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Silicon–Carbon Unsaturated Compounds. 49. Nickel-Catalyzed Reactions of 2-Adamantyl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)silene

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Summary: Heating a benzene solution of adamantoyltris(trimethylsilyl)silane (1) with a catalytic amount of $Ni(PEt_3)_4$ afforded the benzene adducts 2-[adamantyl(trimethylsiloxy)methyl]hexamethyl-2-phenyltrisilane and 2-[adamantyl(trimethylsiloxy)methyl]-hexamethyl-1-phenyltrisilane in 46 and 31% yields. A similar nickel-catalyzed reaction of 1 with dimethylphenylsilane produced 2-[adamantyl(trimethylsiloxy)-methyl]pentamethyl-2-(trimethylsilyl)-1-phenyltrisilane in 82% yield.

Current interest has focused on the reaction of transition-metal complexes with unsaturated silicon species such as silenes and disilenes.[1-7] Recently, we have reported that the nickel-catalyzed reactions of ethynyldisilanes, ethenyldisilanes, and silicon-containing small-ring compounds afford products which can be best explained by assuming the formation of silene–nickel complexes and nickelasilacycles.[8] It is of considerable interest to us to investigate the chemical behavior of stable silenes toward transition-metal complexes. Our strategy for this study involves the thermal production of stable silenes and the reaction of the resulting silenes with the transition-metal complexes. Brook and his co-workers have demonstrated that the photolysis of acylpolysilanes produces various stable silenes in high yield,[9] and they have also reported that the thermolysis of pivaloyltris(trimethylsilyl)silane in the presence of alcohols or phenylpropyne gives products resulting from trapping of 2-*tert*-butyl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)silene.[10] In this paper we report the nickel-catalyzed reaction of 2-adamantyl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)silene generated thermally from adamantoyltris(trimethylsilyl)silane.

First, we carried out the thermolysis of adamantoyltris(trimethylsilyl)silane (1),[11] in order to check whether or not the silene is produced thermally in this system. Thus, when a benzene solution of 1 was heated in a degassed, sealed glass tube at 120 °C for 24 h, the starting compound 1 was recovered quantitatively. Interestingly, a similar reaction of 1 in the presence of 2,3-dimethylbutadiene afforded a [2 + 4] cycloadduct (3)[12] in 90% yield, indicating that 2-adamantyl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)silene (2)[11] was obviously produced in this thermolysis. When a benzene solution of 1 was heated at 120 °C in the presence of a catalytic amount of $Ni(PEt_3)_4$ under the same conditions, the wholly unexpected compounds 2-[adamantyl(trimethylsiloxy)methyl]hexamethyl-2-phenylsilane (**4a**)[13] and a diastereomeric mixture of 2-[adamantyl(trimethylsiloxy)methyl]hexamethyl-1-phenyltrisilane (**5a**)[14] were obtained in 57% and 23% yields,[15] together with 56% of the unreacted starting compound 1. The ^1H NMR spectrum of **5a** shows that this compound consists of a mixture of diasteromers in a ratio of 3:1. All attempts to separate each diastereomer in pure form were unsuccessful. However, the structures of isomers were confirmed by spectrometric analysis of the mixture, as well as by elemental analysis. The ^{29}Si NMR spectrum of **5a** shows four resonances at −47.2, −17.1, −14.9, and 14.4 ppm for the major diastereomer and at −47.8, −17.2, −10.0, and 14.4 ppm for the minor isomer. The location of the methyl groups on the trisilane unit was determined by the ^1H–^{29}Si COSY spectrum. Thus, for the major isomer, the signal at −47.2 ppm due to the

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(13) Compound **4a**: MS m/z 473 ($M^+ - Me$); IR ν_{Si-O} 1060 cm^{-1}; ^1H NMR (δ; in $CDCl_3$) −0.31 (s, 9H, Me_3Si), 0.10 (s, 9H, Me_3Si), 0.31 (s, 9H, Me_3Si), 1.60–2.00 (m, 15H, Ad), 3.87 (s, 1H, HCO), 7.24–7.53 (m, 5H Ph); ^{13}C NMR (δ; in $CDCl_3$) 0.6, 0.8, 2.1 (Me_3Si), 28.7, 37.1, 37.9, 41.2 (Ad), 82.8 (CHO), 127.5, 127.6, 136.4, 138.6 (Ph); ^{29}Si NMR (δ; in $CDCl_3$) −41.1 (SiPh), −16.0, −15.8 (Me_3Si), 14.2 (Me_3SiO). Anal. Calcd for $C_{26}H_{48}OSi_4$: C, 63.89; H, 9.89. Found: C, 63.71; H, 9.89.

