ELSEVIER

Journal of Organometallic Chemistry 629 (2001) 44–46

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Reaction of 9,10-dimethyl-9,10-dihydro-9,10-disilaanthracene with alkyne in the presence of palladium

Makoto Oba, Yumi Watanabe, Kazuhiro Iwai, Hideaki Ohtaki, Kozaburo Nishiyama *

Department of Material Science and Technology, Tokai University, 317 Nishino, Numazu, Shizuoka 410-0395, Japan

Received 19 February 2001; received in revised form 26 March 2001; accepted 26 March 2001

Abstract

Reaction of 9,10-dimethyl-9,10-dihydro-9,10-disilaanthracene (**1**) with alkynes in the presence of palladium catalyst was examined. The formal Diels–Alder adduct was isolated from the reaction mixture, indicating the possibility of the intermediacy of 9,10-disilaanthracene, a novel silaaromatic compound. It was found that the [4 + 2] adduct was obtained only from the *cis* isomer of the 9,10-dihydro-9,10-disilaanthracene. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: 9,10-Disilaanthracene; Palladium catalyst; Dehydrogenation; [4 + 2] Adduct

---

1. Introduction

The chemistry of aromatic compounds containing sp^2-silicon atoms has been a major research theme in organosilicon chemistry for over 20 years [1]. Recently, the first isolation of stable silaaromatic compounds was reported [2]. 9,10-Dihydro-9,10-disilaanthracene derivatives have often utilized as precursors of organosilicon reactive intermediates such as silyl radicals [3] and silyl anions [4]. However, generation of 9,10-disilaanthracenes, novel silaaromatic species, from the precursor has not been reported. There have been some reports on the transient generation of the related 9-silaanthracene [5] and 1,4-disilabenzene [6,7] from the corresponding dihydro derivatives. In this paper, we would like to report the reaction of 9,10-dimethyl-9,10-dihydro-9,10-disilaanthracene (**1**) under the dehydrogenative conditions.

2. Experimental

2.1. General

GC measurements were performed on a Shimadzu GC-18A gas chromatograph using a 50 m × 0.25 mm methyl silicone capillary column (Quadrex). TLC was carried out on Merck silica gel 60 F_{254}. Flash column chromatography was performed on Merck silica gel 60 (230–400 mesh). ^{1}H-, ^{13}C- and ^{29}Si-NMR spectra were measured in $CDCl_3$ solution on a Varian UNITY-400 spectrometer. All chemical shifts are reported as δ-values (ppm) relative to residual chloroform (δ_H 7.26), the central peak of deuteriochloroform (δ_C 77.0) or tetramethylsilane δ_{Si} 0.0). *J*-Values are given in Hz. GC-MS (EI) was measured with the direct combination of GC (Hewlett–Packard GC 5890 series II with a 25 m × 0.25 mm methyl silicone capillary column) and a JEOL JMS-AX-500 spectrometer with DA7000 data system.

Preparation and separation of the *cis*- and *trans*-**1** were performed according to the literature [8,9]. All other reagents were of commercial grade.

---

* Corresponding author. Fax: + 81-559-681155.

E-mail address: nishiyam@wing.ncc.u-tokai.ac.jp (K. Nishiyama).

PII: S0022-328X(01)00831-2

2.2. *Reaction of 9,10-dimethyl-9,10-dihydro-9,10-disilaanthracene (**1**) with alkyne*

A degassed mixture of *cis*-**1** (200 mg, 0.83 mmol) and 2-butyne (2 ml) in the presence of 10% palladium on carbon (300 mg) was stirred at room temperature (r.t.) for 72 h. After removal of the catalyst using a Celite pad, the concentrated reaction mixture was chromatographed on silica gel. Elution with hexane gave adduct **4** (25 mg, 10%) as a colorless powder, m.p. 218–219°C. ^{1}H-NMR δ 0.97 (s, 6H), 1.90 (s, 6H), 7.18 (m, 4H), 7.61 (m, 4H). ^{13}C-NMR δ -12.69, 16.64, 126.66, 130.77, 146.42, 151.39. ^{29}Si-NMR δ -33.3. HRMS m/z 292.1080 (M^+, Calc. for $C_{18}H_{20}Si_2$ 292.1104).

A similar treatment of the *cis*-**1** (200 mg, 0.83 mmol) with 3-hexyne (2 ml) afforded the adduct **5** (15 mg, 6%) as a colorless powder, m.p. 123–125°C. ^{1}H-NMR δ 0.87 (t, $J = 7$ Hz, 6H), 0.97 (s, 6H), 2.36 (q, $J = 7$Hz, 4H), 7.16 (m, 4H), 7.59 (m, 4H). ^{13}C-NMR δ -12.53, 14.95, 24.01, 126.51, 130.53, 146.59, 156.38. ^{29}Si-NMR δ -33.7. HRMS m/z 320.1398 (M^+, Calc. for $C_{20}H_{24}Si_2$ 320.1417).

