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Interaction of Hydrosilanes with the Surface of Rhodium

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Received August 26, 1994

Interaction of triethylsilane and diphenylsilane (Ph_2SiH_2, Ph_2SiD_2) with the surfaces of rhodium has been examined by trapping the reaction intermediates with 2,3-dimethyl-1,3-butadiene. 1,4-Hydrosilylation of the diene is predominantly observed to occur under mild condition over the rhodium catalyst. It is inferred from the product analyses that silylene and silyl radicals bonded to rhodium surfaces are the intermediates for addition of silylene to the diene, and for 1,4-hydrosilylation, respectively.

Introduction

Transition metal complexes containing silyl radicals or silylenes as ligands are relatively uncommon; however, some of those complexes have been isolated as stable compounds.[1,2] Also a recent ion beam study of the reactions of transition metal ions with various silanes in the gas phase is quite informative as to detailed mechanistic interpretation of transition metal-catalyzed hydrosilylation and provides estimates of bond energies of transition metal-silylenes.[3] There are numerous reports on the hydrosilylations of olefin and diene catalyzed by transition metals and their complexes.[4-9] Activation of Si-H bonds by transition metal is presumed to play an important role in the catalytic hydrosilylation, and direct evidence for this oxidative addition is shown by spectroscopy at low temperatures.[10,11]

We are concerned about the formation of silyl radicals and silylenes bonded to transition metal under mild reaction condition. Much endeavor has also been made for obtaining the mechanistic information about the behaviors of silylhyd-

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rides on the surfaces of rhodium.

In this study, we examined the heterogenous reactions of triethyl- and diphenylsilanes over rhodium. Particularly diphenylsilane is presumed to be an important precursor for a metal-silylene intermediate since it could undergo consecutive double SiH additions to rhodium with concomitant formation of a metal silicon double bond. A trapping agent of 2,3-dimethyl-1,3-butadiene is employed since it could efficiently trap the silyl radical and silylene bonded to the metal center being formed. A labelling experiment employing a partially deuterized diphenylsilane Ph_2SiD_2 was also performed for clarifying the mechanistic interpretation of the catalytic hydrosilylation.

Experimental

General Data. ^1H NMR spectra were recorded on a Bruker AC-80 FT and/or Bruker AM-300 FT spectrometer. Gas chromatograph-mass spectra (GC-MS) were recorded on a Shimadzu GCMS-QP1000, and/or on a Hewlett Packard GC/MS spectrometer consisting of a HP 5890 series II gas chromatograph and a HP 5970 series mass selective detector (MSD) operating at an ionization voltage of 70 eV. Flame ionization detector (FID) and thermal conductivity detector (TCD) instruments were employed for analytical gas chromatography. The FID instrument was Varian model 3300. The TCD gas chromatograph was Gow-Mac Series 350. The TCD instrument was also used routinely for separation of reaction mixtures and yield determinations. Yields were based on the amount of unrecovered starting precursors and were determined with the use of the precursors as an external standards. Chromatographic response factors in the TCD instrument were determined for isolated products or for hydrocarbons with the similar molecular weight as the observed products. All the products were separated by using a 13 ft×1/4″ 20% OV-17 on Chromorsorb WHP, 105 °C .[12]

All chemical shifts are reported in values as measured in parts per million(ppm) down field from tetramethylsilane (TMS). Coupling constants (J) are given in Hz. Signals in the ^1H NMR spectra are described as : s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

Materials. 5% Rhodium powder on carbon (Aldrich), 98 % 2,3-dimethyl-1,3-butadiene(Aldrich), 99% dichlorodiphenylsilane (Aldrich), and 99% triethylsilane (Aldrich) were used without further purification.

Diphenylsilane and dieuterodiphenylsilane were prepared from reactions of dichlorodiphenylsilane with lithium aluminum hydride and lithium aluminum deuteride, respectively. A conventional method for the preparation is described in the literature.[13,14] The NMR spectrum is the same as reported previously.[15]