(14) Compound **5a** was analyzed as a 3:1 diastereomeric mixture: MS m/z 473 ($M^+ - Me$); IR ν_{Si-O} 1050 cm^{-1}; ^1H NMR (δ; in $CDCl_3$) for the major isomer 0.02 (s, 9H, Me_3Si), 0.05 (s, 3H, MeSi), 0.09 (s, 9H, Me_3SiO), 0.43 (s, 3H, MeSi), 0.48 (s, 3H, MeSi), 1.41–1.91 (m, Ad, overlapping with the signals of the minor isomer), 3.48 (s, 1H, HCO), 7.27–7.51 (m, Ph, overlapping with the signals of the minor isomer); ^1H NMR (δ; in $CDCl_3$) for the minor isomer 0.09 (s, 9H, Me_3Si), 0.11 (s, 9H, Me_3SiO), 0.15 (s, 3H, MeSi), 0.41 (s, 3H, MeSi), 0.42 (s, 3H, MeSi), 3.39 (s, 1H, HCO); ^{13}C NMR (δ in $CDCl_3$) for the major isomer −6.3, −1.0, −0.8 (MeSi), 0.0, 1.26 (Me_3Si), 28.6, 37.0, 37.4, 41.0 (Ad), 81.8 (CHO), 127.4, 127.5, 134.4, 140.5 (Ph); ^{13}C NMR (δ; in $CDCl_3$) for the minor isomer −6.2, −1.6, −1.2 (MeSi), 0.51, 1.26 (Me_3Si), 28.6, 37.0, 37.4, 40.9 (Ad), 81.6 (CHO), 128.21, 128.24, 134.1, 140.5 (Ph); ^{29}Si NMR (δ in $CDCl_3$) for the major isomer −47.2 (SiMe), −17.1 ($SiMe_2Ph$), −14.9 (Me_3SiSi), 14.4 (Me_3SiO); ^{29}Si NMR (δ; in $CDCl_3$) for the minor isomer −47.8 (SiMe), −17.2 ($SiMe_2Ph$), −10.0 (Me_3SiSi), 14.4 (Me_3SiO). Anal. Calcd for $C_{26}H_{48}OSi_4$: C, 63.89; H, 9.89. Found: C, 63.82; H, 10.01.

(15) Yields were calculated by analytical GLC using an internal standard and were based of the reacted starting compound.

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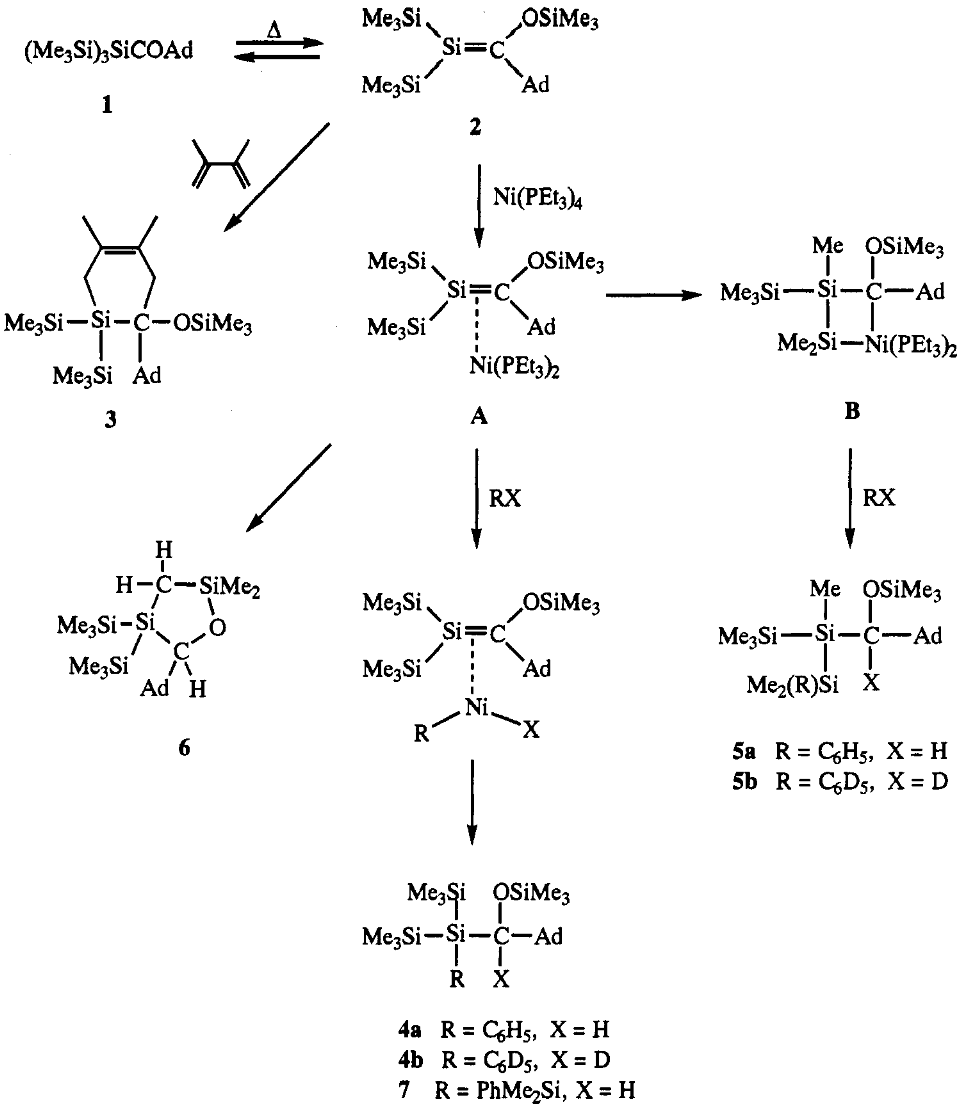
Scheme 1



