New Examples of 1,6- and 1,7-Hydrogen Transfer Promoted by an α-Silyl Group in Rhodium(I)-Catalyzed Radical Reactions of Acyclic Enediynes

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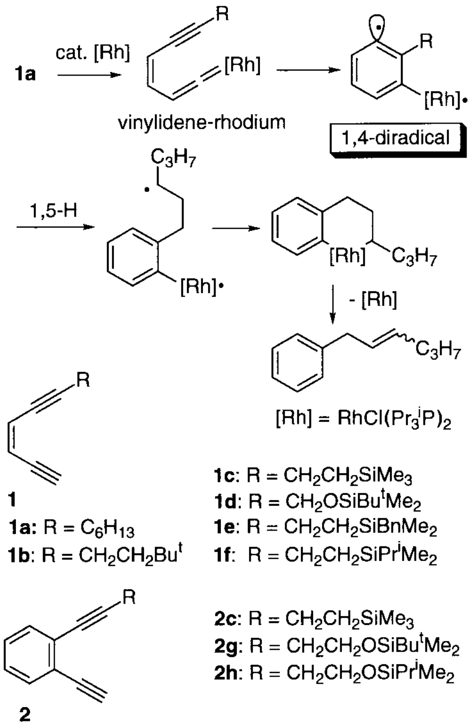
Summary: A rhodium(I) catalyst triggers cycloaromatization of ω-trialkylsilylated acyclic enediynes to afford benzosilacycloalkane or vinylsilane products via 1,6- and/or 1,7-hydrogen transfer, presumably effected by radical stabilization by an α-silyl moiety and via a seven- and/or eight-membered rhodacycle intermediate. The addition of a catalytic amount of dimethyl maleate is essential to obtain better yields of the products.

It is well-known that a carbanion located α to the silicon atom is stabilized, and hence, the deprotonation of a C−H bond α to a silyl group is a very useful and important process.[1] Similarly, a carbocation located β to a silicon atom is stabilized by $\sigma-\pi$ hyperconjugation between the C−Si σ-bond and a cation center.[2] This interaction is responsible for the regioselective addition of an electrophile to vinylic and allylic silanes, which leads to a carbocation β to the silicon atom.[3] Analogously, much attention has been paid to radical species located α and β to a silicon atom to clarify the question of their respective stabilities. The β-stabilization of a silyl moiety is understood,[4] while the extent of α-stabilization is ambiguous and remains an open question.[5,6] Because of the increasing usefulness of radical reactions in organic synthesis,[7,8] it is of importance to make use of the stabilizing effect of a silyl moiety on a radical center.

Recently, we reported a rhodium(I)-catalyzed reaction of an acyclic enediyne (**1**) via Saito-Myers[9] type cycloaromatization of a vinylidene−rhodium intermediate (Scheme 1).[10] In this reaction, the 1,4-organorhodium diradical intermediate, like an α,3-didehydrotoluene,[11] can act as the active species. As shown in Scheme 1, (Z)-1,5-dodecadiyn-3-ene (**1a**) afforded 1-phenylhex-2-ene via 1,5-hydrogen transfer and a rhodacyclohexane intermediate. During our work on cycloaromatization

Scheme 1



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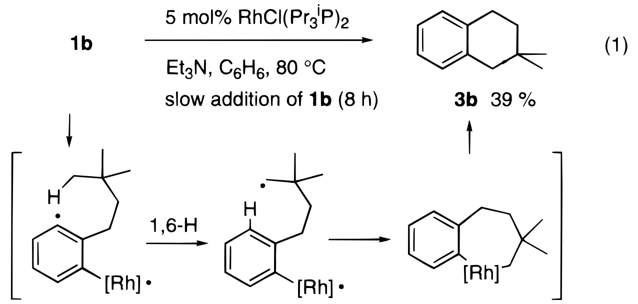
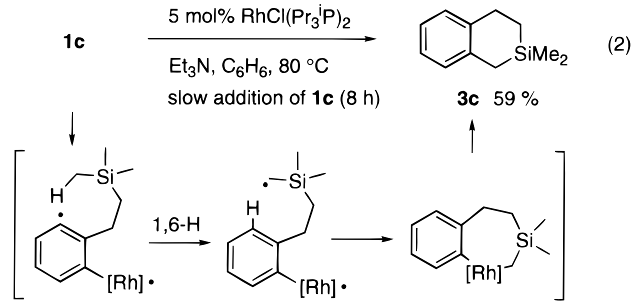
of various acyclic enediynes, we found a new catalytic process involving a 1,*n*-hydrogen transfer ($n = 6, 7$) and subsequent reductive coupling. Although several reports of 1,6-transfer have been published,[12] the example of 1,7-transfer is extremely rare to the best of our knowledge.[13] We report herein the Rh(I)-catalyst-triggered cycloaromatization of ω-trialkylsilylated acyclic enediynes followed by 1,6- and 1,7-hydrogen transfer, leading to six- and seven-membered ring products or vinylsilanes.