Pyrolysis of triethylsilane and dideuterodiphenylsilane on the surface of rhodium. 1.0 g (5.4 mmol) dideuterodiphenylsilane, 0.31 g (2.7 mmol) triethylsilane and 0.1 g powdered rhodium on carbon were placed in a pyrex tube (o.d. : 13 mm, length : ca. 120 mm). The reaction mixture was degassed using the freeze-pump-thaw cycle. The sample was pyrolyzed at 150 °C for 2 hr. The rhodium on carbon was removed by passing through a silicagel column. 45 and 100% of the protiated and deuteriated diphenylsilane and triethylsilane were recovered, respectively. Mass of a

mixture of Ph_2SiH_2, Ph_2SiHD, Ph_2SiD_2 : 186 (38), 185 (39), 184 (23), 183 (8.5), 182 (8.5) 181 (10), 180 (3.8), 107 (88), 106 (100), 105 (49), 79 (13), 53 (25). Mass of a mixture of Et_3SiH and Et_3SiD : 117 (5.7), 116 (2.2), 115 (2.4), 88 (85), 87 (34), 86 (34), 60 (100), 59 (90), 58 (22), 57 (12), 55 (9.4), 43 (19).

Pyrolysis of triethylsilane and 2,3-dimethyl-1,3-butadiene on the surface of rhodium on carbon. A mixture of 0.49 g (4.2 mmol) triethylsilane, 0.73 g (8.9 mmol) 2,3-dimethyl-1,3-butadiene and 0.1 g rhodium on carbon was pyrolyzed at 150 °C for 10 min in the same manner described above. All triethylsilanes were decomposed. The products obtained were 2,3-dimethyl-5,5-diethyl-5-silahept-1-ene (I) (6%) and 2,3-dimethyl-5,5-diethyl-5-silahept-2-ene(II) (56 %). The products were identified from ^1H NMR and mass spectra. 2,3-Dimethyl-5,5-diethyl-5-silahept-1-ene(I); 200 MHz FT ^1H NMR (C_6D_6) : δ 0.56 (q, 6H, J = 7.8 Hz, $SiCH_2$), 0.60 (d, 2H, J = 5.9 Hz, $SiCH_2$), 0.96 (t, 9H, J = 7.8 Hz, $Si-C-CH_3$), 1.03 (d, 3H, J = 6.8 Hz, $SiCH_2CHCH_3$), 1.64 (s, 3H, $=C-CH_3$), 2.36 (m, 1H, $CH_2CHC=$), 4.70 (s, 1H, $=CH$), 4.82 (S, 1H, $=CH$); mass : $(M^+ - 29)$ 169 (93), 141 (36), 127 (81), 115 (32), 113 (55), 99 (47) 87 (100), 85 (21), 59 (87). 2,3-dimethyl-5,5-diethyl-5-silahept-2-ene(II); 80 MHz FT ^1H NMR $(C_6D_6$: δ 0.62 (m, 6H, $SiCH_2$) 0.97 (m, 9H, $Si-C-CH_3$), 1.58 (s, 2H, CH_2), 1.65 (s, 9H, CH_3); mass : M^+ 198 (12), 169 (2.1), 115 (68), 87 (100), 59 (39).

Pyrolysis of diphenylsilane and 2,3-dimethyl-1,3-butadiene on the surface of rhodium on carbon. A mixture of 1.0 g (5.4 mmol) diphenylsilane and 1.3 g (16 mmol) 2,3-dimethyl-1,3-butadiene and 0.1 g powdered rhodium on carbon was pyrolyzed at 150 °C for 5 min. in the same manner. 98% of diphenylsilane was decomposed. The products obtained were 3,4-dimethyl-1,1-diphenyl-1-silapent-3-eme(III) (45%), 3,4-dimethyl-1,1-diphenyl-1-silacyclopent-3-ene(IV) (4%), and 2,3,7,8-tetramethyl-5,5-diphenyl-5-silanona-2,7-diene(V) (2%). The pyrolysis experiment was performed with various reaction times. Variation of the product yields with reaction time is shown in Table 1. The products were identified from ^1H NMR and mass spectra. 3,4-Dimethyl-1,1-diphenyl-1-silapent-3-ene(III); 80 MHz FT ^1H NMR (C_6D_6) : δ 1.43 (s, 3H, CH_3), 1.52 (s, 6H, CH_3, CH_3), 2.06 (d, 2H, J = 3.9 Hz, CH_2), 5.07 (t, 1H, J = 3.9 Hz, SiH), 7.17 (m, 6H, C_6H_5), 7.53 (m, 4H, C_6H_5); mass : M^+ 266 (4.4), 224 (76), 183 (35), 182 (100), 181 (70), 146 (55), 105 (47), 79 (75), 53 (11). 3,4-Dimethyl-1,1-diphenyl-1-silacyclopent-3-ene(IV); 80 MHz FT ^1H NMR (C_6D_6) : δ 1.73 (s, 6H, CH_3), 1.85 (s, 4H, CH_2), 7.21 (m, 6H, C_6H_5), 7.53 (m, 4H, C_6H_5); mass : M^+ 264 (100), 186 (92), 181 (45), 171 (21), 145 (9.2), 105 (40), 79 (9.4), 53 (11). 2,3,7,8-Tetramethyl-5,5-diphenyl-5-silanona-2,7-diene(V); 80 MHz FT ^1H NMR (C_6D_6) : δ 1.38 (s, 6H, CH_3), 1.55 (s, 12H, $SiCH_3$), 2.19 (s, 4H, CH_2), 7.20 (m, 6H, C_6H_5), 7.53 (m, 4H, C_6H_5); mass : M^+ 348 (5.3), 265 (62), 223 (9.4), 197 (9.4), 187 (100), 183 (92), 105 (24).

