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RHODIUM CARBENE COMPLEXES AS HYDROSILYLATION CATALYSTS

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Summary

The catalytic activity of various rhodium carbene complexes has been investigated. These complexes are active for the hydrosilylation of a wide variety of unsaturated organic molecules such as olefins, acetylenes and dienes. Their activity is comparable to other rhodium(I) complexes previously used as hydrosilylation catalysts. The yield of products is found to vary with catalyst, silane and organic substrate.

Introduction

The recent reports that transition metal carbene complexes are active in the catalysis of the olefin metathesis reaction [1,2], has focussed attention on the catalytic activity of this type of complex. We have utilized the complexes I—IV, prepared from the electron-rich olefins (for example eqn. 1), or prepared by three fragment oxidative addition reactions (for example eqn. 2), as catalysts for hydrosilylation reactions. As many rhodium compounds such as Wilkinson's compound [5], $[RhCl(PPh_3)_3]$, and chlorocarbonylbis(triphenylphosphine)-rhodium(I) [6], $[RhCl(CO)(PPh_3)_2]$, are active hydrosilylation catalysts, we decided to investigate the catalytic activity of various rhodium carbene complexes, to see if the carbene ligands enhanced or modified the catalytic activity.

$$[RhCl(PPh_3)_3] + [Me_2NCHCl]Cl \xrightarrow[-PPh_3]{CHCl_3,20^\circ C}$$

$$[RhCl_3(CHNMe_2)(PPh_3)_2] \xrightarrow{reduction} [RhCl_2H(CNMe_2)(PPh_3)_2]\ [4] \qquad (2)$$

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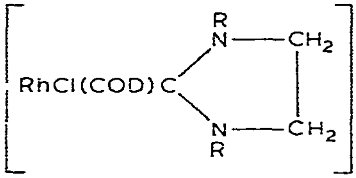
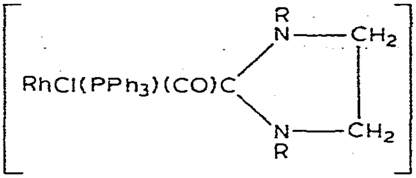
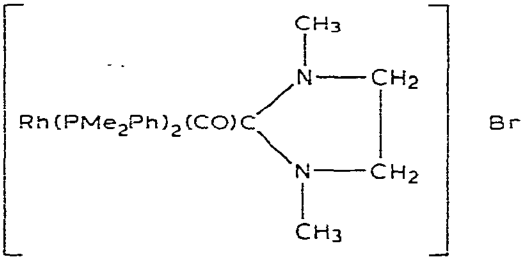


(Ia) R = C_6H_5
(Ib) R = CH_3



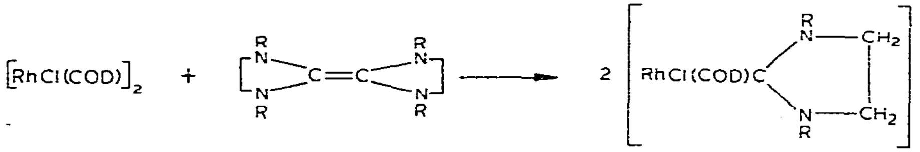
(IIa) R = p-$C_6H_4CH_3$
(IIb) R = p-$C_6H_4OCH_3$



(III)

$[RhCl_2H(CHNMe_2)(PPh_3)_2]$

(IV)



[3] (1)

Results and discussion

The results of the hydrosilylation of various unsaturated species are summarized in Tables 1 and 2. All reactions were carried out under standard conditions, i.e. 100°C for 8 h. No attempt was made to maximize yields.

Hydrosilylation of terminal olefins

The catalytic activity of the complexes I—IV was investigated for the hydrosilylation of 1-octene by a variety of silanes (eqn. 3). The results are summarized in Table 1, together with results previously reported for other rhodium complexes.

