Cationic Palladium Complex-catalyzed Cyclization–Hydrosilylation of 1-Alkene-6,11-diyne Derivatives: Facile Cyclization at the Enyne Part than at the Diyne Counterpart

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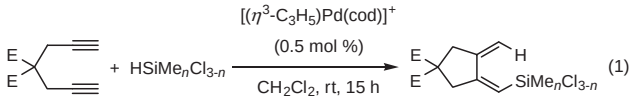
A palladium complex, $[(\eta^3\text{-}C_3H_5)Pd(cod)]^+[PF_6]^-$ (**C**), catalyzes hydrosilylation of 1-dodecene-6,11-diyne (**5**) or 1-tridecene-6,11-diyne (**7**), and of their 9-oxo congeners (**9** or **11**), with $HSiCl_3$ to form regioisomeric cyclization products (**6**, **8**, **10**, and **12**, respectively), which arise between the diyne part (path a) to form **A** series or between the enyne counterpart (path b) to form **B** series. The formation of product **B** is markedly favored with 1-tridecene-6,11-diyne derivatives as compared with 1-dodecene-6,11-diyne ones that possess a terminal alkyne.

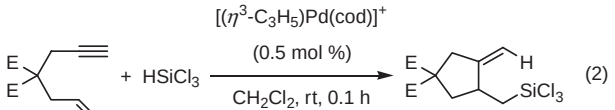
We have reported that a cationic palladium complex, $[(\eta^3\text{-}C_3H_5)Pd(cod)]^+[PF_6]^-$ (**C**) (cod = 1,5-cyclooctadiene), catalyzes the cyclization–hydrosilylation of 1,6-alkadiyne, typically dimethyl dipropargylmalonate (**1**), with $HSiCl_3$, under mild conditions to afford (*Z*)-1-methylene-2-(trichlorosilyl)methylene-4,4-bis(methoxycarbonyl)cyclopentane (**2**) in 80% yield (eq 1).[1,2] It was also found that $HSiMe_nCl_{3-n}$ (n = 0–2) can equally be employed for the reaction to give the corresponding products in comparable yields.



(1)

1 (E = CO_2Me) (n = 0,1, 2) **2** (n = 0) (80%)

The protocol of the Pd complex **C**-catalyzed hydrosilylation is equally applicable to some 1,6-alkenynes. It is especially worthy to note that the cyclization–hydrosilylation of diethyl allylpropargylmalonate (**3**) proceeded much faster than that of **1** under standard conditions for a few minutes to form the corresponding product **4** in 95% yield (eq 2).[3] On this line of research, we have recently found that an intriguing hydrosilylative cross-coupling of 1-alkynes with 1-alkenes can also be catalyzed by the Pd complex **C**, an intermolecular version of the cyclization–hydrosilylation of 1,6-alkenynes as mentioned above.[4]



(2)

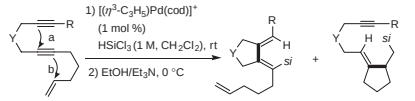
3 (E = CO_2Et) **4** (95%)

We wish to demonstrate herein that even more intriguing reactivity pattern was observed in a typical reaction of 1-dodecene-6,11-diyne (**5**) to afford two cyclization–hydrosilylaiton products indicative of a competitive five-membered ring formation either at the diyne moiety (path a) or at the enyne counterpart (path b), respectively, as depicted in Table 1. Thus, the Pd complex **C**-catalyzed hydrosilylation of **5** using $HSiCl_3$ (1 equiv.) was carried out at room temperature for 4 h to form two products, **6A** and **6B**,[5] the latter being predominating in up to **A**/**B** = 23/77, though the combined yield as triethoxysilyl derivatives was rather poor (35%) (Table 1, Entry 1). In this reaction, although intramolecular carbopalladation by path a followed by the second carbopalladation by path b was conceptually possible, such a domino cyclization did not take place. The reaction of homologous 1-tridecene-6,11-diyne (**7**) under essentially the same conditions as above revealed that both combined yield of cyclization products (73%, **8A** and **8B**)[6] and regioselectivity of **A**/**B** = 8/92 were found to be much enhanced (Entry 2).[7] Furthermore, the Pd complex **C**-catalyzed reaction of **7** with $HSiMeCl_2$, instead of $HSiCl_3$, required longer reaction time to proceed, affording cyclization products (**8A′** and **8B′**)[8] in up to 42% combined yield, while high regioselectivity for **A**/**B** was maintained (Entry 3). These results, contrary to our sense, clearly indicate that path b predominates over path a.

