observed in **3**.

The values of the coupling constants which could be observed in **1** and all of

TABLE 1  
<sup>1</sup>H NMR RESULTS<sup>a</sup>

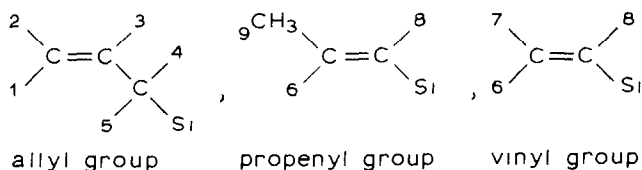
Compound	$\delta(\text{ppm})^b$									
	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	H(8)	H(9)	Si-Me
<b>1</b>	1.83	ca. 3.8 <sup>c</sup>	ca. 3.8 <sup>c</sup>	0.92	ca. 0.2 <sup>c</sup>	2.07	-	2.84	1.65	0.21 0.18
<b>2</b>	2.47	4.23	4.80	1.05	0.37	-	-	-	-	-0.08 0.93
<b>3<sup>e</sup></b>	-	-	-	-	-	1.88	3.58	2.22	-	-0.03 0.23

	$J(\text{Hz})^d$									
	12	13	23	34	35	45	67	68	78	69
<b>1</b>	0	12.9	-	6.0	-	13.7	-	13.3	-	5.8
<b>2</b>	0	13.0	8.3	7.3	9.1	13.2	-	-	-	-
<b>3<sup>e</sup></b>	-	-	-	-	-	-	1.8	14.6	11.3	-

<sup>a</sup> Compounds **1** and **2** observed at 200 MHz; compound **3** observed at 90 MHz, all in C<sub>6</sub>D<sub>6</sub>.

<sup>b</sup> Proton numbering:



<sup>c</sup> Value either approximated or not observed because of overlapping resonances. <sup>d</sup> Small <sup>1</sup>H-<sup>103</sup>Rh coupling (0-2 Hz) also observed in alkenyl proton resonances. <sup>e</sup> Observed at 90 MHz.

those observed in **2** and **3** are of the expected magnitudes based on earlier work [1]. For example, the *trans*, *cis* and *geminal* coupling constants in [(*acac*)-Rh(CH<sub>2</sub>=CHCMe<sub>3</sub>)<sub>2</sub>] are known to be, respectively, 13.0, 8.6 and c.a. 0 Hz, values which are very close to those observed for similar coupling in **1**, **2** and **3**. Because  $J_{68}$  is 13.3 Hz in **1**, the propenyl portion of the ligand molecule must have the *trans* configuration. Further evidence of the *trans* configuration occurs from the observation that H(6), an "inner" proton, resonates at higher field than H(8) as required [2].

<sup>13</sup>C NMR results for **1**, **2** and **3** are collected in Table 2 which also contains the carbon numbering schemes used in the ensuing discussion. Off resonance decoupling techniques were used in making carbon assignments. It will be noted that there is uncertainty in uniquely identifying C(1), C(2) and C(5) in **1** since each of them is attached to only one hydrogen atom. However, assignments were made based on a comparison of values for  $J(^{103}\text{Rh}-^{13}\text{C})$  in compounds **2** and **3**, both of which are assumed to be representative for rhodium(I)-coordinated allyl and vinyl groups in chelating silane ligands. It is noted that C(8) and C(9) are not equivalent in **1** as required by the proposed structure.

Similar alkene isomerizations catalyzed by rhodium(I) are not unprecedented, although they have not been observed for simple allylsilanes before. However, [RhCl(PPh<sub>3</sub>)<sub>3</sub>] is known to isomerize allyl ethers to 1-propenyl ethers [3]. It is also known that 1,4-diene complexes of rhodium(I) are quantitatively isomerized to 1,3-diene complexes when heated in inert solvents.

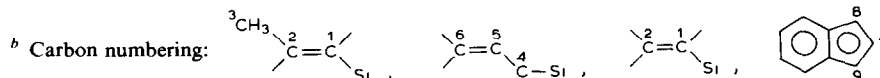
The mechanism of this latter isomerization invokes the intermediacy of an ( $\eta$ -allyl)hydrido species resulting from transfer of an allylic hydrogen to rhodium which subsequently undergoes metal-to-carbon hydrogen transfer at the terminal carbon to generate the isomerized 1,3-diene complex [4].