The yields of 1-octylsilanes (V) seem sensitive to both catalyst and silane. With triethylsilane, high yields of Vd (approximately 95%, with respect to silane) are obtained with complexes Ib, IIa, and IIb, whereas lower yields of Vd were obtained using Ia and IV as catalysts.

$$C_6H_{13}CH{=}CH_2 + HSiX_3 \xrightarrow{100^\circ C,\ 8h} C_6H_{13}CH_2CH_2SiX_3 \qquad (3)$$

(Va) X = OC_2H_5
(Vb) $X_3 = (CH_3)_2C_6H_5$
(Vc) $X_3 = CH_3(OC_2H_5)_2$
(Vd) X = C_2H_5

TABLE 1

HYDROSILYLATION OF 1-OLEFINS USING RHODIUM CARBENE CATALYSTS

Catalyst [a]	Olefin [b]	Silane [c]	Conditions (°C/h)	Yield of 1-alkylsilane [d]
Ia	1-octene	$HSi(OEt)_3$	100/8	92
Ia	1-octene	$HSiMe_2Ph$	100/8	98
Ia	1-octene	$HSiMe(OEt)_2$	100/8	40
Ia	1-octene	$HSiEt_3$	100/8	73
Ib	1-octene	$HSi(OEt)_3$	100/8	62
Ib	1-octene	$HSiMe_2Ph$	100/8	99
Ib	1-octene	$HSiMe(OEt)_2$	100/8	74
IIa	1-octene	$HSiEt_3$	100/8	96
IIb	1-octene	$HSiEt_3$	100/8	98
III	1-octene	$HSiMe_2Ph$	100/8	96
III	1-octene	$HSiMe(OEt)_2$	100/8	52
IV	1-octene	$HSiEt_3$	100/8	61
$[RhCl(PPh_3)_2CO]$	1-hexene	$HSiCl_3$	75/15	90 [17]
$[RhCl(PEt_3)_2CO]$	1-hexene	$HSiCl_3$	55/30	2 [17]
$[RhCl(PPh_3)_3]$	1-hexene	$HSiEt_3$	60/140	60 [18]
$[RhCl(C_2H_4)_2]_2$	1-heptene	$HSiEt_3$	85/2	60 [19]

[a] 2×10^{-2} mmol of catalyst. [b] 6.3 mmol 1-octene used, except for $HSiMe_2Ph$ reactions where 13 mmol of 1-octene used. [c] Quantities of silane used. $HSi(OEt)_3$, 5.4 mmol; $HSiMe_2Ph$, 6.5 mmol; $HSiMe(OEt)_2$, 6.2 mmol; $HSiEt_3$, 6.3 mmol. [d] Based on silane, calculated by quantitative GLC.

TABLE 2

HYDROSILYLATION USING RHODIUM CARBENE CATALYSTS

Catalyst [a]	Unsaturated substrate (mmol)	Silane (mmol)	Product(s)	Yield (%) [b]
Ia	$n\text{-}C_4H_9C{\equiv}CH$ (8.7)	$HSiMe_2Ph$ (6.5)	*cis*- and *trans*-$C_4H_9CH{=}CHSiMe_2Ph$	77
Ia	$n\text{-}C_4H_9C{\equiv}CH$ (8.7)	$HSiEt_3$ (6.3)	*cis*- and *trans*-$C_4H_9CH{=}CHSiEt_3$	49
Ia	$CH_2{=}C(CH_3)C(CH_3){=}CH_2$ (8.8)	$HSi(OEt)_3$ (5.4)	$CH_2{=}C(CH_3)CH(CH_3)CH_2Si(OEt)_3$ $(CH_3)_2C{=}C(CH_3)CH_2Si(OEt)_3$	24 36
Ia	$CH_2{=}C(CH_3)C(CH_3{=}CH_2$ (8.8)	$HSiEt_3$ (6.3)	$CH_2{=}C(CH_3)CH(CH_3)CH_2SiEt_3$ $(CH_3)_2C{=}C(CH_3)CH_2SiEt_3$	12 86
Ib	$CH_2{=}C(CH_3)C(CH_3){=}CH_2$ (8.8)	$HCi(OEt)_3$ (5.4)	$CH_2{=}C(CH_3)CH(CH_3)CH_2Si(OEt)_3$ $(CH_3)_2C{=}C(CH_3)CH_2Si(OEt)_3$	35 35
III	$CH_2{=}C(CH_3)C(CH_3){=}CH_2$ (8.8)	$HSi(OEt)_3$ (5.4)	$CH_2{=}C(CH_3)CH(CH_3)CH_2Si(OEt)_3$ $(CH_3)_2C{=}C(CH_3)CH_2Si(OEt)_3$	4 77
Ia	$\underline{(CH_2)_5C}{=}O$ (9.7)	$HSi(OEt)_3$ (5.4)	$\underline{(CH_2)_5C}HOSi(OEt)_3$	88
Ib	$\underline{(CH_2)_5C}{=}O$ (9.7)	$HSi(OEt)_3$ (5.4)	$\underline{(CH_2)_5C}HOSi(OEt)_3$	60
III	$\underline{(CH_2)C}{=}O$ (9.7)	$HSi(OEt)_3$ (5.4)	$\underline{(CH_2)_5C}HOSi(OEt)_3$	29
Ia	$CH_2{=}C(CH_3)C(O)OCH_3$ (9.5)	$HSiEt_3$ (6.3)	$(CH_3)_2C{=}C(OCH_3)OSiEt_3$	98

