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Hydrosilation of Dienes Catalyzed by $Cp^*{}_2NdCH(SiMe_3)_2$

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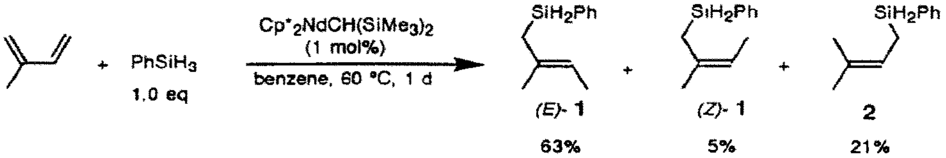
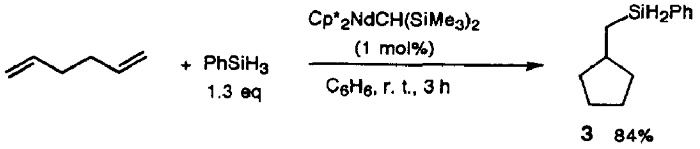
Abstract: $Cp^*{}_2NdCH(SiMe_3)_2$ efficiently catalyzes hydrosilation of 1,3-, 1,5-, and 1,6-dienes under mild conditions with unusual selectivities as compared with later transition metal-catalyzed reactions; hydrosilation of isoprene affords mainly (E)-, not (Z)-, allylsilane. On the other hand, hydrosilation of 1,5- and 1,6-dienes proceeds through intramolecular C-C bond formation to give (silylmethyl)-cyclopentanes.

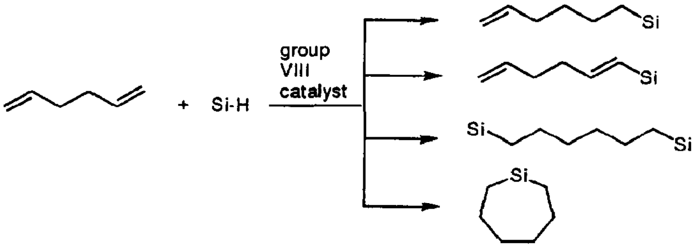
Group VIII metal-catalyzed hydrosilation is one of the most useful reactions to synthesize organosilicon compounds. On the other hand, high activities and selectivities for olefin transformations achieved by group III and IV metallocene catalysts have attracted much interest in the last several years; some asymmetric reactions have also been attained using chiral metallocenes.[1] Based on these backgrounds, growing efforts have recently been devoted to early transition metal-catalyzed hydrosilation.[2] Our previous paper dealt with hydrosilation of olefins catalyzed by $Cp^*{}_2NdCH(SiMe_3)_2$.[2a] The present paper reports diene hydrosilation by the neodymium complex and reveals remarkable difference in selectivities between lanthanoid and d-block transition metal catalysis.

Isoprene reacted with phenylsilane in the presence of $Cp^*{}_2NdCH(SiMe_3)_2$ at the 1,4-positions to give 2-methyl-2-butenylsilane (1) as the major product with concomitant formation of the regio isomer, 3-methyl-2-butenylsilane (2).[3] The high *(E)*-selectivity realized for 1 is unusual because papers on hydrosilation of isoprene with group VI or VIII metals have reported *(Z)*-selectivity; Cr, Mo, Fe, Ru, Co, Rh, Ni, and Pd have so far been investigated as catalysts.[4] The reaction of 2,3-dimethyl-1,3-butadiene by $Cp^*{}_2NdCH(SiMe_3)_2$ also afforded the 1,4-adduct in a selective manner.