It is likely that the isomerizations reported herein occur by a similar mechanism which is summarized below for **1**. The site of coordinative unsaturation at rhodium needed to initiate allylic C-H bond insertion and ultimate formation of **1a** could arise from slippage of the indenyl ligand from  $\eta^5$ - to  $\eta^3$ -coordination [5] in an

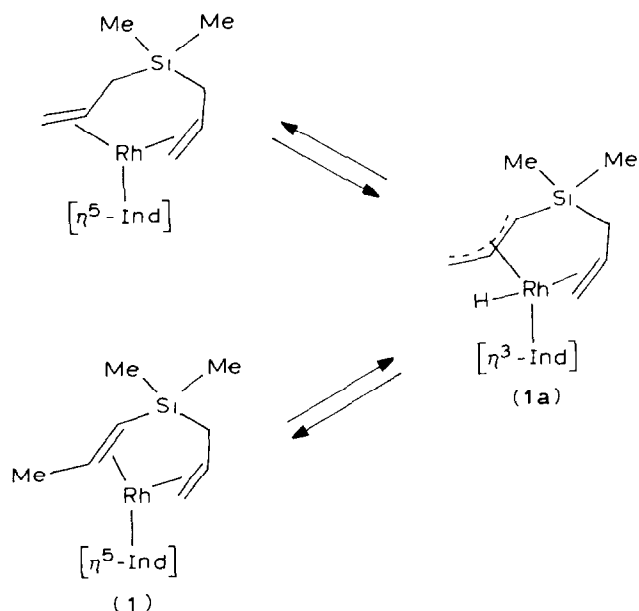
TABLE 2  
<sup>13</sup>C NMR RESULTS<sup>a</sup>

Compound	$\delta$ (ppm) <sup>b</sup>									
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	Si-CH <sub>3</sub>	C(7)	C(8)	C(9)
<b>1</b>	64.5 <sup>c</sup>	69.9 <sup>c</sup>	26.0	16.8	52.7 <sup>c</sup>	46.5	2.2	93.4	78.8	77.7
	(10.8)	(14.6)			(12.7)	(12.7)	2.8	(5.7)	(4.1)	(4.8)
<b>2</b>	-	-	-	20.1	77.0	61.0	-1.8	-	-	-
					(13.5)	(13.0)	-2.4			
<b>3</b>	35.4	53.2	-	-	-	-	-3.8	89.2	76.5	76.5
	(8.9)	(14.5)					3.6	(6.3)	(4.9)	(4.9)

<sup>a</sup> Chemical shifts are reported in ppm downfield from TMS (mean value reported for <sup>103</sup>Rh-coupled peaks; the values of  $J(^{103}\text{Rh}-^{13}\text{C})$  appear in parentheses (Hz); spectra observed in C<sub>6</sub>D<sub>6</sub>.

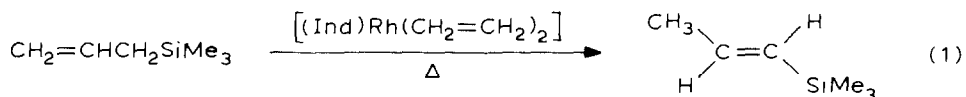


<sup>c</sup> Assignments are tentatively made by comparing <sup>103</sup>Rh-<sup>13</sup>C coupling constants to those in compounds **2** and **3**.



initially formed diallylsilane complex. It will be noticed that the second double bond of the diallylsilane does not need to be released from the metal to maintain an 18 electron count as the  $(\eta\text{-allyl})\text{hydrido}$  intermediate is formed. The isomerization is favored thermodynamically since propenylsilanes are estimated to be about 2 kcal/mol more stable than the isomeric allylsilanes [6]. The failure of the diallylsilane ligand to isomerize completely to the bis-propenylsilane is somewhat puzzling but could be caused by steric constraints which prevent the formation of an intermediate such as **1a** in the (allyl)(propenyl)dimethylsilane-rhodium(I) complex.

Allyltrimethylsilane also reacts with diethylene( $\eta^5\text{-indenyl}$ )rhodium(I) to form *trans*-propenyltrimethylsilane catalytically (see eq. 1). As the reaction proceeded, the solution gradually darkened and no stable rhodium-containing species could be



isolated from it. *trans*-Propenyltrimethylsilane which can not be readily separated from unconverted allyltrimethylsilane by distillation, was identified in the volatiles from the mixture by its characteristic NMR [7]. Both its concentration and that of allyltrimethylsilane in reaction mixtures were routinely monitored using NMR. Interestingly, no *cis*-propenyltrimethylsilane was observed.

