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Cationic palladium-catalyzed hydrosilylative cross-coupling of alkynes with alkenes forming 4-silylated-1-butene frameworks*

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Abstract: A new hydrosilylative cross-coupling reaction of a variety of alkynes with several alkenes, which is catalyzed by a cationic Pd complex $[Pd(\eta^3\text{-}C_3H_5)(cod)]^+[PF_6]^-$ (cod = 1,5-cyclooctadiene) was studied systematically. The reaction using $HSiCl_3$ as an addend afforded more or less two types of products consisting of four possible derivatives, $R^1CH{=}CR^2\text{–}CHR^3\text{–}CHR^4\text{–}SiCl_3$, which always contained 4-trichlorosilyl-1-butene frameworks, in acceptable combined yields. The coupling pattern was markedly dependent both on the precatalyst in the absence or presence of PPh_3 ligand and on the combination of the alkyne and alkene partners employed. A possible catalytic cycle that involves an initial hydropalladation of an alkyne, followed by a facile and specific carbopalladation of an alkene, is proposed. At the same time, the lack of regioselectivity in the latter step is noted.

Keywords: cationic palladium complex; hydrosilanes; alkynes; alkenes; cross-coupling; hydropalladation; carbopalladation.

INTRODUCTION

Cyclization/hydrosilylation of certain alkadiynes has been well known to be catalyzed by either Rh(I) [1], Ni(II) [2], or Pt(II) complex [3], by using trialkylsilane as an addend. However, we have found that a cationic Pd complex $[Pd(\eta^3\text{-}C_3H_5)(cod)]^+[PF_6]^-$ (**A**), (cod = 1,5-cyclooctadiene) is very effective for the reaction only by using trichlorosilane [4]. In addition, we are interested in the fact that a 1,6-alkenyne undergoes the same reaction exothermically, and much faster than the corresponding 1,6-alkadiyne as depicted in Scheme 1.

Taking advantage of the observed rate enhancement for the 1,6-alkenyne cyclization, we have examined an intramolecularly competitive cyclization/hydrosilylation of certain 1-alkene-6,11-diynes. Thus, the results obtained for the cyclization of 1-tridecene-1,6-diyne are particularly of interest as shown also in Scheme 1. There are two products arising from different pathways, and we have detected a quantitative rate difference in the cyclization between a diyne pathway **a** and an enyne pathway **b**: We have found that, on the basis of product composition, pathway **b** proceeds over 10 times faster than pathway **a** [5].

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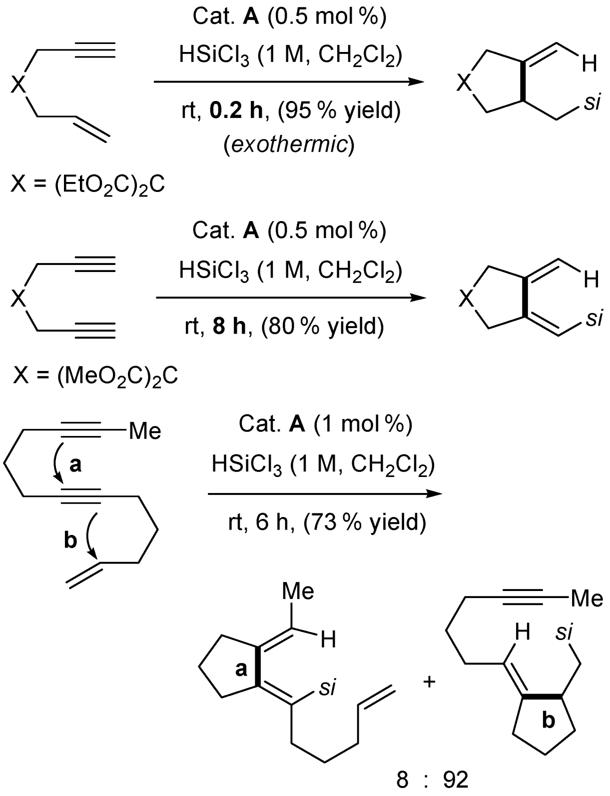
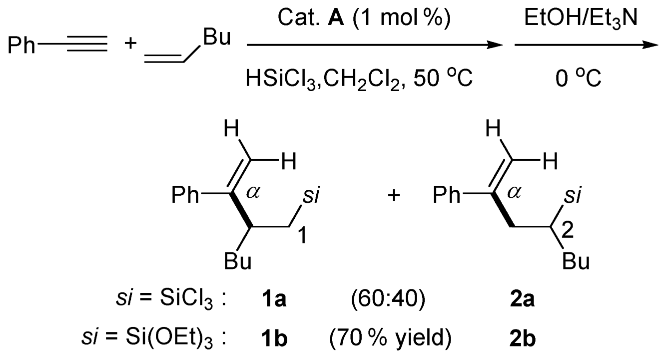


Scheme 1 Facile cyclization of 1,6-enynes compared to 1,6-diynes.