Pyrolysis of dideuterodiphenylsilane and 2,3-dimethyl-1,3-butadiene on the surface of rhodium. A mixture of 1.0 g (5.4 mmol) dideuterodiphenylsilane, 2.2 g (27 mmol) 2,3-dimethyl-1,3-butadiene and 0.1 g powdered rhodium on carbon was pyrolyzed at 150 °C for 2 hr in the same manner. All diphenylsilanes were decomposed. The products obtained were 1,5-dideutero-3,4-dimethyl-1,1-diphenyl-1-silapent-3-ene(III-D₂) (73%), 3,4-dimethyl-1,1-diphenyl-
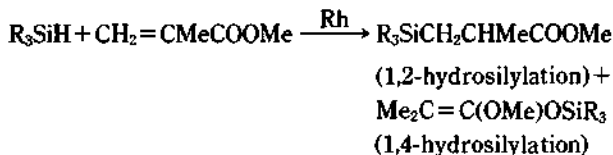
1-silacyclopent-3-ene(IV) (9.0%) and 1,9-dideutero-2,3,7,8-tetramethyl-5,5-diphenyl-5-silanona-2,7-diene(V-D₂) (1.2%). 1,5-Dideutero-3,4-dimethyl-1,1-diphenyl-1-silapent-3-ene(III-D₂); 80 MHz FT ^{1}H NMR (C₆D₆) : δ 1.47 (s, 3H, CH₃), 1.58+1.61 (s, 5H, CH₃, CH₂D), 2.10 (s, 2H, CH₂), 7.17 (m, 6H, C₆H₅), 7.53 (m, 4H, C₆H₅); mass : M⁺ 268 (5.7), 225 (27), 224 (2.8), 184 (100), 183 (21), 182 (13), 181 (15), 105 (36), 79 (5.7), 53 (9.5). 1,9-Dideutero-2,3,7,8-tetramethyl-5,5-diphenyl-5-silanona-2,7-diene(V-D₂); 80 MHz FT ^{1}H NMR (C₆D₆) : δ 1.36 (s, 6H, CH₃), 1.55 (s, 10H, CH₃, CH₂D), 2.19 (s, 4H, CH₂), 7.21 (m, 6H, C₆H₅), 7.53 (m, 4H, C₆H₅): mass : M⁺350 (1.9), 266 (38), 265 (26), 264 (5.7), 225 (4.5), 224 (4.9), 197 (6.6), 188 (72), 187 (27), 184 (25), 183 (100), 182 (23), 105 (26).

Results and Discussion

Triethylsilane reacts with 2,3-dimethyl-1,3-butadiene at 150 ℃ over the rhodium surface for a short reaction time of 10 min. to give an appreciable amount of 1,4-hydrosilylation product II, along with a small quantity of 1,2-hydrosilylation product I.

Et₃SiH + ⤳ $\xrightarrow[\text{Rh}]{150°\text{C, 10 min.}}$ Et₃Si—⤳ + Et₃Si—⤳

I, 6%   II, 56%
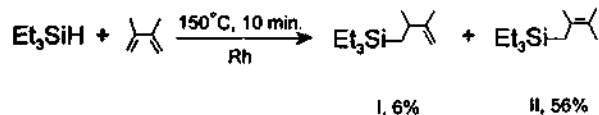
Previously, the similar results were reported by Quirk in the hydrosilylation of methyl methacrylate by several tris- or trialkoxysilanes using rhodium catalyst and 1,2- and 1,4-hydrosilylation products were observed.[6]

$R_3SiH + CH_2 = CMeCOOMe \xrightarrow{Rh} R_3SiCH_2CHMeCOOMe$

(1,2-hydrosilylation)+
Me₂C=C(OMe)OSiR₃
(1,4-hydrosilylation)

R=-OMe, -OEt, -OiPr, -OtBu, -NMe₂

For R=-OMe and -OEt, the product ratio was reported as 1:1, On the contrary, when R is bulky group such as -OiPr, -OtBu and -NMe₂, 1,4-hydrosilylation is a dominant process.

