Communication

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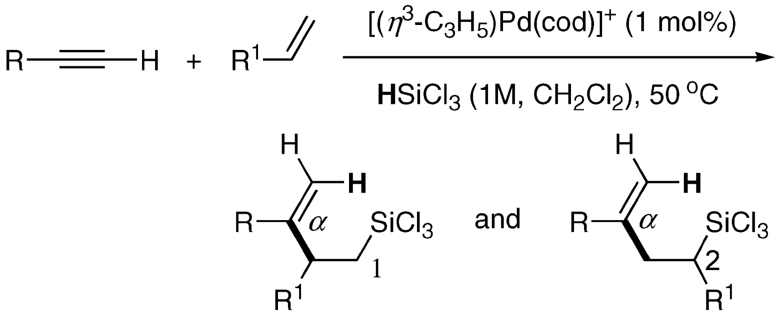

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Cationic Palladium-Catalyzed Hydrosilylative Cross-Coupling of Alkynes with Alkenes

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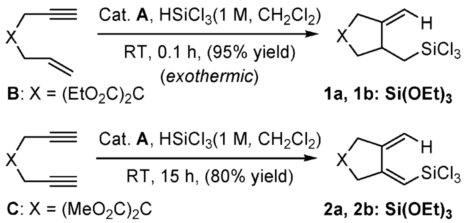
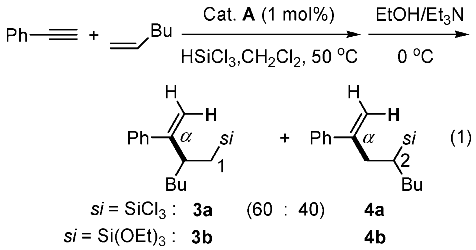
We wish to report herein a palladium complex-catalyzed cross-coupling of alkynes with alkenes, which occurs selectively under the hydrosilylation conditions. The unique findings originated from the fact that, by using trichlorosilane as an addend, a palladium complex, $[(\eta^3\text{-}C_3H_5)Pd(cod)]^+[PF_6]^-$ (**A**) (cod = cyclooctadiene), at a 0.5 mol % level, was found to catalyze the cyclization−hydrosilylation of a 1,6-heptenyne (**B**) evidently faster than that of the corresponding 1,6-heptadiyne (**C**), as depicted in Scheme 1.[1]

Scheme 1

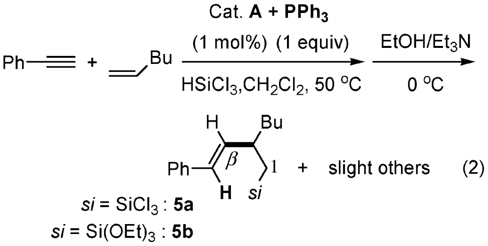


Although there are a variety of examples of the late transition metal (Rh,[2] Ni,[3] Pd,[4] and Pt[5]) complex-catalyzed cyclization−hydrosilylation of α,ω-alkadiynes,[2a,e,g,3a,4i,5b] alkenynes,[1,2c,g] as well as alkadienes,[2f,4d] it is worthy to note that trialkylsilanes are necessarily of choice as addends in these cases, while $HSiMe_nCl_{3-n}$ ($n = 0-2$) and none of trialkylsilanes are applicable for our reactions (Scheme 1).[4i] These facts may imply that the transfer of a trialkylsilyl group to the π-coordinated alkyne site on these metal centers, that is, the initial *syn* silylmetalation, must proceed much easier than that of a trichlorosilyl group, whereas the *syn* hydropalladation must precede under our conditions.

With these intriguing circumstances, we have performed an *intermolecular* version of the hydrosilylation of alkenyne as mentioned above. Thus, in a 5 mL screw-capped test tube with a stirring bar was placed a mixture of phenylacetylene (1.0 mmol), 1-hexene (3 equiv), trichlorosilane (1 M, CH_2Cl_2, 1 mL), and the catalyst **A** (0.01 mmol, 1 mol %) under an argon atmosphere, and the mixture was heated with stirring at 50 °C for 1−3 h. The reaction mixture was either directly subjected to a bulb-to-bulb distillation in vacuo or immediately treated with excess ethanol and triethylamine in CH_2Cl_2 at 0 °C, and the two products were obtained in 70% combined yield as triethoxysilyl derivatives after a usual work up (eq 1).[6] The result revealed that the initial *hydropalladation* must take place at the alkyne site, directing palladium at an α-position regioselectively, while the insertion step of 1-hexene into the resulting vinylpalladium intermediate (*carbopalladation*) did undergo cleanly with rather poor regioselectivity, a terminally silylated product being more or less predominant (vide infra).[7]



However, once triphenylphosphine (1 equiv) was added to the catalyst **A**, the same reaction as above in 3 h exhibited a quite different reaction pattern as shown in eq 2.[6] The initial hydropalladation directed the palladium center toward the β-position of the alkyne regioselectively, resulting in giving almost a single coupling product **5b** in 58% isolated yield. The effect of a phosphine ligand on a reversed regiocontrol in the hydropalladation of 1-alkynes would have a steric origin.