Now we ask: Does intermolecular version of coupling-hydrosilylation of 1,6-alkenyne work? Indeed, we have found that, under hydrosilylation conditions, an unprecedented cross-coupling between an alkyne and an alkene occurs satisfactorily. Herein, we disclose the cationic Pd complex-catalyzed hydrosilylative cross-coupling of alkynes with alkenes [6].

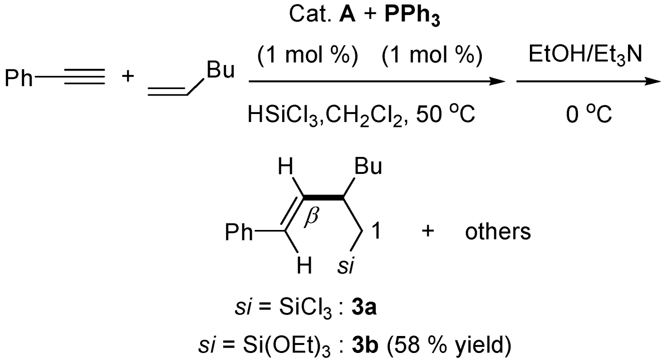
RESULTS AND DISCUSSION

Phenylacetylene and an equimolar amount of 1-hexene were chosen as coupling partners in order to settle the reaction conditions. Hydrosilylative coupling was catalyzed effectively by a 1 mol % catalyst loading of a cationic Pd complex **A** under mild heating for a few hours. Tetrafluoroborate as a counter anion worked equally well. Use of $HSiCl_3$ in 1 M solution of dry CH_2Cl_2 was particularly suitable for the reaction. Two major products, isolated by bulb-to-bulb distillation and identified by ^{1}H and ^{13}C NMR analyses, were found to be regioisomers arising from a reverse coupling of 1-hexene with phenylacetylene in a ratio of **1a**:**2a** = 60:40 as depicted in eq. 1 [7]. On the other hand, the alkyne part underwent regioselectively the coupling. Namely, the initial hydropalladation of phenylacetylene took place in an α-directing manner. By using three-fold excess of 1-hexene, the combined yield, 70 % as triethoxysilyl derivatives **1b** and **2b**, improved, while the isomer ratio was found unchanged.



(1)

However, once triphenylphosphine was added to the precatalyst **A**, the cross-coupling reaction exhibited completely different pattern: Initial hydropalladation makes the Pd center attach at a β-position of phenylacetylene almost exclusively. Of the several bulky phosphines, PPh_3 was found to be the most effective ligand in giving selectively a β-1 [7] type cross-coupling product **3a** (see eq. 2). Combined with other evidence for the coupling of 1-heptyne, the ligand effect on the Pd catalyst may be attributed to a steric origin.



(2)

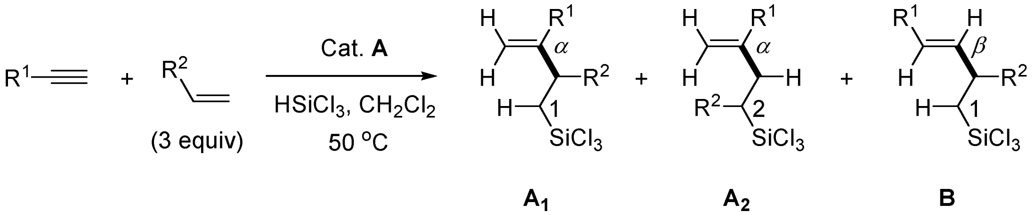
Although the critical species derived from precatalyst **A** that conducts the coupling reaction is not clear yet, we have examined the scope and limitations of the present hydrosilylative cross-coupling reaction. Phenylacetylene, 1-heptyne, or methyl propiolate was employed as a 1-alkyne, while 1-hexene or styrene was used as a 1-alkene partner. In addition, *trans*-3-hexene was also examined. All results are compiled in Table 1.

Under the standard conditions without PPh_3 ligand, the extent of α-directing selectivities for 1-alkynes [($\mathbf{A_1}$ + $\mathbf{A_2}$)/**B**] are about similar, except for propiolate, as seen in entries 1–4 and entry 5. As for the alkene insertion to the vinylpalladium intermediates, the ratios of 1,2- vs. 2,1-insertion ($\mathbf{A_1}$/$\mathbf{A_2}$) for styrene (entries 2 and 4) are a little better than those for 1-hexene (entries 1 and 3), both being not regioselective at all so far examined.