It should be pointed out that the Si-H bond in Et₃SiH can be actually activated by Rh. Therefore we performed a pyrolysis experiment employing a mixture of triethylsilane and dideuterodiphenylsilane with a ratio of 1:2 over Rh to examine whether or not the H/D scrambling occurs between the H atom bonded to Si in Et₃SiH and the D atoms in Ph₂SiD₂. We observe that 72% of the H atoms in the Et₃SiH molecules are replaced by the D atoms. If the scrambling completely occurs, a statistical calculation indicates that 80% of the H atoms in Et₃SiH should be replaced by D atoms by assuming that all the silane precursors are not consumed *via* for example dehydrogenation giving rise to H₂, HD and D₂ losses. This observation indicates that the activation of the Si-H bonds by rhodium plays an important role in the scrambling observed.

Therefore we presume that the hydrosilylations of the diene mecessitate the oxidative addition of Et₃Si-H to the surface of rhodium as shown in Scheme 1.

Et₃SiH
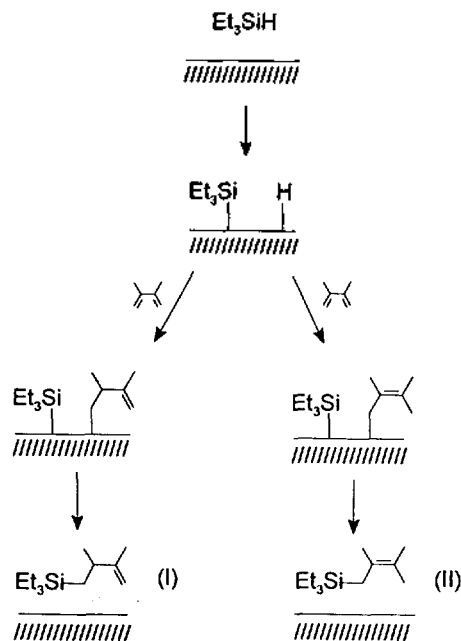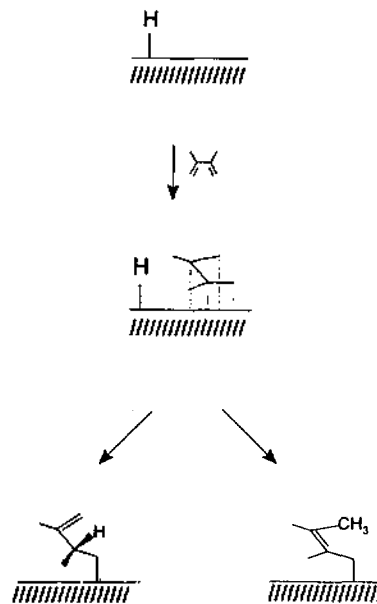
Scheme 1.

Scheme 2.

The sign ⫫ shown in scheme 1 indicates the surface of the rhodium catalyst. The dissociative addition of the Si-H to the catalyst is believed to be efficient since the transition state is symmetry-allowed due to the d orbital participation of Rh in the interaction between the HOMO (d orbital) of Rh and the LUMO in the Si-H bond in Et₃Si-H(Si-H antibonding orbital). It is still a question whether the H atom bonded to the surface of Rh is directly added to the free diene in the solution phase as shown in Scheme 1 or to the diene bonded to the surface of Rh as shown in Scheme 2.

The similar reactivity is observed in the diene hydrosilylation by diphenylsilane over rhodium at 150 ℃ for 5 min.