In order to elucidate further trend, if any, of the observed competitive cyclization of 1-alkene-6,11-diyne systems, we have also examined the cationic Pd complex **C**-catalyzed cyclization–hydrosilylation of two 9-oxa-1-alkene-6,11-diyne congeners and all results obtained are also given in Table 1. Thus, 9-oxa-1-dodecene-6,11-diyne (**9**) was subjected to the present reaction. After prolonged reaction using $HSiCl_3$ followed by ethoxylation, there obtained cyclization–hydrosilylation products (**10A** and **10B**)[9] in a ratio 25:75 in moderate 44% combined yield (Table 1, Entry 4). This **A**:**B** ratio coincides with that obtained for the reaction of the corresponding hydrocarbon **5** (Entry 1).

In the reaction of **9** using $HSiMeCl_2$, the reactivity pattern became exceptional, **A**/**B** = 82/18 (Entry 5), while the combined yield diminished only to 16% due mainly to facile dime-

Table 1. Competitive cyclization–hydrosilylation of 1-en-6,11-diyne systems catalyzed by cationic Pd complex **C**



5: Y = CH_2; R = H
7: Y = CH_2; R = Me
9: Y = O; R = H
11: Y = O; R = Me

6A: R = H
8A: R = Me
10A: R = H
12A: R = Me

6B: R = H
8B: R = Me
10B: R = H
12B: R = Me

Entry	Compd.	$HSiX_3$	Time/h	Yield/%[a]	Composition[b] A:B
1	5	$HSiCl_3$	4	35	23:77
2	7	$HSiCl_3$	6	73	8:92
3	7	$HSiMeCl_2$	19	42	9:91
4	9	$HSiCl_3$	24	44	25:75
5	9	$HSiMeCl_2$	24[c]	16	82:18
6	11	$HSiCl_3$	1.5	51	11:89
7	11	$HSiMeCl_2$	3.5	43	22:78

[a]Isolated as ethoxy derivatives, not optimized.
[b]Peak area ratio by GLC. [c]At 50 °C.

rization at the terminal alkyne.[10] In addition, the cyclization–hydrosilylation of 9-oxa-1-tridecene-6,11-diyne (**11**) using $HSiCl_3$ was also examined (Entry 6), giving rise to both enhanced combined yield (51%, **12A** and **12B**)[11] and regioselectivity (**A**/**B** = 11/89). This reactivity pattern may essentially be comparable to that found in Entry 2. It is evident that introducing a methyl substituent on the terminal alkyne carbon as in both **7** and **11** must play a crucial role to suppress any dimerization otherwise easily proceed.

Finally, the trend found in Entry 6 seems to be applicable to Entry 7 (43%, **12A′** and **12B′**).[12]

In conclusion, our results presented here clearly show that the Pd complex **C**-catalyzed cyclization–hydrosilylation of 1-alkene-6,11-diyne (**7** or **11**) with $HSiCl_3$ reacts at the enyne part (path b) to form **B** faster, at most, by a factor of 8–11 than at the diyne counterpart (path a) to form **A**. To the best of our knowledge, in the metal-catalyzed addition reactions, it may be widely accepted that, regardless of either terminal or internal alkynes, they become activated by means of stronger coordination to the catalyst metal than alkenes. However, our results must be explained by the fact that the Pd-catalyzed hydrosilylation of the enyne part of 1-alkene-6,11-diyne system as well as 1,6-alkenyne with best $HSiCl_3$ might well proceed via an initial alkyne hydropalladation, if any reversible,[13] followed by a fast and selective carbopalladation with an alkene part (path b) to form a cyclic intermediate, which eventually gives rise to the preferred cyclization–hydrosilylation product **B** and regenerates an active HPd catalyst.