Trans-3-hexene reacted similarly with phenylacetylene, but 80/20 of **16a/17a** (entry 6) became diminished as compared with 91/9 for 1-hexene as a coupling partner (entry 1). We believe the difference is significant, being indicative of a reversible hydropalladation to phenylacetylene in an initial step of the catalytic cycle (vide infra).

Furthermore, with added PPh_3 (1 equiv to cat. **A**) under otherwise the same conditions as given in Table 1, highly **B** selective cross-couplings were uniformly attained for entries 1–4: The ratios of ($\mathbf{A_1}$ + $\mathbf{A_2}$)/**B** were found around 4–9/96–91 [6b].

Table 1 Hydrosilylative cross-coupling of alkynes with alkenes catalyzed by complex **A**.



Entry	R^1	R^2	Time/h	Yield/% [a]	Composition [b]	
					A_1/A_2	**$(A_1 + A_2)/B$** [c]
1[d]	C_6H_5	C_4H_9	1.5	70	60/40	91/ 9 (**1a**+**2a**)/**3a**
2	C_6H_5	C_6H_5	3	71	78/22	93/ 7 (**4a**+**5a**)/**6a**
3	C_5H_{11}	C_4H_9	3	56	66/34	89/11 (**7a**+**8a**)/**9a**
4	C_5H_{11}	C_6H_5	2.5	52	81/19	73/27 (**10a**+**11a**)/**12a**
5	CO_2Me	C_4H_9	4	40	88/12 [e]	100/nil (**13a**+**14a**)/**15a**
6	C_6H_5	(*E*)-3-hexene	3	50	($A_1 = A_2$)	80/20 [f] (**16a**/**17a**)

[a] Combined yield as triethoxysilyl derivatives. [b] Glc analysis of trichlorosilyl derivatives.

[c] See Experimental. [d] See eq. 1. [e] Minor product estimated to be A_2.

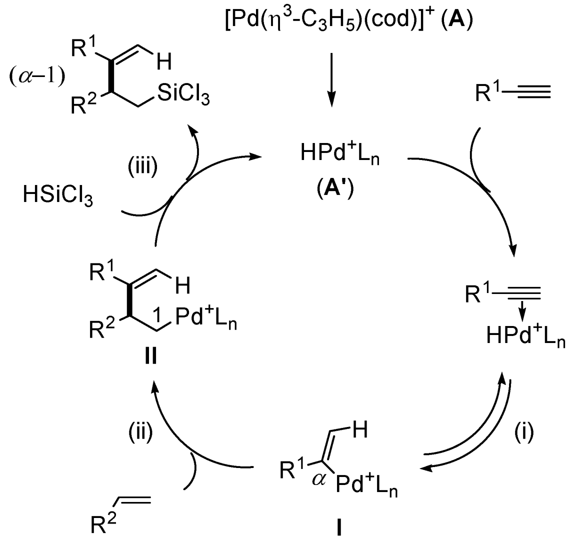
[f] Presumably (*R**,*S**)-diastereomers.

The cross-coupling between certain internal alkynes with 1-alkenes can also be carried out: 1-phenylpropyne, 3-hexyne, and ethyl 2-butynoate were examined as alkyne substrates, these selected examples being to avoid potentially complicated coupling pattern [6b].

Based on the common understandings, the coordination affinity of alkynes to any Pd species must be stronger than the affinity of alkenes. It is probable to presume that alkenes undergo a migratory insertion to the vinylpalladium intermediate much faster than alkynes. As discussed above, we can estimate this rate difference to be about 10 times [5]. Furthermore, according to a theoretical study, alkenes have a weaker coordination to a cationic phenylpalladium(II) compared to the methylpalladium(II) complex, and have a lower insertion barrier [8]. Then, in our case, a vinylpalladium intermediate must play a decisive role to undergo a facile insertion of alkenes that we examined. In addition, without added PPh_3, the regiocontrol at this insertion step may be difficult, at the present time.

A proposed catalytic cycle for the hydrosilylative cross-coupling between alkynes and alkenes is presented here (Scheme 2). As a major path to lead to **A_1** or **A_2** type of coupling (see, Table 1), a real catalyst species, HPd^+L_n (**A'**) may contain a few ligands other than the substrate alkyne. Coordinated alkyne undergoes reversible hydropalladation to form a vinylpalladium intermediate (**I**). Then, a quick migratory insertion of alkene follows to afford a homoallylpalladium intermediate (**II**), which, in turn, reacts with $HSiCl_3$ to give one of 4-trichlorosilyl-1-butenes, and regenerates HPd^+L_n (**A'**).