Table 1. Product yields as a function of reaction time in the reactions of diphenylsilane with 2,3-dimethyl-1,3-butadiene at 150 °C on the surface of Rh

Reaction Time (min)	% Decomposition	Yield (%)[a]		
		III	IV	V
5	98	45	4	2
10	100	0	8	50
20	100	0	8	61
120	100	0	15	65
240	100	0	4	48

[a] Product yield are expressed as % absolute, based on the amount of the unrecovered starting material.
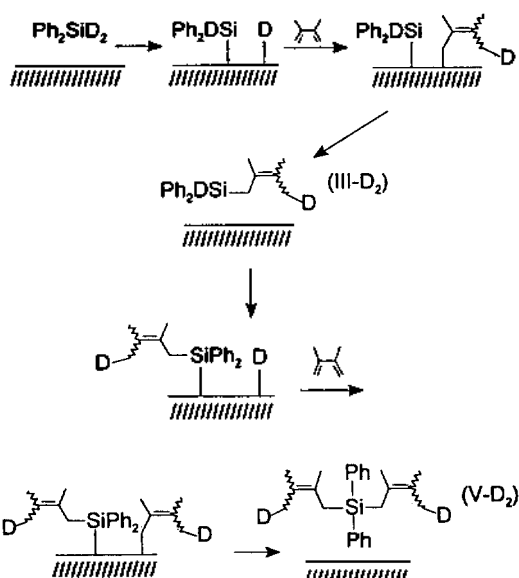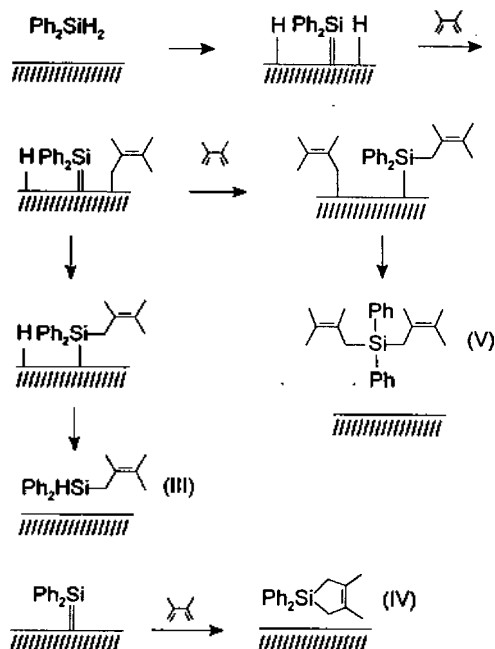
Scheme 3.

Scheme 4.
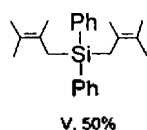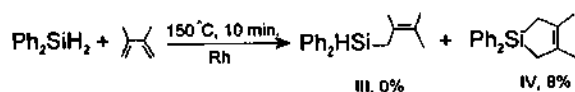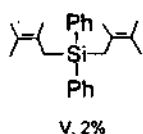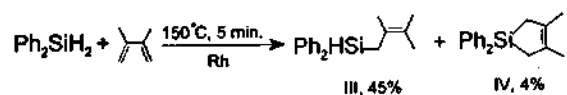
In the longer reaction time, we have also observed product V formed by the consecutive hydrosilylations of the dienes, the incorporation of two diene molecules with one Ph₂SiH₂ molecule. Porduct V is found to be very stable under our reaction condition as shown in Table 1.

In an attempt to elucidate whether of not the catalyst plays an important role in the hydrosilylation, we performed an experiment without the catalyst under the same reaction condition, in which Ph₂SiH₂ is not observed to react with 2,3-dimethyl-1,3-butadiene. In the 5 min. reaction, product III is observed as the major product accounting for over 87% of all the observed products. Formation of III in the diene hydrosilylation implies that the mechanism shown in Scheme 1 also operates in the addition of the diphenylsilane to the diene. Further hydrosilylation of the diene by the primary product III could explain the formation of product V. The possible mechanism is shown in Scheme 3. It should be noted that a partially deuterium labelled Ph₂SiD₂ is represented in Scheme 3 as the reactant to clarify the mechanism.

Alternative mechanism is shown in Scheme 4, which involves the dissociative double additions of Ph₂SiH₂ to the catalyst.

The key intermediate for the formation of IV is the silylene which is doubly bonded to the transition metal. Recently, such metal-silylene complexes are isolated and characterized.[2] A recent ion beam study showed that metal ion-silylene bond energies D° (M⁺-SiH₂) (M=Co⁺, Ni⁺) are fairly large ranging 67±6 kcal/mol.[3] The transition metals form relatively strong metal-silylene bonds by accepting lone pair electrons from silylene and by back-donating electrons to the empty p orbital of silicon.