central silicon atom of the trisilane unit couples with methylsilyl protons at 0.05 ppm and a methyne proton at 3.48 ppm, while a signal at −17.1 ppm couples with methyl protons at 0.43 and 0.48 ppm due to the *Me*$_2$PhSi unit. For the minor isomer, a signal at −47.8 ppm couples with methylsilyl protons at 0.15 ppm, and a silicon signal at −17.2 ppm couples with proton signals at 0.41 and 0.42 ppm due to the *Me*$_2$PhSi group. These results are wholly consistent with the structure proposed for **5a**. The formation of **4a** can be best understood in terms of the reaction of the silene–nickel complex **A** formed from silene **2** and Ni(PEt$_3$)$_4$ with benzene, while **5a** may be explained by the reaction of the nickeladisilacyclobutane species **B**, which would be produced by isomerization of silene–nickel complex **A** with benzene. The C–H bond activation of aromatic compounds by silene–transition-metal complexes has recently been reported.[16]

In this reaction, three products whose mass spectra show their parent ion peak at *m*/*z* 410, corresponding to isomers of **1**, were also produced in 9%, 6%, and 7% yields. The isomerization product obtained in 9% yield was separated from the reaction mixture by gel-permeation chromatography and identified as 2-adamantyl-4,4-dimethyl-1,1-bis(trimethylsilyl)-3-oxa-1,4-disilacyclopentane (**6**)[17] by spectrometric analysis as well as by elemental analysis. The other two products, however, could not be isolated, and attempts to characterize them by way of spectroscopic methods were unsuccessful. The formation of **6** can be explained in terms of the intramolecular addition of a C–H bond of the trimethylsiloxy group across the silicon–carbon double bond of the silene–nickel complex **A**.

As expected, heating **1** in the presence of a nickel catalyst in benzene-d_6 at 120 °C for 24 h gave 2-[adamantyldeuterio(trimethylsiloxy)methyl]-2-(pentadeuteriophenyl)-hexamethyltrisilane (**4b**)[18] and 2-[adamantyldeuterio(trimethylsiloxy)methyl]-1-(pentadeuteriophenyl)-hexamethyltrisilane (**5b**)[19] consisting of two diastereomers in the ratio of 3:1 in 40% and 10% yields, respectively, in addition to 60% of the unreacted starting compound **1**. In

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[16] Ishikawa, M.; Okazaki, S.; Naka, A.; Sakamoto, H. *Organometallics* **1992**, *11*, 4135.

[17] Compound **6**: MS *m*/*z* 410 (M$^+$); IR ν_{Si-O} 1050 cm^{-1}; ^{1}H NMR (δ; in C$_6$D$_6$) −0.01 (d, 1H, CH$_2$, *J* = 14.85 Hz), 0.08 (d, 1H, CH$_2$, *J* = 14.85 Hz), 0.23 (s, 3H, MeSi), 0.26 (s, 9H, Me$_3$Si); 0.33 (s, 9H, Me$_3$Si), 0.46 (s, 3H, MeSi), 1.71–2.10 (m, 15H, Ad), 3.79 (s, 1H, HCAd); ^{13}C NMR (δ; in C$_6$D$_6$) −6.8 (CH$_2$), −0.5, 0.4 (Me$_3$Si), 0.6, 1.0 (MeSi), 28.0, 36.8, 37.2, 40.7 (Ad), 81.6 (CHAd); ^{29}Si NMR (δ; in C$_6$D$_6$) −41.8 (Si(SiMe$_3$)$_2$), −15.4, −14.5 (SiMe$_3$), 28.2 (SiMe$_2$). Anal. Calcd for C$_{20}$H$_{42}$OSi$_4$: C, 58.18; H, 10.74. Found: C, 58.31; H, 10.51.