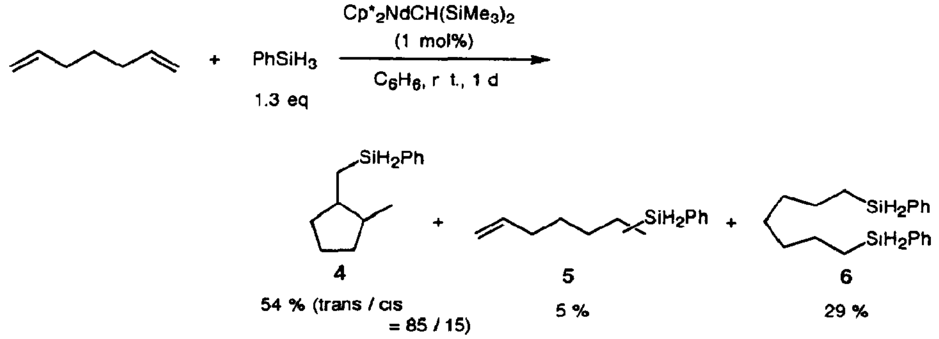


The neodymium-catalyzed reaction of 1,5-hexadiene with $PhSiH_3$ progressed smoothly at room temperature and two 1:1 hydrosilation products were observed by capillary GC (84 and 11 % yields, respectively). The major product was isolated and characterized to be a (silylmethyl)cyclopentane (3).[5,6] The minor one is tentatively assigned to be 2-methyl-1-phenylsilacyclohexane.[7] Thus, the present hydrosilation mainly proceeds through intramolecular carbon-carbon bond formation, whereas group VIII metal-catalyzed hydrosilation of 1,5-hexadiene yielded 5-hexenylsilane, 1,5-hexadienylsilane, 1,6-bis(silyl)hexane, or silacycloheptane depending upon reaction conditions (e.g. diene/silane ratio, types of silanes and catalysts).[8]

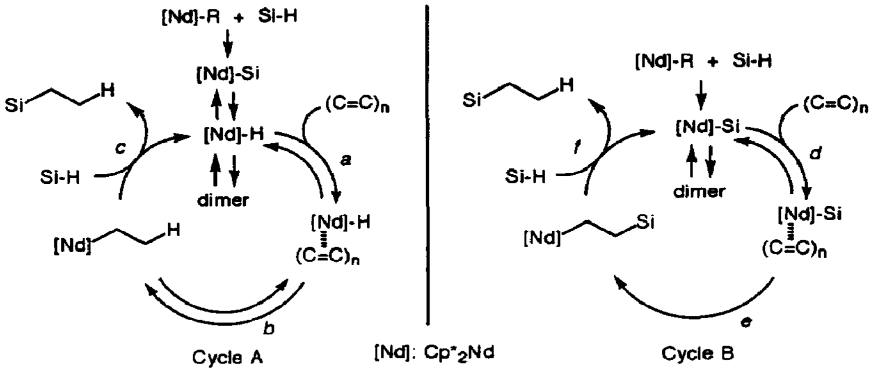




The hydrosilation of 1,6-heptadiene also afforded a (silylmethyl)cyclopentane derivative (4)[9] as the major product although the reaction was somewhat slower than that of 1,5-hexadiene and produced an appreciable amount of 1,7-bis(silyl)heptane (6).[10] The result contrasts with the Cp*$_2$YCH(SiMe$_3$)$_2$-catalyzed hydrosilation, which resulted in selective formation of 1,7-bis(silyl)heptane from 1,6-heptadiene and PhSiH$_3$.[2e] Platinum-catalyzed hydrosilation of 1,6-heptadiene is also known to give a linear adduct, 6-heptenylsilane.[11]