In a typical reaction (allyltrimethylsilane/catalyst = 19/1) the conversion to *trans*-propenyltrimethylsilane was only 43% after 6.5 h, but after 8.5 h the reaction was essentially complete at about 80% conversion (corresponding to 15 catalyst turnovers). The reaction was monitored for an additional 24 h, and the percent conversion did not change. When the catalyst concentration was reduced (allyltrimethylsilane/catalyst 134/1) the number of catalyst turnovers increased to 43, but the conversion dropped to 32% after 8 h.

## Experimental

### *General conditions and starting materials*

All reactions were conducted under an atmosphere of prepurified nitrogen. Hexane and tetrahydrofuran were dried and distilled from calcium hydride prior to use. Diallyldimethyl- and allyltrimethyl-silane were obtained from Petrarch Systems, Inc. and used as received. Dimethyldivinylsilane [8] and diethylene( $\eta^5$ -indenyl)rhodium(I) [5] were prepared by literature methods and showed acceptable physical and spectral properties. Carbon and hydrogen were determined locally on a Perkin-Elmer Model 240C Elemental Analyzer.

Sixty MHz  $^1\text{H}$  NMR spectra were determined on a Perkin-Elmer Model R-12A Spectrometer; 90 MHz spectra were determined on a Varian Model EM-390; 200 MHz spectra were determined on a Nicolet Model NT-200. Carbon-13 NMR spectra were determined on a Varian FT-80A Spectrometer in both the proton-decoupled and off-resonance decoupled modes. Benzene- $d_6$  was used as the solvent, for an internal reference standard and for deuterium lock.

### *Reaction of diethylene( $\eta^5$ -indenyl)rhodium(I) with diallyldimethylsilane*

The ethylene complex (0.50 g, 1.8 mmol) was refluxed with diallyldimethylsilane (2.0 ml, 11 mmol) in a mixture of tetrahydrofuran (2 ml) and hexane (5 ml) for 12 h. Volatiles were removed from the dark mixture which was then taken up in hexane and chromatographed on Florisil. Orange crystals of ( $\eta^4$ -*trans*-propenylallyldimethylsilane)( $\eta^5$ -indenyl)rhodium(I) (0.52 g, 74%, m.p. 53°C) were obtained from the cold (-78°C) concentrated hexane eluate. Anal. Found: C, 57.20; H, 6.59.  $\text{C}_{17}\text{H}_{23}\text{RhSi}$  calcd.: C, 56.98; H, 6.47%.

### *Reaction of diethylene( $\eta^5$ -indenyl)rhodium(I) with divinyl dimethylsilane*

In a procedure analogous to that described above the ethylene complex (0.50 g, 1.8 mmol) reacted with divinyl dimethylsilane (2.0 ml, 13 mmol) to yield ( $\eta^4$ -divinyl dimethylsilane)( $\eta^5$ -indenyl)rhodium(I) (0.40 g, 66%, m.p. 72°C). Anal. Found: C, 54.75; H, 5.70.  $\text{C}_{15}\text{H}_{19}\text{RhSi}$  calcd.: C, 54.54; H, 5.79%.

### *Reaction of diethylene( $\eta^5$ -indenyl)rhodium(I) with allyltrimethylsilane*

In a procedure analogous to that described above the ethylene complex (0.50 g, 1.8 mmol) reacted with allyltrimethylsilane (2.0 ml, 13 mmol) to yield *trans*-propenyltrimethylsilane [7] (52% isolated yield) after 12 h. No rhodium complex could be isolated from the reaction mixture. Other runs under different conditions were routinely monitored and analyzed by  $^1\text{H}$  NMR spectroscopy without prior distillation.

### *Preparation of acetylacetonato( $\eta^4$ -diallyldimethylsilane)rhodium(I) [1]*

Acetylacetonatobis(ethylene)rhodium(I) [2] (0.64 g, 2.5 mmol) was mixed with diallyldimethylsilane (2 ml, 11 mmol) at -78°C. The stirred solution evolved ethylene as it warmed to room temperature. After stirring the reaction for 30 minutes at room temperature the volatiles were removed in vacuo. The residue, taken up in hexane and chromatographed on Florisil, yielded acetylacetonato( $\eta^4$ -diallyldimethylsilane)rhodium(I) (0.41 g, 48%, m.p. 60°C) upon crystallization at -78°C

of the concentrated eluate. Anal. Found: C, 45.22; H, 6.39%.  $C_{13}H_{23}SiO_2Rh$  calcd.: C, 45.62; H, 6.77%.

### Acknowledgements

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