[18] Compound **4b**: MS *m*/*z* 479 (M$^+$ − Me); IR ν_{C-D} 2270, ν_{Si-O} 1060 cm^{-1}; ^{1}H NMR (δ; in CDCl$_3$) −0.31 (s, 9H, Me$_3$Si), 0.10 (s, 9H, Me$_3$Si), 0.31 (s, 9H, Me$_3$Si), 1.60–2.00 (m, 15H, Ad); exact MS calcd for C$_{25}$H$_{39}$D$_6$OSi$_4$ (M$^+$ − Me) 479.2922, found 479.2911.

this reaction, compound 6 and two unidentified isomerization products of 1 were also produced in 15%, 13%, and 12% yields, respectively.

Next, we examined the reaction of silene–nickel complex A with a hydrosilane. Thus, when 1 was treated with dimethylphenylsilane in the presence of $Ni(PEt_3)_4$ at 120 °C for 24 h, the reaction cleanly proceeded to give a hydrosilylation product, 2-[adamantyl(trimethylsiloxy)methyl]pentamethyl-2-(trimethylsilyl)-1-phenyltrisilane (7),[20] with high regiospecificity in 82% yield as the sole volatile product. In this reaction, 39% of the starting compound 1 was recovered unchanged. The IR spectrum of 7 shows no absorptions due to the stretching frequencies of an Si–H bond at about 2100 cm^{-1}, indicating that a dimethylphenylsilyl group adds to the sp^2 silicon of the silene but not to the carbon. In the absence of a nickel catalyst under the same reaction conditions, no product was formed, but the starting compound 1 was recovered quantitatively. The reaction of stable silenes with transition-metal complexes is currently being examined and will be reported elsewhere.

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(19) Compound **5b** was analyzed as a 3:1 diastereomeric mixture: MS *m/z* 479 ($M^+ - Me$); IR ν_{C-D} 2270, ν_{Si-O} 1050 cm^{-1}; ^1H NMR (δ; in $CDCl_3$) for the major isomer 0.02 (s, 9H, Me_3Si), 0.05 (s, 3H, MeSi), 0.10 (s, 9H, Me_3Si), 0.43 (s, 3H, MeSi), 0.47 (s, 3H, MeSi), 1.41–1.91 (m, Ad, overlapping with the signals of the minor isomer); ^1H NMR (δ; in $CDCl_3$) for the minor isomer 0.10 (s, 9H, Me_3Si), 0.11 (s, 9H, Me_3SiO), 0.15 (s, 3H, MeSi), 0.41 (s, 3H, MeSi), 0.42 (s, 3H, MeSi); exact MS calcd for $C_{23}H_{35}D_6OSi_3$ ($M^+ - Me_3Si$) 421.2684, found 421.2784.

(20) Compound 7: MS *m/z* 531 ($M^+ - Me$); IR ν_{Si-O} 1030 cm^{-1}; ^1H NMR (δ; in $CDCl_3$) 0.15 (s, 9H, Me_3Si), 0.19 (s, 18H, $2Me_3Si$), 0.517 (s, 3H, MeSi), 0.520 (s, 3H, MeSi), 1.45–1.93 (m, 15H, Ad), 3.98 (s, 1H, HC), 7.30–7.55 (m, 5H, Ph); ^{13}C NMR (δ; in $CDCl_3$) 1.3, 1.9 (MeSi), 2.8, 3.1, 3.3 (Me_3Si), 28.7, 36.7, 38.4, 40.8 (Ad), 82.2 (HC), 127.6, 128.3, 134.5, 141.7 (Ph); ^{29}Si NMR (δ; in $CDCl_3$) −77.1 ($SiSiMe_3$), −14.5 ($PhMe_2Si$), −12.2, −12.1 (Me_3SiSi), 12.7 (Me_3SiO). Anal. Calcd for $C_{28}H_{54}OSi_5$: C, 61.46; H, 9.95. Found: C, 61.41; H, 9.85.