ORGANIC LETTERS

2002
Vol. 4, No. 17
2825−2827

# Ruthenium-Catalyzed Hydrosilylation of 1-Alkynes with Novel Regioselectivity

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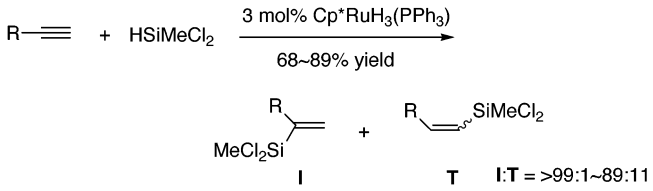
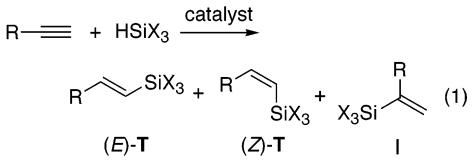
**Received April 27, 2002**

## ABSTRACT




**A ruthenium catalyst precursor bearing a bulky and electron-donating pentamethylcyclopentadienyl (Cp*) ligand, typically Cp*RuH$_3$(PPh$_3$), mediates hydrosilylation of several 1-alkynes with novel regioselectivity to give preferentially 2-silyl-1-alkenes.**

Hydrosilylation of 1-alkynes is a versatile means for preparing 1-alkenylsilanes, which are widely used for organic synthesis.[1] Thus, regio- and stereocontrol of the reaction is indispensable for the synthetic use of 1-alkenylsilanes. Hydrosilylation of 1-alkynes catalyzed by various transition metal complexes such as chloroplatinic acid often gives a mixture of three possible isomers (eq 1).




Both (*E*)- and (*Z*)-1-silyl-1-alkenes are obtained via the addition of a hydrosilane across the carbon−carbon triple bond, where the silicon atom attaches to the terminal carbon, being referred to as terminal adducts. The reversed addition of a hydrosilane to 1-alkynes gives a 2-silyl-1-alkene as an internal adduct. Rigorous stereocontrol to yield either (*E*)- or (*Z*)-1-silyl-1-alkene has been achieved independently by Takeuchi[2] and Ojima,[3] suppressing the formation of an internal adduct in both cases. On the other hand, regiocontrol to yield an internal adduct has received less attention.[4] However, recent reports do describe the selective formation of the internal adduct in the ruthenium complex-catalyzed hydrosilylation of alkynes, either by the necessary functional group-directed addition of trialkyl- and trialkoxysilanes[5] or by a more general Markovnikov-type one.[6] We have already found that the complex Cp*RuH$_3$(PPh$_3$) (**1**)[7] is a unique catalyst precursor for the regiocontrolled hydrosilylation of 1-alkynes with preferably dichloromethylsilane to afford mainly 2-silyl-1-alkenes[8] and report herein our own results.

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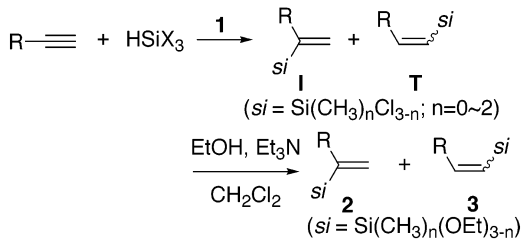
10.1021/ol026089q CCC: $22.00 
**Published on Web 07/27/2002**

A trihydride complex **1** was employed as a catalyst precursor. The reaction of 1-heptyne (2 mmol) and $HSiCl_3$ (3 mmol) in toluene with a catalytic amount of **1** (0.06 mmol, 3 mol % to 1-heptyne) at 80 °C for 24 h (Table 1, entry 1) gave an internal adduct **I**, 2-(trichlorosilyl)-1-heptene, and a terminal adduct **T**, 1-(trichlorosilyl)-1-heptene, in a ratio of 69:31 by GLC analysis. Treatment of the reaction mixture with EtOH and $Et_3N$ in $CH_2Cl_2$ gave the corresponding mixture of 2-(triethoxylsilyl)-1-heptene (**2**) and 1-(triethoxysilyl)-1-heptene (**3**) in 79% yield by bulb-to-bulb distillation. Higher regioselectivity in obtaining the 2-silylated adduct was attained when other chlorosilanes, $HSiMeCl_2$ (entry 2, **I**:**T** = 89:11) and $HSiMe_2Cl$ (entry 3, 85:15), were used instead of $HSiCl_3$. Reactions of several terminal alkynes with $HSiMeCl_2$ were examined: both 1-octyne and functionalized 4-pentynyl acetate also gave the internal adduct with slightly higher selectivity (entries 4 and 5). Excellent selectivity and good yield were achieved with 3-butynyl acetate and phenyl propargyl ether (entries 6 and 7, 97:3 and >99:1, respectively), while the reaction of 3-methylbutyl propargyl ether resulted in lower selectivity with moderate yield (entry 8). The reaction of phenylacetylene proceeded with inferior selectivity, still exhibiting the same tendency (entry 9, 69:31). However, the reaction of *tert*-butylacetylene did exhibit inverted selectivity (entry 10, *17:83*) in contrast to that of trimethylsilylacetylene, which occurred only in low yield (entry 11, 71:29, 18% yield[9]). It should also be noted that, in most reactions that gave internal adducts (**2**) preferentially, the minor terminal adduct (**3**) mainly has the (*Z*)-configuration, which must arise from an overall anti addition of hydrosilane to 1-alkyne.