The reaction of 9,9-dimethyl-1,5-decadiyn-3-ene (**1b**) using a slow addition technique afforded 2,2-dimethyltetralin (**3b**) in 39% yield under catalytic conditions involving Et_3N and 5 mol % $[RhCl(Pr_3{}^iP)_2]$[14] at 80 °C (eq 1). This result shows that the starting enediyne,



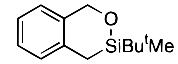
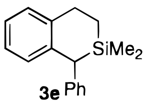
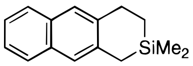
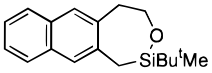
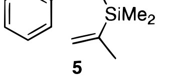
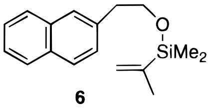
which has no hydrogen capable of transferring in the 1,5-manner, undergoes catalytic cycloaromatization. As shown in eq 1, the formation of **3b** can be rationalized by assuming that the 1,4-organorhodium diradical undergoes 1,6-hydrogen transfer from the *tert*-butyl group to give a 1,7-diradical intermediate. The latter forms a rhodacycloheptane, which undergoes subsequent reductive elimination.[15]

This catalytic reaction also was applied to the enediynes (**1c**–**f** and **2c**,**g**,**h**) bearing an ω-trialkylsilyl group, which is more easily available than a *tert*-alkyl group. Under identical conditions, the reaction of **1c** gave 2,2-dimethyl-2-silatetralin (**3c**) in 59% isolated yield (eq 2). In comparison with these reactions, the

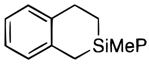


higher yield of **3c** might be attributed to the 1,6-hydrogen transfer facilitated by radical stabilization by the silyl group. Recently, Malacria and co-workers reported that an α-silyl group promotes 1,6-transfer from a methyl group on a silicon to the σ-radical.[12e]

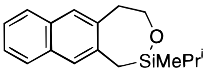
Table 1. Formation of Silacycloalkane and Vinylsilane via 1,6- and 1,7-Hydrogen Transfer

entry	enediyne	products	yield[a] (%)
1	**1c**	**3c**	71
2	**1d**	 **3d**	31 (36)[b]
3	**1e**	 **3e**	0 (51)
4	**2c**	 **4c**	48
5	**2g**	 **4g**	55 (21)
6	**1f**	 **5**	69[c]
7	**2h**	 **6**	42[d](21)

[a] Isolated yields; numbers in parentheses indicate the yield of starting material recovered. [b] The ratio between the starting material and the product was determined by ^1H NMR. [c] **3f** (5%) was also produced. [d] **4h** (4%) was also produced.



3f



4h

Further work showed that the addition of a catalytic amount of dimethyl maleate (DMM) as a π-acid is effective in the formation of silacycloalkanes. In the reaction of **1c**, the addition of DMM (25 mol % to **1c**) increased the yield of **3c** to 71%.[16] The results using other enediynes under optimum conditions are listed in Table 1. The silyl ether **1d** also gave the corresponding **3d** in 31% yield (entry 2). The reaction of **1e** also was carried out, but the expected product **3e** was not obtained and **1e** was recovered (51%) (entry 3). The

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(12) 1,6-Transfer: (a) Wagner, P. J.; Chiu, C. *J. Am. Chem. Soc.* **1979**, *101*, 7134. (b) Aoyama, H.; Arata, Y.; Omote, Y. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1165. (c) Yamazaki, N.; Eichenberger, E.; Curran, D. P. *Tetrahedron Lett.* **1994**, *35*, 6623. (d) Curran, D. P.; Xu, J. *J. Am. Chem. Soc.* **1996**, *118*, 3142. (e) Bogen, S.; Fensterbank, L.; Malacria, M. *J. Am. Chem. Soc.* **1997**, *119*, 5037.