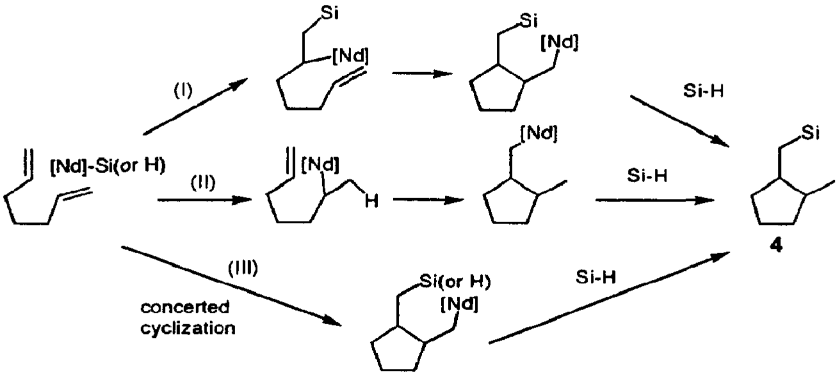
Two different catalytic cycles are possible for the neodymium-catalyzed hydrosilation, one involving hydridometal as a key intermediate and the other being based on silylmetal species (Cycles A and B, Scheme 1). Regarding the olefin insertion steps (*b* and *e*, Scheme 1), [Nd]-H mechanism seems more facile than the [Nd]-Si mechanism as far as the steric factor is concerned. On the other hand, both mechanisms seem plausible for the product forming steps (*c* and *f*, Scheme 1) as judged by Marks' and Tilley's studies; the reaction of Cp*$_2$LnCH(SiMe$_3$)$_2$ (Ln = La, Nd, Sm) with PhSiH$_3$, mesityl-SiH$_3$, or H$_2$Si(SiMe$_3$)$_2$ resulted in nearly quantitative elimination of H$_2$C(SiMe$_3$)$_2$, while Cp*$_2$YMe(THF) converts PhSiH$_3$ to PhMeSiH$_2$.[12]



Scheme 1. Possible reaction cycles for neodymium-catalyzed hydrosilation.

As for the hydrosilation of α,ω-dienes, intermediacy of 9-coordinate hydrido(diene) or silyl(diene) complexes is indicated by the fact that the hydrosilation of 1,5-hexadiene with phenylsilane is much faster than that of 1-hexene; the conversions of $PhSiH_3$ were 94 and 36%, respectively, after 20 min (diene or olefin/silane = 1/1, Nd 1 mol%, r.t.).

There are three possible pathways for the formation of cyclopentane skeleton from 1,6-diene via hydrosilation: [Nd]-Si and [Nd]-H-based stepwise C=C insertions (routes I and II, Scheme 2) and a concerted cyclization (route III, Scheme 2). Hydridometal-based mechanism was proposed for group III metallocene-catalyzed hydrosilation of olefins.[2e] The formation of 4 from 1,6-diene via a hydridometal (route II), however, requires the olefin insertion placing the metal at the internal carbon; the process is both electronically and sterically unfavorable. At present, it is difficult to propose a consistent mechanism that explains all of the experimental and literature data.



Scheme 2. Possible cyclization mechanisms of 1,6-heptadiene.

In summary, the unique characteristics of lanthanocene-catalyzed hydrosilation have been revealed such as selective formation of *(E)*-1,4-adduct from 1,3-diene and hydrosilation-carbocyclization of 1,5- and 1,6-dienes. Application of these reactions to various substrates with functional groups and the utilization of chiral metallocene catalysts will be coming topics.