In conclusion, we have found an unprecedented hydrosilylative cross-coupling of 1-alkynes with 1-alkenes, which is catalyzed by a cationic Pd complex **A** in the absence or presence of added PPh_3 ligand. The reaction, using $HSiCl_3$ as an addend, afforded more or less two types of coupling products consisting of 4-trichlorosilyl-1-butene frameworks, in acceptable combined yields.



Scheme 2 Possible catalytic cycle of cross-coupling.

EXPERIMENTAL [6b,9]

Typical procedure for eq. 1: 2-phenyl-3-(trichlorosilyl)methyl-1-heptene (1a) and 2-phenyl-4-trichlorosilyl-1-octene (2a)

A mixture of phenylacetylene (1 mmol), 1-hexene (3 mmol), and the catalyst **A** (1×10^{-2} mmol, 1 mol %) dissolved in dry CH_2Cl_2 (1 mL) was placed in a 5-mL screw-capped test tube under an argon atmosphere. To this solution was added $HSiCl_3$ (1 M, CH_2Cl_2, 1 mL), and the mixture was heated at 50 °C in a thermostated oil bath for 4 h. Color change of the reaction mixture was diagnostic of the end-point of reaction. GLC analysis of the reaction mixture [$3\ \mathrm{mm}^{\phi} \times 3$ m column packed with SE-30 grease on Celite (10 %) under programmed heating at a rate 10 °C/min from 100 °C (for 2 min) to 280 °C] revealed clearly that the reaction was complete, and that the peak area ratio of the cross-coupling products containing a trichlorosilyl group [T_R = 17.0 (**1a**) and 17.2 (**2a**) min] was estimated to be 60:40. A small amount of hydrosilylation products from 1-hexene, which were usually neglected, were also obtained. The products were directly subjected to bulb-to-bulb distillation under reduced pressure to give the regioisomeric products consisting of **1a** and **2a** (0.223 g, 70 % combined yield). Little change in the ratio **1a** to **2a** except combined yields was observed by using 1 or 5 equiv of 1-hexene to phenylacetylene. They were separated by preparative GLC for the spectral identification. Spectral data for **1a**: ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 0.85 (t, J = 7.1 Hz, 3H), 1.2–1.4 (m, 6H), 1.67 (dd, J = 15.5, 7.3 Hz, 1H), 1.79 (dd, J = 15.5, 6.9 Hz, 1H), 3.03 (quint, J = 6.9 Hz, 1H), 5.12 (s, 1H), 5.29 (d, J = 0.7 Hz, 1H), 7.3–7.4 (aromatic H, 5H). ^{13}C NMR (67.8 MHz): δ 14.0, 22.6, 28.7, 29.8, 31.4, 39.1, 113.6, 126.9, 127.5, 128.3, 141.9, 151.8. Spectral data for **2a**: ^{1}H NMR: δ 0.85 (t, J = 7.1 Hz, 3H), 1.45–1.65 (m, 6H), 1.19 (quint, J = 7.1 Hz, 1H), 2.55 (ddd, J = 14.5, 10.2, 0.7 Hz, 1H), 3.09 (ddd, J = 14.5, 4.3, 0.7 Hz, 1H), 5.17 (d, J = 0.7 Hz, 1H), 5.36 (q, J = 0.7 Hz, 1H), 7.3–7.4 (aromatic H, 5H). ^{13}C NMR: δ 13.8, 22.8, 27.4, 29.9, 34.1, 35.8, 115.4, 126.5, 127.8, 128.5, 139.7, 145.8. The corresponding triethoxysilyl compounds **1b** and **2b** were derived from **1a** and **2a** for analytical purpose. The distilled sample obtained above was treated with an excess EtOH and Et_3N dissolved in CH_2Cl_2 in an ice-cooled bath for 1 h. Salt Et_3N/HCl formed was removed by repeated trituration with cold hexane and filtration through a short celite plug, and the filtrates were concentrated using a coolnit evaporator. The residual oil was purified by a bulb-to-bulb distillation under a reduced pressure to give products. If necessary, they were purified by a preparative GLC. Spectral data for **1b**: ^{1}H NMR: δ 0.83_4 (t, J =