2.3. *9,9′,10,10′-Dioxy-9,9′,10,10′-tetrahydro-9,9′,10,10′-tetramethyl-9,9′,10,10,-tetrasiladianthracene (**6**)*

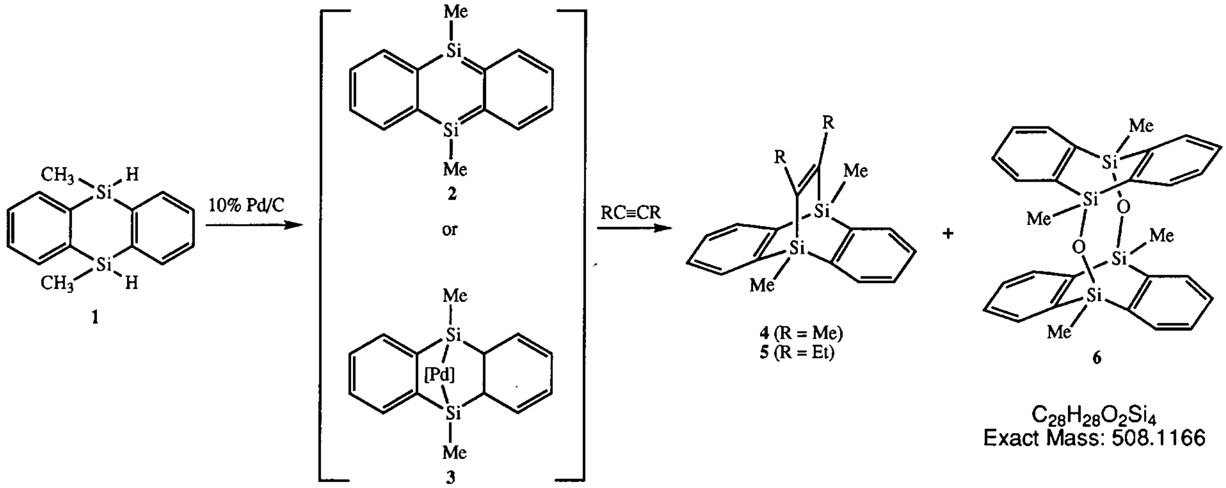
A *cis*/*trans* (44/56) mixture of **1** (260 mg, 1.08 mmol) and 10% palladium on carbon (260 mg) was stirred at r.t. for 24 h. After removal of the catalyst using a Celite pad, the concentrated reaction mixture was triturated with acetone to give a dimer **6** (10.0 mg, 8%) as a colorless powder, m.p. > 320°C. ^{1}H-NMR δ 0.67 (s, 12H), 7.11 (m, 8H), 7.44 (m, 8H). ^{13}C-NMR δ -2.90, 128.57, 132.98, 143.28. ^{29}Si-NMR δ -19.7. HRMS m/z 508.1143 (M^+, Calc. for $C_{28}H_{28}O_2Si_4$ 508.1166). The filtrate was concentrated and the residue was chromatographed on silica gel. Elution with hexane gave *trans*-**1** (120 mg, 46%).

3. Results and discussion

First of all, we carried out the flow thermolysis of a *cis*/*trans* (44/56) mixture of 9,10-dimethyl-9,10-dihydro-9,10-disilaanthracene (**1**) in the presence of various trapping reagents, since the thermal generation of the related 1,4-disilabenzene from the corresponding dihydro derivative was reported [7]. However, we were unable to isolate the products which would indicate the formation of the expected silaaromatics. Therefore, our attention was next denoted to the catalytic dehydrogenation reactions.

When a degassed mixture of the 9,10-dihydro-9,10-disilaanthracene (**1**) (*cis*/*trans* = 44/56) and 2-butyne in the presence of 10% palladium on carbon was stirred at r.t. for 72 h, the starting material was completely consumed and an adduct **4** was isolated from the complex reaction mixture in 4% yield along with a trace amount of a dimeric product **6**. Most of the product was polymeric material and could not be characterized. The adduct **4** can be explained as arising from the Diels–Alder reaction of the generated 9,10-dimethyl-9,10-disilaanthracene (**2**) with 2-butyne as shown in Scheme 1. Elevated temperatures or the use of solvent did not improve the yield of the adduct **4**. In the absence of 2-butyne, the dimer **6** was the only volatile and isolable product.

To investigate the difference in the reactivity between the *cis* and *trans* isomers, we examined the isolation of both isomers in pure form. The *trans*-**1** was obtained as colorless needles by repeated recrystallizations from ethanol, while the *cis*-**1** was isolated by the Corey's procedure [9]. Then, the palladium catalyzed dehydro-



Scheme 1.

genation reactions of both isomers were separately performed under the similar reaction conditions as described above. It was found that the formal Diels–Alder adduct **4** was obtained in 10% yield only from the *cis* isomer, indicating the elimination of the hydrogen atoms was a concerted process.