[a] 2×10^{-2} mmol catalyst, 100° for 8 h. [b] Based on silane; calculated by quantitative GLC. containing small amounts of other products.

Variation in silane also causes changes in yield, dependent on catalyst. For example the yields of V, using Ia, decrease from 98% using phenyldimethylsilane, through 92% for triethoxysilane, 73% for triethylsilane to 40% for diethoxymethylsilane. A similar order of activity ($HSi(CH_3)_2C_6H_5 > HSi(OC_2H_5)_3 > HSi(C_2H_5)_3$) has been found for the hydrosilylation of 1-hexene catalyzed by $[RhH(PPh_3)_4]$ [7]. However, the order of activity is different for other catalysts, for example for Ib the order of activity is $HSi(C_2H_5)_3 \sim HSi(CH_3)_2C_6H_5 > HSi(OC_2H_5)_3$. This is similar to that reported for Wilkinson's compound [5]. The effect of ligands on the stability of the catalytic intermediates, proposed for Wilkinson's compound and its analogs, $[RhH(SiX_3)ClL_2]$, was found to be a subtle balance of steric and electronic factors, dependent both on the nature of the ligands, L, and the substituents X, on silicon [8,9]. As the yield of products from hydrosilylation have been postulated [8,9] to depend inversely on the stability of this adduct, it follows that the yield of products should also be influenced by similar subtle effects in silane and ligands. Our results seem to reflect this subtle balance of effects.

Hydrosilylation of terminal acetylenes

The hydrosilylation of 1-hexyne catalyzed by Ia leads to a mixture of *cis*- and *trans*-mono adducts (eqn. 4). This reaction is unusual in that transition metal-catalyzed hydrosilylation normally leads only to the *trans*-olefin by *cis*-addition. In the case of triethylsilane the ratio of *cis*/*trans* was estimated by GLC to be 80/20. Mixtures of isomers in similar ratios have been found using Wilkinsons's compound as a catalyst [10] and other rhodium catalysts [11], although the yields and ratios of isomers were found to be very sensitive to reaction conditions and ligands.

$$n\text{-}C_4H_9C{\equiv}CH + HSiX_3 \xrightarrow{100^\circ C,\ 8h} cis\text{- and } trans\text{-}n\text{-}C_4H_9CH{=}CHSiX_3 \qquad (4)$$

(VIa) $X = C_2H_5$
(VIb) $X_3 = (CH_3)_2C_6H_6$

Hydrosilylation of dienes

The complexes, Ia, Ib, and III were investigated for the hydrosilylation of 2,3-dimethyl-1,3-butadiene. The results are included in Table 2. All three catalysts gave moderate yields of 1/1 diene/silane adducts and both 1,2- and 1,4-adducts were formed (eqn. 5). The proportion of each product formed being dependent on catalyst; the ratio of VIIIb/VIIb being 60/40 for Ia, 50/50 for Ib, and 95/5 for III. Wilkinson's compound is reported to give only the 1,4-adduct, *cis*-2-(1-triethoxysilyl)butene, when 1,3-butadiene reacts with triethoxysilane [12]. When triethylsilane reacts with 2,3-dimethyl-1,3-butadiene catalyzed by Ia, an

$$CH_2{=}C(CH_3)C(CH_3){=}CH_2 + HSiX_3 \xrightarrow{100^\circ C,\ 8\,h}$$

$$CH_2{=}C(CH_3)CH(CH_3)CH_2SiX_3 + (CH_3)_2C{=}C(CH_3)CH_2SiX_3 \qquad (5)$$

(VIIa) $X = C_2H_5$
(VIIb) $X = OC_2H_5$

(VIIIa) $X = C_2H_5$
(VIIIb) $X = OC_2H_5$

excellent yield of 1/1 adducts (1,4-/1,2-adduct ratio, 87/13) was obtained. Small amounts (~3%) of higher boiling products were detected in these reactions.

