Rhodium-catalyzed silylative coupling of olefins with vinylsilanes

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$RhH(CO)(PPh_3)_3$ appeared to be a very effective catalyst for disproportionation of vinylsilanes and their co-disproportionation with styrene and 1-decene. The insertion of vinylsilane (or bis(silyl)ethene) into the Rh–H bond followed by β-silyl transfer to form a Rh–Si bond and elimination of ethylene (or vinylsilane), in combination with a MS study of the product of the reaction of styrene-d_8 with vinylsilane and well-known insertion of alkene into the Rh–Si bond accounts for a non-metallacarbene mechanism of a new rhodium-catalyzed silylation of olefins with vinylsilanes.

Keywords: rhodium-complex catalysis, silylative coupling of olefins, vinylsilane

Recent reports on the migratory insertion of ethylene [1], vinylsilane [2] and styrene [3] into the Ru–Si bond in $RuCl(SiR_3)(CO)(PPh_3)_2$ suggest the disproportionation of vinyltrisubstituted silanes and their co-disproportionation with olefins to occur via a mechanism involving the insertion of olefin into the Ru–Si (and vinylsilane into Ru–H) bonds followed by β-H (and β-Si) elimination to yield bis(silyl)ethene or silyl(organyl)ethene (and ethylene). This new type of olefin conversion – silylation (coupling) of olefins with vinylsilanes – occurs by C_{vinyl}–Si and C_{vinyl}–H bond cleavage according to scheme 1 [2,3].

A preliminary study on the rhodium-catalyzed disproportionation of vinylsilanes using the following systems: $RhCl_3$ – hydride donor [5] and $RhCl(PPh_3)_3 + LiAlH_4$ [11] suggests that also complexes containing initially Rh–H bonds can be new catalysts for the olefin silylation by vinylsilanes.

In the communication, we report that $RhH(CO)(PPh_3)_3$ (**4**) is a very effective catalyst in the silylation (coupling) of some olefins with vinyltrisubstituted silanes occurring according to the equation of scheme 1. Selected catalytic data on homocoupling of various vinyltrisubstituted silanes ($R' = SiR_3$) compiled in table 1 show that the reaction yields two isomers: E-1,2-bis(silyl)ethene (**2**) and 1,1-bis(silyl)ethene (**3**) earlier spectroscopically characterized [6]. The products of silylation are accompanied predominantly by the products of hydrogenation of vinylsilanes ($EtSiR_3$ – up to 8%) and 1,2-bis(silyl)ethane ($R_3SiCH_2CH_2SiR_3$ – traces). Also products of the substituent exchange at the silicon and siloxanes are observed in the reaction mixture but no *cis*-isomer was detected. The presence of (**3**) in the reaction products indicates the non-metallacarbene mechanism of the vinylsilane disproportionation.

The insertion of ethylene into the Rh–Si bond as a step of hydrosilylation and dehydrogenative silylation pathway has been known and thoroughly discussed [12–16], but the first striking proof of its occurrence was given by Thorn and Harlow [17].

Therefore, in order to provide additional evidence for such a mechanism, the stoichiometric reaction of complex (**4**) with vinyltrimethylsilane (in the ratio 1 : 5) was carried out to occur according to the equation:

$$\begin{aligned} &RhH(CO)(PPh_3)_3 + Me_3SiCH{=}CH_2 \\ &\quad\to Rh(SiMe_3)(CO)(PPh_3)_n + CH_2{=}CH_2, \\ &\quad n = 2, 3 \end{aligned} \tag{1}$$

The Rh–Si complex was detected by NMR spectroscopy. Evolution of ethylene was confirmed by GLC analysis. In the particular experiment 0.1 g (1.09×10^{-4} mol) of $RhH(CO)(PPh_3)_3$ and 0.08 ml (5.51×10^{-4} mol) of $ViSiMe_3$ were added subsequently to 5 ml of warm (50 °C) benzene. Then the solution was refluxed for 1.5 h. Evaporation of an excess of vinylsilane and benzene under reduced pressure followed by addition of pentane gave a brown precipitate. The latter was filtered off washed with cold pentane and dried under vacuum. The air sensitive solid was analysed by ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectrum evidences the formation of the silyl complex in the mixture with other Rh complexes. The signals ^1H NMR (300 MHz, benzene) $\delta = 0.315$ (s) and ^{13}C NMR (75 MHz, benzene) $\delta = 2.45$ were assigned to the trimethylsilyl group in the Rh–Si complex formed. Ethylsilane, the product of vinylsilane (**1**) hydrogenation, as well as molecular hydrogen also were detected in the reaction mixture. The above explains why an attempt to isolate a pure Rh–Si complex failed.