Further trapping of the intermediate **2** was accomplished by the reaction of the *cis*-**1** with 3-hexyne to give the corresponding [4 + 2] adduct **5** in 6% yield. The only trace amount of the adduct **5** was detected when the reaction was carried out with the *cis*/*trans* mixture of **1**.

For the formation of the adduct **4** or **5**, an alternative reaction pathway, the palladium catalyzed dehydrogenative double silylation of alkyne via a bis(silyl)palladium complex **3**, cannot be ruled out at the present stage. Because Tanaka and coworkers reported a similar reaction of alkynes with bis(hydrosilane) species in the presence of platinum complex catalysts to give disilacyclic compounds [10]. Although we tried to obtain the adduct **4** using various platinum catalysts, we could not ascertain the formation of the adduct.

Finally, we also carried out the copyrolysis of the adduct **4** with methanol or 3-hexyne, however, any expected trapping products could not be detected in the reaction mixture. Further investigations on the generation of 9,10-disilaanthracene are currently under way.

References

[1] (a) G. Rabbe, J. Michl, Chem. Rev. 85 (1985) 419;
(b) G Rabbe, J. Michl, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Organosilicon Compounds, Wiley, New York, 1989, pp. 1102–1108;
(c) A.G. Brook, M.A. Brook, Adv. Organomet. Chem. 39 (1996) 71.

[2] (a) K. Wakita, N. Tokitoh, R. Okazaki, S. Nagase, Angew. Chem. Int. Ed. Engl. 39 (2000) 634;
(b) K. Wakita, N. Tokitoh, R. Okazaki, N. Takagi, S. Nagase, J. Am. Chem. Soc. 122 (2000) 5648;
(c) N. Tokitoh, K. Wakita, R. Okazaki, S. Nagase, P.v.R. Schleyer, H. Jiao, J. Am. Chem. Soc. 119 (1997) 6951.

[3] (a) M. Oba, K. Nishiyama, J. Chem. Soc. Chem. Commun. (1994) 1703;
(b) T. Gimisis, M. Ballestri, C. Ferreri, C. Chatgilialoglu, Tetrahedron Lett. 36 (1995) 3897;
(c) M. Oba, Y. Kawahara, R. Yamada, H. Mizuta, K. Nishiyama, J. Chem. Soc. Perkin Trans. 2 (1996) 1843;
(d) S. Kyushin, T. Shinnai, T. Kubota, H. Matsumoto, Organometallics 16 (1997) 3800;
(e) K. Nishiyama, M. Oba, H. Takagi, T. Saito, Y. Imai, I. Motoyama, S. Ikuta, H. Hiratsuka, J. Organomet. Chem. 626 (2001) 32.

[4] (a) W. Ando, K. Hatano, R. Urisaka, Organometallics 14 (1995) 3625;
(b) K. Hatano, K. Morihashi, O. Kikuchi, W. Ando, Chem. Lett. (1997) 293.

[5] (a) Y. van den Winkel, B.L.M. van Baar, F. Bickelhaupt, W. Kulik, C. Sierakowski, G. Maier, Chem. Ber. 185 (1991) 124;
(b) H. Hiratsuka, M. Tanaka, T. Okutsu, M. Oba, K. Nishiyama, J. Chem. Soc. Chem. Commun. (1995) 215;
(c) K. Nishiyama, M. Oba, H. Takagi, I. Fujii, N. Hirayama, N.H. Horiuchi, T. Okutsu, H. Hiratsuka, J. Organomet. Chem. 604 (2000) 20;
(d) H. Hiratsuka, M. Tanaka, N.H. Horiuchi, T. Yoshinaga, M. Oba, K. Nishiyama, J. Organomet. Chem. 611 (2000) 71.

[6] (a) J.D. Rich, R. West, J. Am. Chem. Soc. 104 (1982) 6884;
(b) G. Maier, K. Shottler, H.P. Reisenauer, Tetrahedron Lett. 26 (1985) 4079.

[7] K.M. Welsh, J.D. Rich, R. West, J. Organomet. Chem. 325 (1987) 105.

[8] (a) J.Y. Corey, W.Z. McCarthy, J. Organomet. Chem. 271 (1984) 319;
(b) W.Z. McCarthy, J.Y. Corey, E.R. Corey, Organometallics 3 (1984) 255.

[9] K.M. Welsh, J.Y. Corey, Organometallics 6 (1987) 1393.

[10] (a) M. Tanaka, Y. Uchimaru, H.-J. Lautenschlager, Organometallics 10 (1991) 16;
(b) M. Tanaka, Y. Uchimaru, Bull. Soc. Chim. Fr. 129 (1992) 667.