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References and Notes

1 T. Uno, S. Wakayanagi, Y. Sonoda, K. Yamamoto, *Synlett* **2003**, 1997.

2 For closely related cyclization–hydrosilylation of 1,6-alkadiynes with $HSiR_3$ catalyzed by a cationic Pt complex, see: X. Wang, H. Chakrapani, J. W. Madine, M. A. Keyerleber, R. A. Widenhoefer, *J. Org. Chem.* **2002**, *67*, 2778, and references therein; For Ni(0)-catalyzed reaction using $HSiR_3$, see: K. Tamao, K. Kobayashi, Y. Ito, *J. Am. Chem. Soc.* **1989**, *111*, 6478; K. Tamao, K. Kobayashi, Y. Ito, *Synlett* **1992**, 539; Also, for the preceding Rh-catalyzed silylative cyclization of 1,6-heptadiynes with $HSiR_3$, see: T. Muraoka, I. Matsuda, K. Itoh, *Organometallics* **2002**, *21*, 3650; T. Muraoka, I. Matsuda, K. Itoh, *Tetrahedron Lett.* **1998**, *39*, 7325; I. Ojima, A. T. Vu, J. V. McCullagh, A. Kinoshita, *J. Am. Chem. Soc.* **1999**, *121*, 3230; I. Ojima, S.-Y. Lee, *J. Am. Chem. Soc.* **2000**, *122*, 2385; For a related work, see: C. Liu, R. A. Widenhoefer, *Organometallics* **2002**, *21*, 5666.

3 S. Wakayanagi, T. Shimamoto, M. Chimori, K. Yamamoto, *Chem. Lett.* **2005**, *34*, 160.

4 T. Shimamoto, M. Chimori, H. Sogawa, K. Yamamoto, *J. Am. Chem. Soc.* **2005**, *127*, 16410.

5 NMR data for **6B** ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.53 (dd, J = 15.2, 10.9 Hz, 1H), 1.05 (dd, J = 15.2, 4.0 Hz, 1H), 1.23 (t, J = 6.9 Hz, 9H), 1.4–1.8 (m, 4H), 1.59 (quint, J = 7.3 Hz, 2H), 1.94 (t, J = 2.6 Hz, 1H), 2.09 (qd, J = 7.3, 1.3 Hz, 2H), 2.1–2.4 (m, 3H), 2.18 (td, J = 7.3, 2.6 Hz, 2H), 3.83 (q, J = 6.9 Hz, 6H), 5.13 (tq, J = 7.3, 2.3 Hz, 1H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 15.0, 18.2, 18.3 (×3), 23.9, 28.3, 28.5, 28.6, 35.3, 39.2, 58.3 (×3), 68.1, 84.8, 114.2, 149.6.

6 **8B** ^{1}H NMR: δ 0.52 (dd, J = 15.2, 10.6 Hz, 1H), 1.05 (dd, J = 15.2, 3.6 Hz, 1H), 1.23 (t, J = 6.9 Hz, 9H), 1.4–1.8 (m, 4H), 1.53 (quint, J = 7.3 Hz, 2H), 1.78 (t, J = 2.4 Hz, 3H), 1.9–2.4 (m, 3H), 2.06 (brq, J = 7.3 Hz, 2H), 2.13 (tq, J = 7.3, 2.4 Hz, 2H), 3.82 (q, J = 6.9 Hz, 6H), 5.14 (tq, J = 7.3, 2.3 Hz, 1H). ^{13}C NMR: δ 3.5, 15.0, 18.28 (×3), 18.29, 23.9, 28.5, 28.6, 29.1, 35.3, 39.2, 58.3 (×3), 75.4, 79.4, 118.3, 149.3.

7 Typical procedure: In a 10 mL screw-capped test tube with a stirring bar was placed a mixture of **7** (349 mg, 2 mmol) dissolved in dry CH_2Cl_2 (2 mL), $HSiCl_3$ (1 M, CH_2Cl_2, 2 mL), and the catalyst **C** (8 mg, 1 mol %), under an argon atmosphere, and the mixture was stirred at ambient temperature for 6 h. The reaction mixture was analyzed by GLC to determine the regioisomer ratio. Then, the reaction mixture was either directly subjected to a bulb-to-bulb distillation in vacuo or immediately treated with excess dry ethanol and triethylamine in CH_2Cl_2 at 0 °C, and the two products were obtained in 73% combined yield as triethoxysilyl derivatives (**8A** and **8B**) after a usual work up (Table 1, Entry 2). The regioisomers were isolated by a careful bulb-to-bulb distillation. Anal. (**8B**) Calcd for $C_{19}H_{34}O_3Si$: C, 67.40; H, 10.12%. Found: C, 67.15; H, 9.93%.