Hydrosilylation of carbonyl compounds

The ketone, cyclohexanone, was hydrosilylated in good yields by triethyl- and triethoxy-silane by catalysts Ia and Ib, but in poor yield using III. The results are included in Table 2. The hydrosilylation of methyl methacrylate by triethylsilane, catalyzed by complex Ia, gave high yields of the 1,4-adduct (eqn. 6). A similar reaction has been reported using Wilkinson's compound [13].

$$CH_2{=}C(CH_3)C(O)OCH_3 + HSi(C_2H_5)_3 \xrightarrow{100^\circ C, 8\,h} (CH_3)_2C{=}C[OSi(C_2H_5)_3]OCH_3 \qquad (6)$$

Experimental

General procedures

All reactions were carried out under pure nitrogen, using freshly distilled, dry liquids. ^{1}H NMR spectra were recorded on a Varian Associates T60 spectrometer. IR spectra were taken with a Perkin—Elmer 457 grating spectrophotometer as thin films. The GLC analysis of the reaction products was carried out on a Varian Aerograph A-700 "Autoprep" Gas Chromatograph, using a 6 ft column of 10% SE30 on Chromosorb G, using indane or dodecane as internal standards. Preparative GLC separations were carried out on the same machine using a 20 ft column of 15% SE 30 on Chromosorb G. The silanes were purchased or prepared according to literature methods [14]. All the unsaturated organic compounds were commercial products, dried over molecular sieves and distilled prior to use, with the exception of 2,3-dimethyl-1,3-butadiene which was prepared by the dehydration of pinacol, by the literature method [15]. The rhodium carbene complexes were gifts from Dr. P.L. Pye, Dr. M.J. Doyle, and Dr. K. Turner, with the exception of Ia, which was synthesized by the standard method [3]. Microanalyses were performed by Integral Microanalytical Laboratories, Inc. of Raleigh, North Carolina.

The product of the hydrosilylation of methyl methacrylate by triethylsilane was identified by its ^{1}H NMR spectra [13].

Hydrosilylation of 1-octene

These reactions were carried out using the same method. The general procedure will be outlined for the hydrosilylation of 1-octene by triethoxysilane catalyzed by Ia.

Ia (50 mg, 0.1 mmol) was added to a mixture of 1-octene (5.7 g, 50 mmol) and triethoxysilane (4.4 g, 27 mmol) under nitrogen. The mixture was then heated with stirring to 100°C (oil bath temperature), and maintained at that temperature for 8 h. The mixture was allowed to cool to room temperature and the unreacted silane and 1-octene removed under reduced pressure, distillation yielded 1-(triethoxysilyl)octane (6.2 g, 83% based on silane), b.p. 106°C/4 mmHg. (Found: C, 61.0; H, 12.0. $C_{14}H_{32}O_3Si$ calcd.: C, 60.8; H, 11.7%.) ^{1}H NMR: τ

(ppm) 6.27 (6H, quartet J 7 Hz, Si—O—CH_2—C), 8.71 (12 H, singlet, C—$(CH_2)_6$—C), 8.85 (9H, triplet, J 7 Hz, Si—O—C—CH_3), 8.87—9.38 (5H, broad multiplet, CH_3—C and C—CH_2—Si).

Also prepared using a similar method: 1-(dimethylphenylsilyl)octane, b.p. 72—75°C/0.4 mmHg. (Found: C, 76.9; H, 11.6. $C_{16}H_{28}Si$ calcd.: C, 77.3; H, 11.4%.) ^1H NMR: τ (ppm) 2.62—2.79 (5H, broad multiplet, Si—C_6H_5), 8.7—9.4 (17H, multiplet, Si—$(CH_2)_7$—CH_3), 9.71 (6H, singlet, Si—CH_3).

1-(Diethoxymethylsilyl)octane: b.p. 86—88°C/2 mmHg. (Found: C, 62.7; H, 12.3. $C_{13}H_{30}O_2Si$ calcd.: C, 63.3; H, 12.3%.) ^1H NMR: τ (ppm) 6.28 (4H, quartet, J 7 Hz, Si—O—CH_2—C), 8.7—9.4 (17H, multiplet, Si—$(CH_2)_7$—CH_3, 8.87 (6H, triplet, J 7 Hz, Si—O—C—CH_3), 10.06 (3H, singlet, Si—CH_3).

