

Journal of Organometallic Chemistry, 439 (1992) 19–21
Elsevier Sequoia S.A., Lausanne
JOM 22836

Nickel-catalyzed reactions of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene

Mitsuo Ishikawa, Hiromu Sakamoto, Shougo Okazaki and Akinobu Naka

*Department of Applied Chemistry, Faculty of Engineering, Hiroshima University,
Higashi-Hiroshima 724 (Japan)*

(Received March 13, 1992)

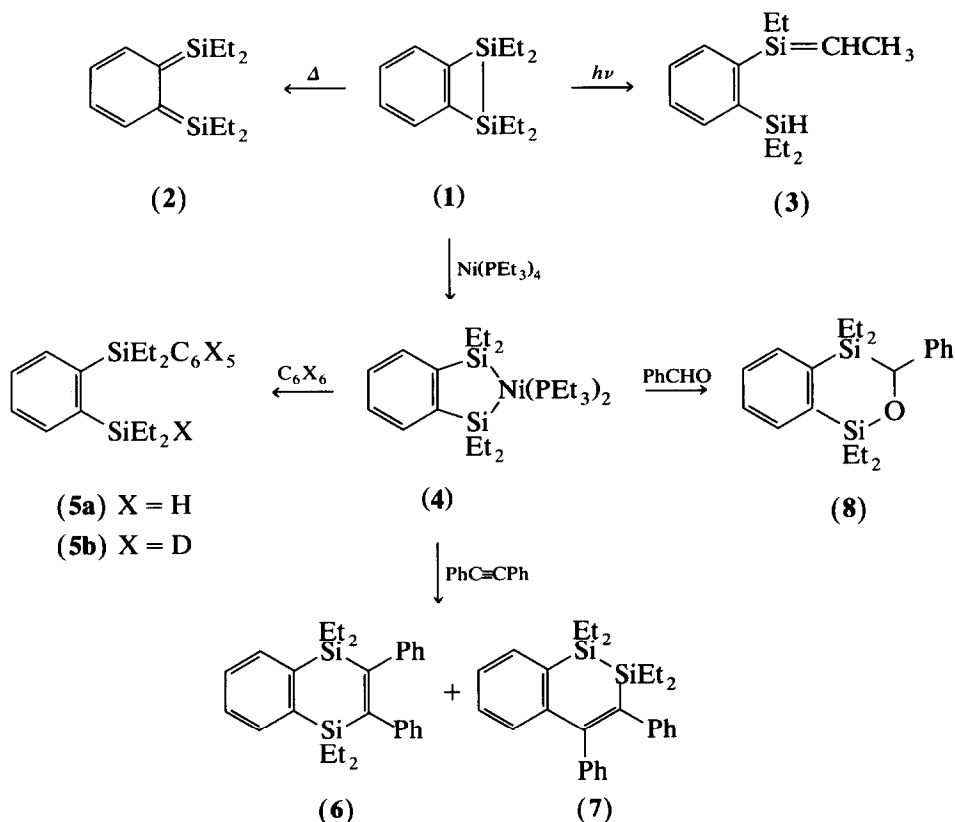
Abstract

The reaction of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene (**1**) with benzene in the presence of a catalytic amount of $\text{Ni}(\text{PEt}_3)_4$ afforded 1-diethylphenylsilyl-2-(diethylsilyl)benzene, while reaction with diphenylacetylene and benzaldehyde gave the respective products arising from insertion of **1** into an Si–Si bond.

3,4-Benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene (**1**) shows unique chemical behaviour. The thermolysis of **1** produces an *o*-quinodisilane (**2**) which reacts with acetylenes to give 2,3-benzo-1,4-disilacyclohexa-2,5-dienes resulting from [4 + 2] cycloaddition [1]. The photolysis of **1**, however, affords 1-ethyl-1-(2-diethylsilylphenyl)-1-silapropene (**3**) arising from homolytic scission of a silicon–silicon bond, followed by intramolecular disproportionation of the resulting silyl radicals [2]. In this paper, we report the nickel-catalyzed reaction of **1** with benzene, diphenylacetylene and benzaldehyde.

When compound **1** (0.5616 g, 2.26 mmol) was heated to reflux in the presence of tetrakis(triethylphosphine)nickel(0) (59 mg, 0.11 mmol) in 10 ml of dry benzene for 17 h, a completely unexpected product, 1-diethylphenylsilyl-2-(diethylsilyl)benzene (**5a**) [MS m/e 297 ($\text{M}^+ - \text{Et}$). IR 2139 cm^{-1} . ^1H NMR (δ , in CDCl_3) 0.51–1.24 (m, 20H, EtSi); 4.22 (quint, 1H, $J = 3.3\text{ Hz}$); 7.27–7.67 (m, 9H, phenyl and phenylene ring protons). ^{13}C NMR (δ in CDCl_3) 4.26, 5.01, 7.51, 8.19 (EtSi), 127.48, 127.80, 127.92, 128.59, 134.90, 134.99, 136.10, 138.47, 143.07, 143.67 (phenyl and phenylene ring carbons)] was obtained in 97% yield (Scheme 1). Compound **5a** is probably formed from coordination of a benzene molecule to 3,4-benzo-2,2,5,5-tetraethyl-1-nickela-2,5-disilacyclopent-3-ene (**4**) arising from insertion of a nickel species into an Si–Si bond of **1**, followed by C–H bond activation of the coordinated benzene. That hydrogen on a silicon atom in compound **5a** came from the benzene molecule

Correspondence to: Dr. M. Ishikawa.