7.1 Hz, 3H), 0.86 (dd, $J = 15.2, 8.2$ Hz, 1H), 0.95 (dd, $J = 15.2, 6.4$ Hz, 1H), 1.20 (t, $J = 6.9$ Hz, 9H), 1.3–1.4 (m, 6H), 2.81 (quint, $J = 6.8$ Hz, 1H), 3.79 (q, $J = 6.9$ Hz, 6H), 5.06 (d, $J = 1.0$ Hz, 1H), 5.18 (d, $J = 1.3$ Hz, 1H), 7.2–7.4 (m, aromatic, 5H). **2b**: ^{1}H NMR: δ 0.82_6 (t, $J = 7.1$ Hz, 3H), 1.22 (t, $J = 6.9$ Hz, 9H), 1.43–1.53 (m, 7H), 2.35 (ddd, $J = 14.5, 10.7, 0.7$ Hz, 1H), 2.93 (ddd, $J = 14.5, 4.0, 0.8$ Hz, 1H), 3.84 (q, $J = 6.9$ Hz, 6H), 5.06 (d, $J = 1.0$ Hz, 1H), 5.27 (q, $J = 1.3$ Hz, 1H), 7.2–7.4 (m, aromatic, 5H). Anal. found: C, 68.25; H, 9.51 %. Calcd. for $C_{20}H_{34}O_3Si$ (**1b**): C, 68.52; H, 9.78 %.

The procedure was applied for all other cross-coupling reactions catalyzed by the precursor **A** in the absence of PPh_3 (see Table 1).

Typical procedure for eq. 2: (*E*)-1-phenyl-3-(triethoxysilyl)methyl-1-heptene (3b)

A catalyst system consisting of the Pd complex **A** and PPh_3 (1 equiv) was employed, and the reaction of phenylacetylene (1 mmol) and 1-hexene (3 mmol) with $HSiCl_3$ (1 M, CH_2Cl_2, 1 mL) was conducted at 50 °C for 4 h, in exactly the same manner as for eq. 1. The products of trichlorosilyl derivatives were detected by GLC analysis [$T_R = 16.7$ min (**3a**)], and isolated as triethoxy derivative **3b**. In the case of eq. 2, the distilled product **3a** was substantially a single one (0.203 g, 58 % yield). Spectral data for **3a**: ^{1}H NMR: δ 0.89 (t, $J = 6.6$ Hz, 3H), 1.23–1.37 (m, 6H), 1.58 (dd, $J = 15.2, 8.9$ Hz, 1H), 1.68 (dd, $J = 15.2, 5.3$ Hz, 1H), 2.63 (qt, $J = 8.9, 5.3$ Hz, 1H), 5.95 (dd, $J = 15.5, 9.2$ Hz, 1H), 6.43 (d, $J = 15.5$ Hz, 1H), 7.2–7.4 (m, aromatic, 5H). **3b**: ^{1}H NMR: δ 0.80 (dd, $J = 15.2, 7.4$ Hz, 1H), 0.87 (t, $J = 6.9$ Hz, 3H), 0.89 (dd, $J = 15.2, 6.6$ Hz, 1H), 1.20 (t, $J = 6.9$ Hz, 9H), 1.17–1.45 (m, 6H), 2.31–2.45 (m, 1H), 3.80 (q, $J = 6.9$ Hz, 6H), 6.06 (dd, $J = 15.7, 8.9$ Hz, 1H), 6.33 (dd, $J = 15.7, 0.3$ Hz, 1H), 7.1–7.4 (m, aromatic, 5H). ^{13}C NMR: δ 14.1, 17.5, 18.3, 22.7, 29.6, 37.6, 38.1, 58.3, 126.0, 126.6, 128.2, 128.4, 137.0, 138.0. Anal. found: C, 68.56; H, 9.77 %. Calcd. for $C_{20}H_{34}O_3Si$ (**3b**): C, 68.52; H, 9.78 %.

For spectral data of **4a–17a** listed in Table 1, see [6b].

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This paper is dedicated to the late Prof. Emeritus Makoto Kumada of Kyoto University (deceased on 28 June 2007).

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7. In the chemical formula, the designations α or β and 1 or 2 refer to the *carbopalladation* that occurs at α or β position of the 1-alkyne employed, and C–Si bond occurring at terminal or internal carbon of the 1-alkene counterpart, respectively.

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9. Throughout this section, all chemical names for the products of hydrosilylative cross-coupling of alkynes with alkenes are given on the basis of common 4-organosilyl-1-butene frameworks, $\mathrm{R^1CH{=}CR^2{-}CHR^3{-}CHR^4{-}SiX_3}$ (X = Cl or OEt), and not consonant with those by CAS (9CI).