8 **8B′** ^{1}H NMR: δ 0.15 (s, 3H), 0.54 (dd, J = 15.2, 10.6 Hz, 1H), 1.05 (dd, J = 15.2, 4.0 Hz, 1H), 1.22 (t, J = 6.9 Hz, 6H), 1.4–2.0 (m, 4H), 1.53 (quint, J = 7.3 Hz, 2H), 1.78 (t, J = 2.6 Hz, 3H), 2.06 (brq, J = 7.6 Hz, 2H), 2.11 (tq, J = 7.1, 2.6 Hz, 2H), 2.2–2.4 (m, 3H), 3.77 (q, J = 6.9 Hz, 4H), 5.13 (tq, J = 6.9, 2.3 Hz, 1H). ^{13}C NMR: δ −3.8, 3.5, 18.3 (×2), 18.4, 18.5, 24.0, 28.5, 28.5$_5$, 29.1, 35.3, 39.3, 58.0 (×2), 75.4, 79.4, 118.3, 149.3.

9 NMR spectral data of **10A** and **10B** have been given in Ref. 3 (Also, see Supporting Information).

10 Y. Kawanami K. Yamamoto, *Synlett* **1995**, 1232; Also, see: T. Sonoda, M. S. Thesis, Tokyo University of Science, Yamaguchi, **2003**.

11 **12B** ^{1}H NMR: δ 0.56 (dd, J = 15.2, 10.9 Hz, 1H), 1.08 (dd, J = 15.2, 3.6 Hz, 1H), 1.22 (t, J = 6.9 Hz, 9H), 1.7–2.5 (m, 7H), 1.86 (t, J = 2.3 Hz, 3H), 3.82 (q, J = 6.9 Hz, 6H), 4.04 (brd, J = 6.9 Hz, 2H), 4.08 (q, J = 2.3 Hz), 5.37 (tq, J = 6.9, 2.4 Hz, 1H). ^{13}C NMR: δ 3.6, 14.7, 18.4 (×3), 23.9, 28.7, 34.8, 39.6, 57.5, 58.3 (×3), 67.5, 75.5, 82.1, 115.1, 154.2.

12 **12A′** ^{1}H NMR: δ 0.25 (s, 3H), 1.22 (t, J = 6.9 Hz, 6H), 1.45 (quint, J = 7.6 Hz, 2H), 1.66 (d, J = 5.9 Hz, 3H), 2.05–2.20 (m, 4H), 3.80 (q, J = 6.9 Hz, 4H), 4.45 (t, J = 2.0 Hz, 2H), 4.57 (s, 2H), 4.95 (dq, J = 10.2, 2.0 Hz, 1H), 5.01 (dq, J = 16.2, 2.0 Hz, 1H), 5.12 (brq, J = 6 Hz, 1H), 5.81 (ddt, J = 16.2, 10.2, 6.6 Hz, 1H). **12B′** ^{1}H NMR: δ 0.15 (s, 3H), 0.57 (dd, J = 14.8, 10.9 Hz, 1H), 1.07 (dd, J = 14.8, 3.6 Hz, 1H), 1.22 (t, J = 7.1 Hz, 6H), 1.4–1.8 (m, 4H), 1.86 (t, J = 2.3 Hz, 3H), 1.95–2.05 (m, 1H), 2.2–2.4 (m, 2H), 3.76 (q, J = 7.1 Hz, 4H), 4.05 (dd, J = 6.9, 1.3 Hz, 2H), 4.08 (q, J = 2.3 Hz, 2H), 5.37 (dq, J = 6.9, 2.6 Hz, 1H).

13 Reversibility of the hydropalladation in Pd-catalyzed cyclization–hydrosilylation of alkadiynes has not been established. However, *reversible* silylpalladation in the case of alkadienes under similar reaction conditions are discussed: X. Wang, H. Chakrapani, C. N. Stengone, R. A. Widenhoefer, *J. Org. Chem.* **2001**, *66*, 1755.

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