Scheme 1.

was confirmed by the fact that a similar reaction of **1** with deuteriobenzene afforded 2-(deuteriodiethylsilyl)-1-[(deuteriophenyl)diethylsilyl]benzene (**5b**) [MS m/e 303 ($M^+ - \text{Et}$). ^2H NMR (δ in $(\text{CD}_3)_2\text{CO}$) 4.2 (br s, D-Si); 7.3 (br s, C_6D_6)] in 59% yield as the sole reaction product, in addition to 12% of the starting compound **1**. The formation of 3,4-benzo-1-metala-2,5-disilacyclopent-3-enes has been reported to date [3–7].

Interestingly, the reaction of **1** (0.3853 g, 1.55 mmol) with diphenylacetylene (0.4170 g, 2.34 mmol) in the presence of nickel(0) catalyst (40 mg, 0.075 mmol) in refluxing benzene gave two isomers of the adduct composed of **1** and diphenylacetylene, 2,3-benzo-1,1,4,4-tetraethyl-5,6-diphenyl-1,4-disilacyclohexa-2,5-diene (**6**) [m.p. 116–117°C. MS m/e 426 (M^+). ^1H NMR (δ in CDCl_3) 0.70–0.95 (m, 20H, EtSi); 6.79–7.62 (m, 14H, phenyl and phenylene ring protons). ^{29}Si NMR (δ in CDCl_3) –13.33] and 3,4-benzo-1,1,2,2-tetraethyl-5,6-diphenyl-1,2-disilacyclohexa-3,5-diene (**7**) [MS m/e 426 (M^+). ^1H NMR (δ in CDCl_3) 0.52–1.18 (m, 20H, EtSi); 6.75–7.49 (m, 14H, phenyl and phenylene ring protons)] in 65 and 15% yields, respectively, in addition to 17% of the starting compound **1**. No other products such as **5a** were detected by either spectrometric analysis or GLC analysis.

The structures of **6** and **7** were confirmed by spectroscopic analysis, as well as by elemental analysis. The ^{13}C NMR spectrum of **6** reveals two resonances at δ 5.25

and 7.68 ppm, seven resonances at 125.01, 127.37, 127.98, 128.03, 133.37, 142.61, and 143.45 ppm, and a single resonance at 157.32 ppm, attributed to ethyl carbons, phenyl and phenylene carbons, and olefinic carbons, respectively. The ^{13}C NMR spectrum of **7** shows four resonances at δ 3.51, 4.33, 8.92, and 9.01 ppm, and two resonances at 148.32 and 152.96 ppm, due to ethyl carbons and olefinic carbons, as well as fourteen resonances at 124.28, 125.66, 126.27, 127.21, 127.49, 128.32, 128.66, 130.60, 131.70, 133.46, 134.52, 140.70, 144.40, 144.76 ppm, due to phenyl and phenylene carbons as expected. The ^{29}Si NMR spectrum indicates signals at δ -21.54 and -20.81 ppm, indicating the presence of two nonequivalent silicon atoms. These results are consistent with the structure proposed for **7**. The formation of **6** can best be explained by the reaction of intermediate **4** with diphenylacetylene, while for compound **7**, it is necessary to consider the presence of another intermediate such as 4,5-benzo-2,2,3,3-tetraethyl-1-nickela-2,3-disilacyclohex-4-ene. Unfortunately, evidence for this intermediate has not yet been obtained.

Carbonyl compound also react with **1** in the presence of a catalytic amount of tetrakis(triethylphosphine)nickel(0) to give an addition product. Thus, treatment of **1** with benzaldehyde in the presence of a nickel catalyst in a degassed sealed tube at 150°C for 24 h, afforded 5,6-benzo-1,1,4,4-tetraethyl-2-oxa-3-phenyl-1,4-disilacyclohex-5-ene (**8**) in 75% yield. All spectral data obtained for **8** were identical with those of an authentic sample [1,2].

Acknowledgement

This research was supported in part by a Grant-in-Aid for Scientific Research on Priority Area of Organic Unusual Valency from the Ministry of Education, Science and Culture. We also thank Shin-Etsu Chemical Co. Ltd., Nitto Electric Industrial Co. Ltd., Dow Corning Japan Ltd., and Toshiba Silicone Co. Ltd. for financial support.

References

- 1 M. Ishikawa, H. Sakamoto and T. Tabuchi, *Organometallics*, 10 (1991) 3173.
- 2 H. Sakamoto and M. Ishikawa, *J. Organomet. Chem.*, in press.
- 3 T.D. Tilley, in S. Patai and Z. Rappoport (Eds.), *The Chemistry of Organic Silicon Compounds*, Part 2, Wiley, New York, 1989, Chap. 24.
- 4 C. Eaborn, T.N. Metham and A. Pidcock, *J. Organomet. Chem.*, 63 (1973) 107.
- 5 W. Fink, *Helv Chim. Acta*, 59 (1976) 606.
- 6 R.J.P. Corriu, J.J.E. Moreau and M. Pataud-Sat, *Organometallics*, 4 (1985) 623.
- 7 M. Tanaka, Y. Uchimaru and H.-J. Lautenschlager, *Organometallics*, 10 (1991) 16.