Cationic Palladium Complex-catalyzed Cyclization–Hydrosilylation of Alkadiynes and Enynes

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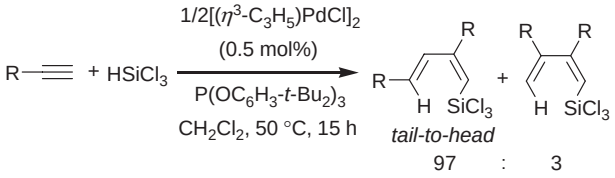
A cationic π-allylpalladium complex, $[(\eta^3\text{-}C_3H_5)Pd(cod)]^+[PF_6]^-$, catalyzes hydrosilylation of 1,6-heptadiyne derivatives to form 1-methylene-2-(silylmethylene) cyclopentanes, $HSiMe_nCl_{3-n}$ ($n = 0$–2) being equally applicable to this cyclization–hydrosilylation. Certain 1,6-enynes react faster than 1,6-diynes under same reaction conditions, and 9-oxa-1-dodecene-6,11-diyne undergoes competitive cyclization–hydrosilylation at either diyne or enyne moiety, indicative of an unexpectedly high-reactive ene counterpart.

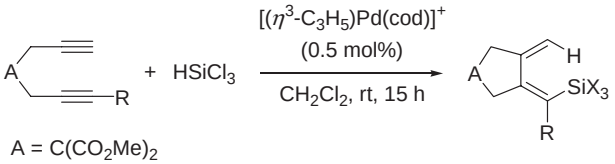
We have reported that a selective dimerization–hydrosilylation of a variety of 1-alkynes with trichlorosilane takes place under the catalysis of $1/2[(\eta^3\text{-}C_3H_5)PdCl]_2$ (**A**) with two equivalents of a bulky phosphite, typically tris(2,4-di-*t*-butylphenyl) phosphite in dichloromethane solution (Scheme 1).[1]



Scheme 1.

It was found that the above catalyst system was not satisfactorily effective to the intramolecular reaction of α,ω-alkadiynes, which may well undergo cyclization–hydrosilylation, and, in fact, an attempted reaction of dimethyl dipropargylmalonate (**1**) under similar conditions as above resulted in giving both cyclization and dimerized hydrosilylation products.[2]

We have recently found that a cationic palladium complex, $[(\eta^3\text{-}C_3H_5)Pd(cod)]^+[PF_6]^-$ (**B**) (cod = cyclooctadiene), catalyzes the cyclization–hydrosilylation of **1** with $HSiCl_3$, even at room temperature for 15 h, to afford (*Z*)-1-methylene-2-(trichlorosilyl)methylene-4,4-bis(methoxycarbonyl)cyclopentane (**2a**), but isolated as a more stable triethoxy derivative (**2b**) in 56% yield (Scheme 2). Thus, no phosphorus ligand was required for the catalyst **B**. It was also found that $HSiMe_nCl_{3-n}$ ($n = 0$–2) can be equally employed for the cyclization–hydrosilylation to give the corresponding products in comparable yields.

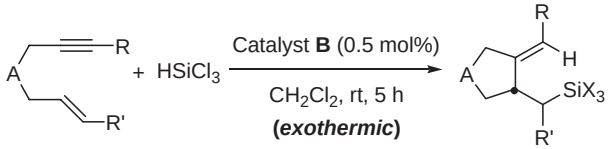


Scheme 2.

The palladium complex **B**-catalyzed hydrosilylation of dimethyl (2-butynyl)propargylmalonate (**3**) was also carried out. Thus, cyclization–hydrosilylation of **3** took place cleanly using $HSiCl_3$ to afford (*Z*)-1-methylene-2-(1-trichlorosilylethylidene)-4,4-bis(methoxycarbonyl)cyclopentane (**4a**), whose structure was identified as its triethoxy derivative (**4b**), obtained in 53% yield, by ^{1}H NMR spectrum (Scheme 2).

Dipropargyl ether (**5**) or unsymmetrical 2-butynyl propargyl ether (**7**) underwent cyclization-hydrosilylation with $HSiCl_3$ in the same manner as **1** to give the corresponding 1,2-dimethylene-cyclopentane **6b** (33% yield) and **8b** (40% yield), respectively. There remained some intractable residue by distillation. The fact that the silyl substituent is exclusively introduced into the internal alkyne site in substrates **3** and **7** clearly indicates that the hydropalladation takes place first at the terminal alkyne site, giving rise to form **4b** and **8b**, respectively (see also Scheme 2).[3,4]

Now, we wish to report that the protocol of the cationic complex **B**-catalyzed reaction is equally applicable to some alkenynes. It is worthy to note that the cyclization-hydrosilylation of both 4,4-bis(ethoxycarbonyl)-1-hepten-6-yne (**9**) and (*E*)-5-oxa-2-nonen-7-yne (**11**) proceeded faster than that of **1** or **3** under standard conditions for 5 h (Scheme 3). An attempted addition of (*S*)-MeO-MOP (1 equiv.)[5] to complex **B**, however, did not induce any optical activity in **10b**,[6] though the reaction rate was apparently enhanced, the yield of **10b** being even higher (in 3.5 h, 90%). Compound **12b**[7] was also obtained in 74% combined yield as a 4:1 diastereoisomer mixture.[7]



Scheme 3.