Hydrosilylation of cyclohexanone by triethoxysilane

Ia (50 mg, 0.1 mmol) was added to a mixture of cyclohexanone (3.8 g, 39 mmol) and triethoxysilane (3.5 g, 21 mmol) under nitrogen. After the mixture had been heated at 100°C for 8 h, unreacted silane was removed under reduced pressure at room temperature. Fractional vacuum distillation yielded cyclohexanoxytriethoxysilane (4.1 g, 75% based on silane), b.p. 100°C/4 mmHg. (Found: C, 54.8; H, 10.0. $C_{12}H_{26}O_4Si$ calcd.: C, 54.9; H, 10.0%.) ^1H NMR: τ (ppm) 6.24 (6H, quartet, J 7 Hz, Si—O—CH_2—C), 6.32 (1H, broad multiplet. CH—O—Si), 7.9—9.1 (10H, broad multiplet, C—$(CH_2)_5$), 8.83 (9H, triplet, J 7 Hz, Si—O—C—CH_3).

Hydrosilylation of 1-hexyne

(a) By triethylsilane. To 1-hexyne (4.3 g, 52 mmol) and triethylsilane (4.4 g, 38 mmol) in a flask was added (50 mg, (0.1 mmol of Ia). The reaction mixture was heated to 100°C and maintained at that temperature for 8 h. After cooling volatiles were removed under reduced pressure, and vacuum distillation yielded 1-(triethylsilyl)-1-hexene (3.2 g, 42% based on silane), b.p. 58°C/0.3 mmHg. (Found: C, 71.9; H, 13.1. $C_{13}H_{26}Si$ calcd.: C, 72.6; H, 13.2%.) GLC analysis of the product showed that it consisted of two isomers in a 80/20 ratio. Pure samples of the two isomers were obtained by preparative GLC using a Varian Aerograph 700 "Autoprep" Gas Chromatograph using a 20′ by 3/8″ column of 15% SE 30 on Chromosorb G at 200°C. The major isomer was identified as *cis*-1-(triethylsilyl)-1-hexene from its ^1H NMR: τ (ppm) 3.66 (1H, overlapping doublet of triplets; J 14 Hz, J^1 7 Hz, C—CH=C—Si), 5.67 (1H doublet, J 14 Hz, C—C—CH—Si), 7.62—8.29 (2H, borad multiplet, C=C—CH_2—C), 8.29—9.87 (22H, complex pattern $CH_3CH_2CH_2C$—C=C—Si—CH_2CH_3). The minor component was identified as *trans*-1-(triethylsilyl)-1-hexene from its ^1H NMR: τ (ppm) 3.90 (1H, doublet of triplets, J 19 Hz, J^1 6 Hz, C—CH=C—Si; literature values [16] 5.01, J 18.7 Hz, J^1 6 Hz), 4.50 (1H doublet, J 19 Hz, C—C=CH—Si; literature values [16] 4.50, J 18.7 Hz), 7.61—8.14 (2H, broad multiplet, C=C—CH_2—C), 8.14—9.71 (22 H, complex pattern $CH_3CH_2CH_2C$—C=C—Si—CH_2—CH_3).

(b) By dimethylphenylsilane. The reaction between 1-hexyne and dimethylphenylsilane was carried out in a similar fashion yielding 1-(dimethylphenylsilyl)hexenes. b.p. 74—75°C/0.3 mmHg. The ^1H NMR spectrum indicated that the product was a mixture of isomers, as three distinct resonances for the

Si—CH_3 protons could be distinguished (τ 9.58, 9.67, and 9.71 ppm, all singlets), in the ratio of 77/18/5. However, the mixture could not be resolved or separated by GLC. The ^1H NMR spectrum in the region τ 3.4—4.7 ppm consisted of a series of peaks. Peaks assigned to *cis*-1-(dimethylphenylsilyl)-1-hexene, at τ (ppm) 3.63 (overlapping doublet of triplets, J 14 Hz, J^1 7 Hz) and 4.44 (doublet, J 14 Hz), could easily be distinguished, and accounted for the majority of the integral in this region. Thus the major product is *cis*-1-(dimethylphenylsilyl)-1-hexene. The minor peaks in this region are in good agreement with the literature [16] values for a mixture of *trans*-1-(dimethylphenylsilyl)-1-hexene (τ (ppm) 3.90, doublet of triplets, J 18 Hz, J^1 5 Hz, and 4.23 doublet J 18 Hz) and 2-(dimethylphenylsilyl)-1-hexene (4.60 and 4.33), although some are obscured. From the values of the integrals for these peaks the product formed in intermediate amounts is *cis*-1-(dimethylphenylsilyl)-1-hexene and the minor product is 2-(dimethylphenylsilyl)-1-hexene. The ^1H NMR spectrum also contains the expected peaks for the Si—C_6H_5 moiety (τ 2.44—2.94 ppm) and C=C—$CH_2CH_2CH_2CH_2CH_3$ protons (τ 7.74—9.39 ppm).