An additional experiment involving the stoichiometric reaction of (**4**) with small excess of one of the products, E-1,2-bis(silyl)ethene (**2**) (ratio 1 : 3), enabled us to also prove the occurrence of the insertion of (**2**) into the Rh–H

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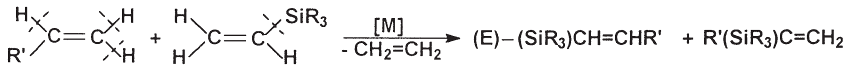

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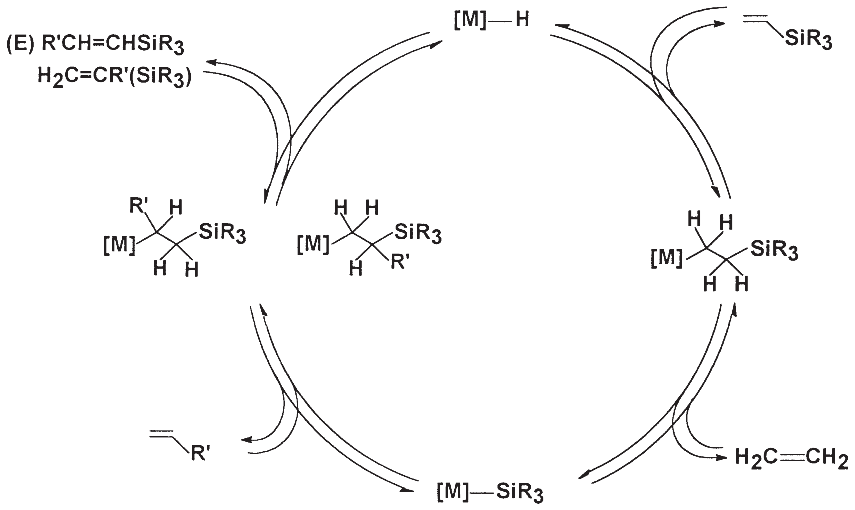


Scheme 1. Catalysis of silylative coupling of olefins with vinylsilanes. M = Ru; R′ = SiR_3 [2,4–7], alkyl [8–10], Ph [3,10]; R = alkyl, alkoxy, Ph.

Table 1
Disproportionation of vinylsilanes catalyzed by $RhH(CO)(PPh_3)_3$.[a]

R_3	Conversion of $H_2C{=}CHSiR_3$ (%)	Yield of bis(silyl)ethenes (%)	(**2**) : (**3**)
Me_3	62	59	4 : 1
Me_2Ph	52	35	5 : 1
Me_2Ph^b	54	31	2 : 1
Me_2OEt	70	67	1 : 1
$Me(OEt)_2$	74	48	2 : 1
$Me(OEt)_2^b$	79	70	2 : 1
$(OEt)_3$	69	48	5 : 1
$(OEt)_3^b$	63	53	10 : 1

[a] 130 °C, ampoules, $[Rh] : [H_2C{=}CHSiR_3] : [C_6H_6] = 1 : 100 : 150$, argon.

[b] 100 °C, open system, 48 h.

Table 2
Silylative coupling of styrene and 1-decene with vinylsilanes catalyzed by $RhH(CO)(PPh_3)_3$.[a]

R_3	Conversion of $H_2C{=}CHSiR_3$ (%)	Yield of E-silylstyrene (**2a**) (silyldecenes (**2b** + **3b**)) (%)
Me_3^b	93	85
Me_2Ph^c	100	100
$Me(OEt)_2$	77	60
$(OEt)_3^b$	52	32
$(OEt)_3$	60	48
Me_2Ph^d	54	(38) (**2b**) : (**3b**) = 12 : 1

[a] 100 °C, open system, 24 h, $[Rh] : [H_2C{=}CHSiR_3] : [styrene] = 1 : 100 : 1000$.

[b] Ampoules.

[c] 0.5 h.

[d] Reflux, 24 h; $[Rh] : [H_2C{=}CHSiR_3] : [1\text{-decene}] = 1 : 100 : 2000$.

bond followed by elimination of the respective vinylsilane and Rh–Si complex (**5**) according to the equation:

$$RhHCO(PPh_3)_3 + Me_3SiCH{=}CHSiMe_3 \rightarrow Rh[SiMe_3](CO)(PPh_3)_n + CH_2{=}CHSiMe_3, \quad n = 2, 3 \qquad (2)$$

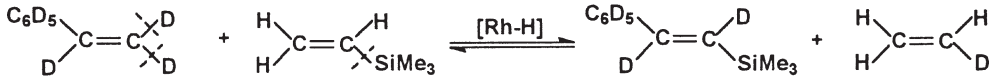
Detection of vinylsilane is a proof for this process. This stoichiometric process indicates reversibility of the vinylsilane disproportionation (see scheme 1).