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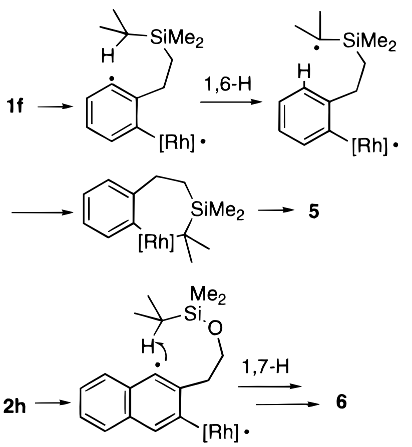
(15) Even in the absence of Et_3N, **3b** was obtained in 27% yield. We have proposed that Et_3N is required for the rapid conversion of the acetylene terminus to the vinylidene–rhodium group; otherwise there is undesired oligomerization of the enediyne.[10]

(16) Typical procedure: In a flame-dried 10 mL two-necked flask was placed $[RhCl(C_8H_{14})_2]_2$ (7.2 mg, 0.01 mmol) under argon. C_6H_6 (1 mL) and $Pr_3{}^iP$ (10 μL, 0.05 mmol) were successively added into the vessel by syringe, and the mixture was stirred at room temperature for 0.5 h. To the solution were added Et_3N (70 μL, 0.5 mmol) and DMM (14.4 mg, 0.1 mmol), and then the mixture was heated to 80 °C. To the stirred solution was added a solution of **1c** (70 mg, 0.4 mmol) in C_6H_6 (2 mL) at 80 °C over a period of 8 h, using a syringe pump. Filtration through Florisil and further purification by column chromatography using hexane as an eluent gave 51 mg (0.29 mmol, 71%) of **3c**: ^1H NMR (270 MHz, $CDCl_3$) δ 7.0–7.1 (m, 4H), 2.71–2.76 (m, 2H), 1.96 (s, 2H), 0.71–0.77 (m, 2H), 0.04 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 141.7, 138.3, 129.5, 127.8, 126.2, 124.8, 29.6, 20.8, 11.6, −2.0; HRMS for $C_{11}H_{16}Si$ (M^+) calcd 176.1021, found 176.1018.

reaction of **2c** resulted in the formation of 1,3,4-trihydro-2,2-dimethyl-2-silaanthracene (**4c**) in 48% yield (entry 4). Surprisingly, the reaction of **2g** gave the seven-membered-ring product **4g** in 55% yield (entry 5). The formation of **4g** suggests that 1,7-hydrogen transfer from the methyl group of the *t*-BuMe$_2$Si group occurred to give a rhodacyclooctane intermediate en route to the product. A theoretical study of 1,6- and 1,7-hydrogen transfer from an sp^3 carbon to a σ-radical has not been reported thus far, but these processes have been assumed to be favored.[17] Thus, the anticipated lower activation energies of 1,6- and 1,7-transfer and the stabilizing effect of the silicon α to a radical center can compensate for the activation entropies in larger cyclic transition states for hydrogen transfer and facilitate the catalytic reaction. The addition of DMM is essential to obtain higher yields of silacycloalkanes. These results strongly support our assumption that the rhodacycle intermediate intervenes in the present reaction and that DMM facilitates the reductive elimination[18] leading to the silacycloalkanes.

Scheme 2



We also examined a similar catalytic reaction of **1f**. The product was not the silacycloalkane; rather, the vinylsilane **5** was obtained in 69% yield (entry 6). Interestingly, the reaction of **2h** gave the vinylsilane **6** (42%), which is produced via 1,7-hydrogen transfer (entry 7). This vinylsilane formation also supports the presence of the rhodacycle intermediate produced by 1,6- and/or 1,7-hydrogen transfer from the *i*-Pr group (Scheme 2). Although the extent of the stabilization of a carbon radical with an α-silicon atom is ambiguous,[5,6] compared with β-stabilization,[4] the silacycloalkane formation, i.e., **3d** and **4g**, suggests the preferred formation of α- vs β-silyl radicals.

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Supporting Information Available: Text giving synthesis details and characterization data for ω-(trialkylsilyl)-alkylacetylenes and **1b**−**f**, **2c**,**g**,**h**, **3b**−**f**, **4c**,**g**,**h**, **5**, and **6** and figures giving ^{1}H NMR and ^{13}C NMR spectra (26 pages). Ordering information is given on any current masthead page.

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(17) The theoretical study on the radical reaction of aliphatic chains shows that activation enthalpies calculated for 1,5-, 1,6-, and 1,7-hydrogen transfer from a methyl group to an sp^3-carbon-centered radical are 20.9, 21.0, and 23.0 kcal mol^{-1}, respectively; see: Dorigo, A. E.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 2195. Huang, X. L.; Dannenberg, J. J. *J. Org. Chem.* **1991**, *56*, 5421.

(18) Some π-acids accelerate the reductive elimination of some 16-electron organopalladium species, providing C−C bonds: Kurosawa, H.; Emoto, M.; Ohnishi, H.; Miki, K.; Kasai, N.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1987**, *109*, 6333.