Even more intriguing reactivity pattern was observed in the reaction of 9-oxa-1-dodecene-6,11-diyne (**13**) as depicted in Scheme 4. Namely, using $HSiCl_3$, there formed two cyclization products, **14**[8] and **15**,[9] the latter being predominating in up to 75%, with 46% combined yield, while $HSiMeCl_2$ afforded mainly the expected product **14** analog, though the combined yield was rather poor (40%).[10]

At present, it is difficult to explain the reason why an anomalous cyclization product **15** predominates over the expected **14** only by using $HSiCl_3$. The fact that the alkene moiety partici-

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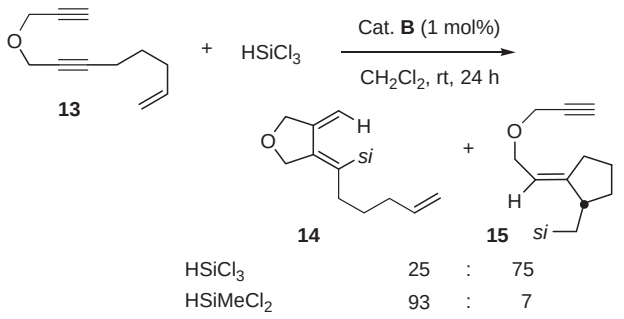
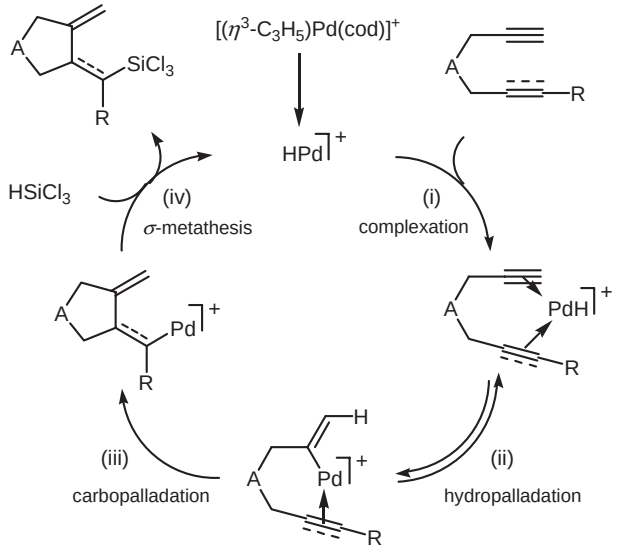


Scheme 4.

pates as easily as the alkyne counterpart in the carbopalladation to undergo cyclization is exemplified in the case of substrates **9** and **11** under the conditions shown in Scheme 3.

Furthermore, the formation of an anomalous product **15**, which must proceed with the terminal alkyne moiety *intact* during the cyclization–hydrosilylation of the particular endiyne **13** with $HSiCl_3$, very likely suggests that the reaction involves an initial *reversible* hydropalladation[11] step in the plausible catalytic cycle.

Thus, the cyclization–hydrosilylation of either alkadiynes or alkenynes may well proceed as follows (Scheme 5): Following (i) complexation, (ii) probably *reversible* hydropalladation, and (iii) intramolecular carbopalladation (presumably easy for the alkene moiety), the cyclized (*Z*)-alkenylpalladium (or the chiral alkylpalladium) intermediate is formed, and finally undergoes (iv) a possible σ-metathesis with a hydrosilane[12] to give the silylated product, regenerating the cationic catalyst. Further examination of the *intermolecular* cross reaction of alkynes with alkenes under similar conditions will be reported elsewhere in due course.



Scheme 5. Other ligands on palladium are omitted for clarity.

In conclusion, we have found that a cationic palladium catalyst (**B**) is remarkably effective for the cyclization–hydrosilylation of several 1,6-diynes to form (*Z*)-1-methylene-2-(silylmethylene)cyclopentane derivatives in moderate yields. Also, alkenynes (**9** and **11**) and a particular endiyne (**13**) can participate in this catalytic reaction with ease. A plausible catalytic cycle was suggested on the basis of the intriguing reaction with endiyne **13**.