The two types of experiments allowed us to show not only the addition of Rh–H into the C=C bond of vinylsilane and bis(silyl)ethene, respectively, which is a well-known process but, above all, to provide evidence for the first β-transfer of a silyl group to a rhodium atom with elimination of the olefin (ethylene, vinylsilane) (see also scheme 1 for M = Ru).

The self-disproportionation of vinylsilanes implies the application of the rhodium catalyst (**4**) for cross-disproportionation with other olefins, i.e., silylative coupling of the olefins with vinylsilanes yielding alkenylsilanes (1-silyl-1-alkenes) (known as "vinylsilanes"), which find considerable synthetic applications in organic synthesis [18].

Coupling of vinylsilanes with exemplary hydrocarbons, i.e., styrene (R′ = Ph) and alkene ($R' = C_8H_{17}$) allows, under optimal conditions, a synthesis of the corresponding E-silylstyrene (**2a**) and silyl(alkyl)ethenes (two isomers, (**2b**) and (**3b**)), respectively. The conversion of vinylsilane, yield and selectivity of the products are presented in table 2. Hydrogenation products, $PhCH_2CH_2SiR_3$, products of vinylsilanes homocoupling, $R_3SiCH_2CH_2SiR_3$ and siloxanes are detected as by-products.

The effect of the coupling of vinylsilane with $C_6D_5CD{=}CD_2$ used in place of $C_6H_5CH{=}CH_2$ was additionally



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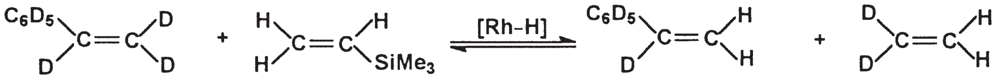

(4)

studied. If the reaction was to occur according to a non-metallacarbene mechanism (i.e., silylation of styrene) the process shown in equation (3) would take place, leading to formation of the product containing seven deuterium atoms, but if the cross-metathesis of vinylsilanes with d-styrene occurs then the process shown in equation (4) would take place leading to silylstyrene-d_6.

A GC-MS study of the deuterated styrene in the preliminary stage of its reaction with vinyltrimethylsilane showed the exclusive formation of a product – d_7. The peaks m/z 183 (M^+) recorded after 15 min of the reaction of styrene-d_8 with $Me_3SiCH{=}CH_2$, i.e., where the yield of the product does not exceed 2%, are convincing evidence for the formation of product containing seven deuterium atoms. No m/z 182 signal was detected at the beginning step of the reaction.

All the results of catalytic disproportionation of vinylsilanes and their co-disproportionation with olefins as well as stoichiometric reactions of the Rh–H complex with the substrate and the product, together with the experiments showing insertion of ethylene into the Rh–Si bond reported earlier [17], and MS study of the product of the deuterated styrene with vinyltrimethylsilane are convincing proofs for a mechanism of the process catalyzed by (**4**) the same as for the ruthenium-catalyzed reaction presented in scheme 1.

Appendix

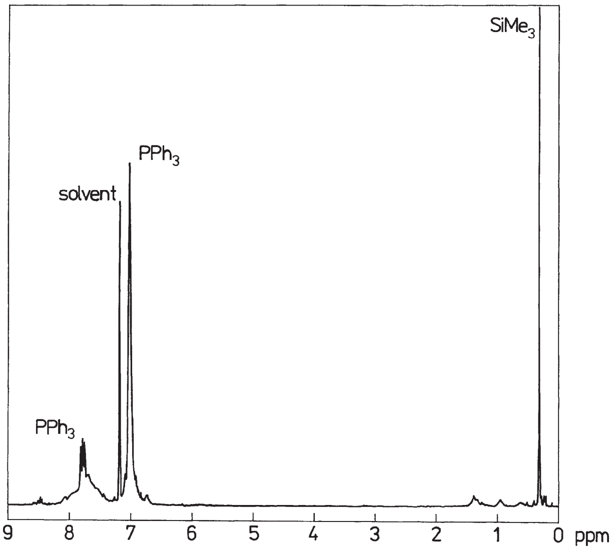

Figure 1. ^1H NMR spectrum of rhodium–silyl complex (the brown precipitate).

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