Hydrosilylation of 2,3-dimethyl-1,3-butadiene

(a) By triethylsilane. Ia (50 mg, 0.1 mmol) was added to a mixture of 2,3-dimethyl-1,3-butadiene (3.6 g, 44 mmol) and triethylsilane (3.7 g, 32 mmol) under nitrogen. After the mixture had been heated, with stirring, for 8 h at 100°C, the unreacted silane and diene were removed under reduced pressure at room temperature. Fractional vacuum distillation yielded triethylsilyl-2,3-dimethylbutenes (5.0 g, 79% based on silane b.p. 55°C/0.3 mmHg. (Found: C, 72.2; H, 12.8. $C_{12}H_{26}Si$ calcd.: C, 72.6; H, 13.2%.) GLC analysis of the product showed that it consisted of two isomers in a 87/13 ratio. Pure samples of the two isomers were separated by preparative GLC using a Varian Aerograph 700 "Autoprep" Gas Chromatograph using a 20′ by 3/8″ column of 15% SE 30 on Chromosorb G at 200°C. The major isomer was identified as 1-(triethylsilyl)-2,3-dimethyl-2-butene from its ^1H NMR spectrum: τ (ppm) 8.41 (9H, singlet, $(CH_3)_2C{=}C(CH_3)$—C), 8.55 (2H, singlet, C=C—CH_2—Si), 8.79—9.76 (15 H, characteristic complex pattern, $Si(CH_2{-}CH_3)_3$). The minor isomer was identified as 4-(triethylsilyl)-2,3-dimethyl-1-butene from its ^1H NMR spectrum: τ (ppm) 5.46—5.59 (2H, broad multiplet, C=CH_2), 7.44—8.11 (1H, broad multiplet, C=C—CH—C), 8.41 (3H, broad singlet, C=C—CH_3), 8.81—9.77 (20H, complex pattern C=C—$C(CH_3)$—CH_2—$Si(CH_2CH_3)_3$). GLC of the pot residue indicated the presence of small amounts of higher boiling products.

(b) By triethoxysilane. The hydrosilylation of 2,3-dimethyl-1,3-butadiene was carried out in a similar fashion to yield triethxoysilyl-2,3-dimethylbutenes (55% based on silane) b.p. 110°C/8 mmHg. (Found: C, 57.8; H, 10.7. $C_{12}H_{26}O_3Si$ calcd.: C, 58.5; H, 10.6%.) GLC analysis of the product mixture showed that it consisted of two isomers in a 60/40 ratio. Pure samples of the isomers were isolated by preparative GLC using the same conditions as above. The major isomer was identified as 1-(triethxoysilyl)2,3-dimethyl-2-butene from its ^1H NMR spectrum: τ (ppm) 6.25 (6H, quartet, J 7 Hz, Si—O—CH_2—C), 8.33 (9H, singlet, $(CH_3)_2C{=}C(CH_3)$—C), 8.43 (2H, singlet, C=C—CH_2—Si), 8.88 (9H, triplet, J 7 Hz, Si—O—C—CH_3). The minor isomer was identified as 4-(triethoxysilyl)2,3-dimethyl-1-butene from its ^1H NMR spectrum: τ (ppm) 5.04—5.24

(2H, broad multiplet, —C=CH$_2$), 6.31 (6H, triplet, J 7 Hz, Si—O—CH$_2$—C), 7.51—8.11 (1H, broad multiplet, C=C—CH—C), 8.21—8.41 (3H, broad multiplet, C=C—C(CH$_3$)—Si), 8.73—9.51 (14 H, complex pattern, C=C—C(CH$_3$)—CH$_2$Si(O—C—CH$_3$)$_3$). GLC of the pot residue indicated the presence of small amounts of higher boiling products.

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