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References and Notes

1 Y. Kawanami and K. Yamamoto, *Synlett*, **1995**, 1232.
2 Y. Kawanami and K. Yamamoto, 43rd Symposium on Organometallic Chemistry, Osaka, Japan, 1996, Abstr., No. PB114.
3 T. Uno, S. Wakayanagi, Y. Sonada, and K. Yamamoto, *Synlett*, **2003**, 1997.
4 For recent and closely related cyclization/hydrosilylation, which is catalyzed by a cationic platinum complex containing bidentate nitrogen ligands, see: X. Wang, H. Chakrapani, J. W. Madine, M. A. Keyerleber, and R. A. Widenhoefer, *J. Org. Chem.*, **67**, 2778 (2002), and references cited therein; Also, for the preceding rhodium-catalyzed silylative cyclization of 1,6-heptadiyne dertivatives with trialkylsilanes, see T. Maruoka, I. Matsuda, and K. Itoh, *Organometallics*, **21**, 3650 (2002); T. Maruoka, I. Matsuda, and K. Itoh, *Tetrahedron Lett.*, **39**, 7325 (1998); I. Ojima, A. T. Vu, J. V. McCullagh, and A. Kinoshita, *J. Am. Chem. Soc.*, **121**, 3230 (1999); C. Liu and R. A. Widenhoefer, *Organometallics*, **21**, 5666 (2002).
5 (*S*)-2′-Methoxy-2-diphenylphosphino-1,1′-binaphthyl: We thank Professor Hayashi (Kyoto Univ.) for his help.
6 NMR spectral data for **10b**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.60 (dd, $J = 15.2$, 10.6 Hz), 1.10 (dd, $J = 15.2$, 3.6 Hz), 1.23 (t, $J = 6.9$ Hz), 1.24 (t, $J = 7.1$ Hz), 1.25 (t, $J = 7.3$ Hz), 1.81 (dd, $J = 12.4$, 11.1 Hz), 2.72 (dd, $J = 12.0$, 7.6 Hz), 2.62 (centered, m), 2.90 (dq, $J = 16.8$, 2.0 Hz), 3.06 (br d, $J = 16.8$ Hz), 3.83 (q, $J = 6.9$ Hz), 4.19 (q, $J = 7.0$ Hz), 4.16 (q, $J = 7.2$ Hz), 4.86 (q, $J = 2.3$ Hz) and 4.91 (q, $J = 2.3$ Hz). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 13.9 (q), 14.3 (t), 18.2 (q), 37.6 (d), 40.0 (t), 41.7 (d), 58.0 (s), 58.3 (t), 61.3 (t), 106.1 (t), 154.1 (s), 171.9 (s), 171.8 (s).
7 NMR spectral data for **12b**: ^{1}H NMR δ 0.92 (d, $J = 7.6$ Hz), 1.04 (m), 1.23 (t, $J = 6.9$ Hz), 1.60 (dq, $J = 6.9$, 1.7 Hz), 2.90 (centered, m), 3.70 (dd, $J = 8.7$, 7.7 Hz), 3.84 (q, $J = 6.9$ Hz), 3.97 (dd, $J = 8.7$, 7.7 Hz), 4.18–4.39 (m), 5.25 (qd, $J = 6.9$, 2.3 Hz). ^{13}C NMR δ 8.1, 14.6, 17.9, 18.3, 42.8, 58.5, 69.8, 70.7, 115.2, 142.2. The major component may have (*R**,*R**) on the basis of *cis*-carbopalladation to take place.
8 NMR spectral data for **14** as a triethoxy derivative: ^{1}H NMR δ 1.21 (t, $J = 6.9$ Hz), 1.4–2.5 (three peaks m), 3.81 (q, $J = 6.9$ Hz), 4.45 (t, $J = 2.0$ Hz), 4.59 (s), 4.97 (dq, $J = 10.2$, 2.0 Hz), 5.02 (dq, $J = 16.8$, 2.0 Hz), 5.10 (t, $J = 2$ Hz), 5.82 (ddt, $J = 16.8$, 10.2, 6.6 Hz), 6.02 (t, $J = 2.0$ Hz). ^{13}C NMR δ 18.1, 28.7, 34.1, 34.2, 58.4, 72.8, 74.3, 108.4, 114.7, 126.4, 138.6, 143.2, 150.5.
9 NMR spectral data for **15** as a triethoxy derivative: ^{1}H NMR δ 0.56 (dd, $J = 15.2$, 10.9 Hz), 1.08 (dd, $J = 15.2$, 3.6 Hz), 1.23 (t, $J = 6.9$ Hz), 1.4–2.5 (four peaks m, 7H), 2.42 (t, $J = 2.3$ Hz), 3.82 (q, $J = 6.9$ Hz), 4.09 (br dd, $J = 6.9$, 1.3 Hz), 4.13 (d, $J = 2.3$ Hz), 5.37 (m). Characterized by a ^{1}H–^{1}H COSY measurement. ^{13}C NMR δ 14.8. 18.3, 23.9, 28.7, 34.8, 39.7, 56.8, 58.3, 67.5, 74.1, 80.1, 114.8, 154.8. Characterized by an OFR measurement.
10 The substrate containing a terminal alkyne site tends to give an expected cyclization product in a poor yield, due to high bp byproduct.
11 To the best of our knowledge, *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, and R. A. Widenhoefer, *J. Org. Chem.*, **66**, 1755 (2001).
12 Y. Maruyama, K. Yamamura, T. Sagawa, H. Katayama, and F. Ozawa, *Organometallics*, **19**, 1308 (2002); For a pertinent review, see F. Ozawa, *J. Organomet. Chem.*, **611**, 332 (2000).

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