Although the exact nature of the catalysis is not clear yet, certain scope and limitations as to the present *hydrosilylative cross-coupling between alkynes and alkenes* are examined, and results obtained are listed in Table 1. As is seen in Table 1, similar reaction patterns to eqs 1 and 2 were substantially observed in most reactions of 1-heptyne (entries 1 and 2), methyl propiolate (entry 3), and again phenylacetylene (entries 5 and 6) with 1-hexene or styrene, respectively. However, the α-directing hydropalladation was found to be not always exclusive, as shown in entry 1, even under conditions of eq 1 (without PPh_3). In addition, a reaction between methyl propiolate and 1-hexene under added PPh_3 (1 or 2 equiv) to the palladium catalyst was exceptional (entry 4), where an α-1 coupling product predominated over a β-1 product. Reaction of phenylacetylene with (*E*)-3-hexene (entry 7) again afforded a β-isomer significantly without added PPh_3 to the catalyst. In addition, the major product is suggested to contain a single diastereoisomer by an NMR analysis. Furthermore, reaction of 3-hexyne, an internal alkyne, with allylbenzene (entry 8) did undergo the cross-coupling under hydrosilylation conditions, while attempted reaction of 3-hexyne with (*E*)-3-hexene was found to be very sluggish. Finally, in some of the above reactions, a small

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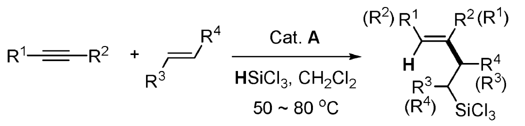
Table 1. Hydrosilylative Cross-Coupling of Alkynes with Alkenes



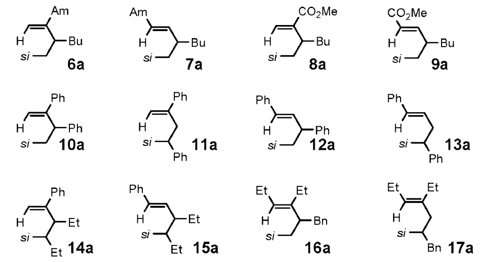
Entry	R^1	R^2	R^3	R^4	Yield(%)[a)]	Ratio
1[b)]	H	C_5H_{11}	H	C_4H_9	63	**6a 7a** 81 :19
2[c)]	C_5H_{11}	H	H	C_4H_9	57	**7a** 100 : nil[d)]
3[b)]	H	CO_2Me	H	C_4H_9	40	**8a** 83 :17[e)]
4[c)]	H	CO_2Me	H	C_4H_9	58	**8a 9a** 63 : 37
5[b)]	H	C_6H_5	H	C_6H_5	75	**10a 11a** 79 : 21
6[c)]	C_6H_5	H	H	C_6H_5	68	**12a 13a** 70 : 30
7[b)]	H	C_6H_5	C_2H_5	C_2H_5	50	**14a 15a** 80 : 20
8[b)]	C_2H_5	C_2H_5	H	CH_2Ph	40	**16a 17a** 80 :20

[a)] Isolated yield as triethoxysilyl derivatives (**b** series).

[b)] Without phosphine (cf. eq 1). [c)] With phosphine (cf. eq 2).

[d)] Dimerization/hydrosilylation of 1-heptyne was observed.

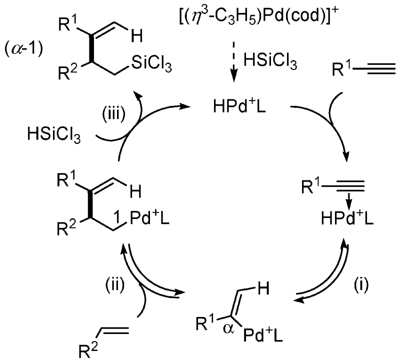
[e)] Minor product estimated to be *α*-2.



amount of simple hydrosilylation product from alkenes, but not from alkynes, was usually observed. Especially, in the case of hydrosilylation of allylbenzene, there was found an extensive hydrosilylation product at the expense of diminished cross-coupling with 3-hexyne (entry 8).

In conclusion, although further study must be undertaken before extensive discussion, the unique reaction presented here might be well understood in terms of (i) initial hydropalladation of a given alkyne to form an alkenylpalladium species, (ii) the latter, in turn, undergoes *quickly and specifically an alkene insertion*, and (iii) the resulting homoallylic organopalladium species terminates one catalytic cycle by undergoing substitution at the palladium center with a trichlorosilyl group to give product(s), regenerating most probably a hydrido-palladium species as an active catalyst (see Scheme 2).[8]

Scheme 2. Proposed Catalytic Cycle



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Supporting Information Available: Experimental procedures and compound characterization data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) In the chemical formula, the designations α or *β* and 1 or 2 refer to the *carbopalladation* at the α or *β* position of the alkyne employed, and C−Si bond occurring at the terminal or internal carbon of the alkene counterpart, respectively.

(7) Immediate reaction products consist of α's (90%) and little *β* isomers (~8%), the latter being hardly isolated at this stage.

(8) Although the circumstantial evidence for intervention of $HPdL^+$ species in the proposed catalytic cycle appears to be quite probable, any premise for the catalyst activation from a precatalyst **A** is problematic. We have examined a stoichiometric reaction of complex **A** with $HSiCl_3$ (2 equiv) dissolved in CD_2Cl_2 in an NMR tube, which is sealed under freeze−thawing, and observed rather slow evolution of both *propene* and *free* cyclooctadiene by monitoring with ^1H (270 MHz), the mixture forming dark precipitates in an hour. However, by ^{29}Si NMR (100 MHz, TMS external standard), no significant data have been obtained.

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