References and Notes

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3. Compounds *(Z)*-**1** and **2** were converted to phenyldimethylsilyl-derivatives with methyllithium and characterized by comparison with authentic samples (see ref. 4a). Spectral data of *(E)*-1 after methylation: ^{1}H NMR (CDCl$_3$) δ 0.32 (s, 6H, SiMe$_2$), 1.55 (s, 3H, Me), 1.59 (d, J = 6.6 Hz, 3H, $\underline{\mathrm{CH_3}}$-CH=), 1.75 (s, 2H, CH$_2$), 5.06 (q, J = 6.6 Hz, 1H, Me$\underline{\mathrm{H}}$C=), 7.40-7.60 (m, 5H, Ph). *(E)*-Configuration was confirmed by NOESY technique. ^{13}C NMR (CDCl$_3$) δ -2.7, 13.6, 18.4, 28.9, 117.1, 127.7, 128.8, 132.7, 133.6, 139.6. HRMS obsd. 176.1005, calcd for $C_{11}H_{16}Si$, 176.1017. The yields of products were determined by GC with internal standards.
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5. Spectral data of **3**: ^{1}H-NMR (C$_6$D$_6$) δ 0.91 (dt, J = 7.1, 3.8 Hz, 2H, CH$_2$Si), 0.95-1.13 (m, 2H), 1.32-1.62 (m, 4H), 1.65-1.92 (m, 3H), 4.52 (t, J = 3.8 Hz, 2H, SiH$_2$), 7.15-7.55 (m, 5H, Ph). ^{13}C NMR (C$_6$D$_6$) δ 17.2, 25.3, 35.7, 37.2, 128.3, 129.7, 133.1, 135.5. HRMS obsd. 190.1178, calcd for $C_{12}H_{18}Si$, 190.1173
6. P L. Watson also reported the occurrence of carbocyclization in lutetium-catalyzed hydrosilation of 1,5-hexadiene in a patent; see ref. 2b.
7. Spectral data of the minor product: ^{1}H NMR (C$_6$D$_6$) δ 0.63-1.35 (m, 7H), 0.86 (d, J =5.9 Hz, 3H), 1.86-1.98 (m, 2H), 4.50-4.60 (m, 1H, SiH), 7.15-7.60 (m, 5H, Ph). HRMS obsd. 190.1165, calcd for $C_{12}H_{18}Si$, 190.1173.
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9. Spectral data of trans-**4**: ^{1}H NMR (C$_6$D$_6$) δ 0.55-0.70 (m, 1H, HC$\underline{\mathrm{H}}$Si), 0.91 (d, J = 6.2 Hz, 3H, Me), 0.94-1.95 (m, 9H), 4.74-4.57 (m, 2H, SiH$_2$), 7.14-7.60 (m, 5H, Ph). ^{13}C NMR (C$_6$H$_6$) δ 15.2, 18.8, 23.3, 34.5, 43.7, 44.7, 128.3, 129.8, 133.1, 135.5. MS m/z 204 (M$^+$), 107 (M$^+$ - C$_7$H$_{13}$). Spectral data of cis-**4**: ^{1}H NMR (C$_6$D$_6$) δ 0.75 (d, J = 6.7 Hz, 3H, Me), 0.75-2.30 (m, 10H), 4.51-4.55 (m, 2H, SiH$_2$), 7.15-7.65 (m, 5H, Ph). ^{13}C NMR (C$_6$H$_6$) δ 11.4, 15.0, 22.8, 32.2, 33.2, 37.9, 40.2, 128.3, 130.1, 133.1, 135.5. MS m/z 204 (M$^+$), 107 (M$^+$ - C$_7$H$_{13}$). Elemental analysis (mixture of **4** and **5**): Calcd for $C_{13}H_{20}Si$: C, 76.40; H, 9.86. Found: C, 76.14; H, 9.95. Structures of trans- and cis-**4** were assigned by comparison of the spectral data with those of trans- and cis-1-methyl-2-{[tris(trimethylsilyl)silyl]metyl}cyclopentane; see Kulicke, K. J.; Chatgilialoglu , C.; Kopping, B.; Giese, B. *Helv. Chim. Acta* **1992**, *75*, 935-939.
10. Product **6** was identified as 1,7-bis(silyl)heptane by comparison of spectral data with literature values; see ref. 2e. Another 1:2 adduct is also observed in a small amount (5% yield), although the structure is not yet fully characterized. Spectral data: ^{1}H NMR (C$_6$D$_6$) δ 0.74-0.84 (m, 2H), 1 03 (br s, 4H), 1.13-1.54 (m, 8H), 4.41-4.48 (m, 2H, SiH), 4.51 (t, J = 3.7 Hz, 2H, SiH), 7.15-7.58 (m, 10H, Ph). ^{13}C NMR (C$_6$H$_6$) δ 10.3, 16.3, 16.6, 25.3, 28.5, 33.1, 33.7, 128.3, 129.8, 135.5, 136 0 MS (CI) m/z 311 (M$^+$-H).
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