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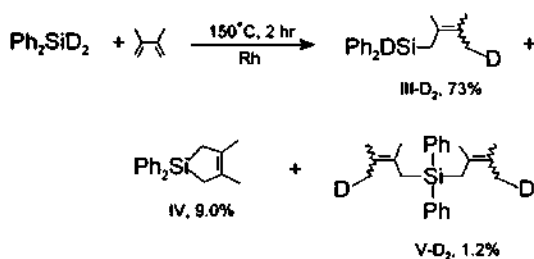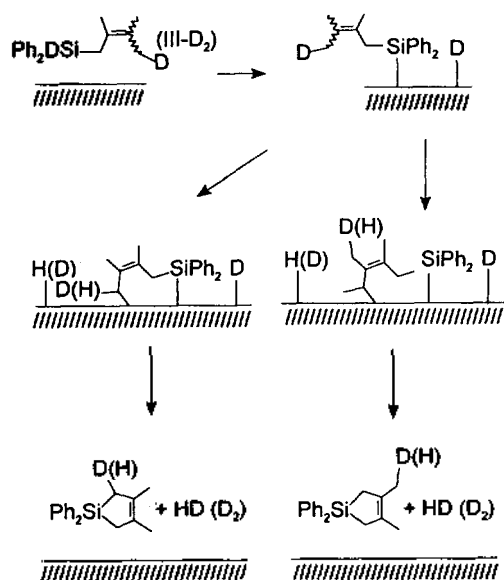
Scheme 5.

Under our catalytic hydrosilylation condition, the mechanism shown in Scheme 3 may operate dominantly for the 1,4-hydrosilylation to yield product III. This explanation is based on time dependence of the product yield as described in Table 1. In the 5 min. reaction, product III has been almost exclusively observed as the predominant product. After longer reaction time, product V is dominantly observed due to the consecutive double hydrosilylation. This correctly reflects the time dependence of the product yield. After the longer reaction time, we have also observed a cyclic product of IV. This product could be accounted for in terms of a cyclization process of product III with concomitant extrusion of H_2.

It is interesting that in the diene hydrosilylation by Ph_2SiH_2, 1,2-hydrosilylation is not observed. This is presumably because the bulky groups such as phenyl ring on the silicon may hinder the 1,2-hydrosilylation *via* the interaction between the phenyl rings and the hydrogen atom, the methyl group on the 2-position of the 2,3-dimethyl-3-butenyl rhodium as shown in Scheme 2.

Labelling experiment was performed by employing Ph_2SiD_2 as the precursor to obtain expected products in which D atoms are incorporated in the expected positions of the products. As shown in Scheme 3, we have observed the expected products in which the deuterium atoms are incorporated in the appropriate positions. But the spectroscopic data indicate that such a replacement of the deuterium atoms in product IV is not observed.

Note that if product IV is formed from III-D_2 as shown in Scheme 5, one can observe deuterium atoms in product IV.

Failure to find deuterium atoms implies that product IV may be formed *via* the reaction of $Ph_2Si=(Rh)_n$ with the diene shown in Scheme 4. But this reaction pathway is minor comparing with the pathway for the double hydrosilylation. It is also interesting that III-D_2 is stable toward another hydrosilylation to form V-D_2 even in the 2 hr pyrolysis. This observation is contrasted with those of the protiated system. We invoke that the drastic isotope effect in the formation

of V may be reflected from the primary isotope effect which is specifically great in a reaction involving the M-H(D) bond cleavage (M=Si, Rh etc.). The ratio of k_H/k_D is estimated to be about 3 at 423 K (150 °C) if the Si-H(D) bond cleavage is the rate-determining step and ν(Si-H)=2200 cm^{-1}. The k_H/k_D ratio of 3 may not be large enough to explain the large value of (yield of III-D_2)/(yield of V-D_2)=73%/1.2%. Thus we presume that the other steps including for example the Rh-H(D) bond cleavages also contribute the yield ratios observed here.

Conclusions

Hydrosilylation of the diene over the rhodium catalyst is observed to occur under the mild condition. Rhodium shows a rather selective reactivity of 1,4-hydrosilylation. This indicates that Si-H bond activations by the rhodium catalyst plays an important role in the diene hydrosilylation. It is inferred from the product studies that diphenylsilylene intermediate bonded to rhodium surfaces $Ph_2Si=(Rh)_x$ is formed. Evidence for the formation of such complex is supported from the labelling experiment employing dideuterodiphenylsilane as the precursor.

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