**Table 1.** Ruthenium-Catalyzed Hydrosilylation of Terminal Alkynes with Chlorosilanes[a]




| entry | alkyne R | silane $X_3$ | **I**:**T** (*E*:*Z*)[b] | yield, % (**2** + **3**)[c] |
|---|---|---|---|---|
| 1 | *n*-$C_5H_{11}$ | $Cl_3$ | 69:31 (1:1) | 79 |
| 2 | | $MeCl_2$ | 89:11 (1:7) | 89 |
| 3 | | $Me_2Cl$ | 85:15 (1:9) | 65 |
| 4 | *n*-$C_6H_{13}$ | $MeCl_2$ | 92:8 (0:1) | 89 |
| 5 | $AcO(CH_2)_3$ | $MeCl_2$ | 93:7 (0:1) | 68 |
| 6 | $AcO(CH_2)_2$ | $MeCl_2$ | 97:3 (0:1) | 83 |
| 7 | $PhOCH_2$ | $MeCl_2$ | >99:1 | 78 |
| 8[d] | *i*-$AmOCH_2$ | $MeCl_2$ | 83:17 (1:1) | 71 |
| 9 | Ph | $MeCl_2$ | 69:31 (1:1) | 81 |
| 10 | $Me_3C$ | $MeCl_2$ | 17:83 (1:0) | 82 |
| 11 | $Me_3Si$ | $MeCl_2$ | 71:29 (1:0) | 18 |

[a] Reaction conditions: alkyne (2 mmol) and silane (3 mmol) in toluene (4 mL) at 80 °C for 24 h under an argon atmosphere. Cp*$RuH_3(PPh_3)$ (0.06 mmol) was a catalyst unless otherwise noted. [b] Determined by GLC and $^1H$ NMR. [c] Isolated yield. [d] *i*-Am = $(CH_3)_2CH(CH_2)_2$.

When the reactions of 1-heptyne were carried out with trialkylsilanes instead of chlorosilanes, simple dimerization of 1-heptyne took place along with the hydrosilylation of 1-heptyne in each case. For example, reaction of 1-heptyne and $Et_2MeSiH$, under the otherwise same conditions as described above, was sluggish and gave both a regioisomeric mixture of dimers[10] (48% yield) and adducts of hydrosilane (34% yield), the latter consisting mainly of an internal adduct (**I**:**T** = 82:18). This kind of dimer formation has already been reported for ruthenium-catalyzed reactions in the absence of hydrosilane.[11,12]

The effect of various ruthenium complexes on the catalytic activity for the hydrosilylation of 1-heptyne with $HSiMeCl_2$ was examined (Table 2). Reactions catalyzed by Cp*Ru(II) species exhibited high selectivities for the internal adduct (entries 1 and 2), while the catalyst precursors without a Cp* ligand were less effective in terms of both reactivity and regioselectivity. The bulkier and more electron-donating phosphorus ligand $PCy_3$ (Cy = cyclohexyl) was found to enhance the regioselectivity (entry 2, **I**:**T** = 93:7) in comparison with $PPh_3$.

**Table 2.** Hydrosilylation of 1-Heptyne with Dichloromethylsilane Using Various Ruthenium Catalysts

| entry | catalyst | **I**:**T** (*E*:*Z*)[a] | yield, % (**2** + **3**)[b] |
|---|---|---|---|
| 1 | Cp*$RuH_3(PPh_3)$ | 89:11 (1:7) | 89 |
| 2 | Cp*$RuH_3(PCy_3)$ | 93:7 (0:1) | 93 |
| 3 | Cp$RuH(PPh_3)_2$ | 30:70 (1:2) | 29[c] |
| 4 | Cp$RuCl(PPh_3)_2$ | 39:61 (1:1) | 7[d] |
| 5 | $Ru(OAc)_2(PPh_3)$ | 25:75 (1:4) | 49 |

[a] Determined by GLC and $^1H$ NMR measurement. [b] Isolated yield. [c] Reaction time: 7 days. [d] Reaction time: 3 days.

Salient features of the present Cp*Ru(II)-catalyzed hydrosilylation of 1-alkynes are (i) the anomalous regioselectivity of preferentially giving 2-silyl-1-alkenes (internal adducts **I**) rather than 1-silyl-1-alkenes (terminal adducts **T**), (ii) formal anti addition that selectively gives the (*Z*)-isomer of **T**, and (iii) that the ruthenium catalyst bearing a Cp* ligand is essential for the reaction.

On the basis of these features and an NMR observation of the stoichiometric mixture of **1** and $HSiMeCl_2$ for liberation of hydrogen, a plausible catalytic loop of the present hydrosilylation of 1-alkyne is depicted as Figure 1, where the key intermediate **A** would originate from the precursor **1**, the hydrosilane, and the substrate alkyne. Thus,

(9) Most of trimethylsilylacetylene remained unchanged after 24 h. The adducts **I** and **T** decomposed after a prolonged reaction time (up to 72 h).

(10) $^1H$ NMR signals of the vinylic protons of the dimers obtained were consistent with the reported spectral data for ruthenium-catalyzed dimerization of 1-hexyne. See Yi's (ref 11) and Kirchner's (ref 12) reports.

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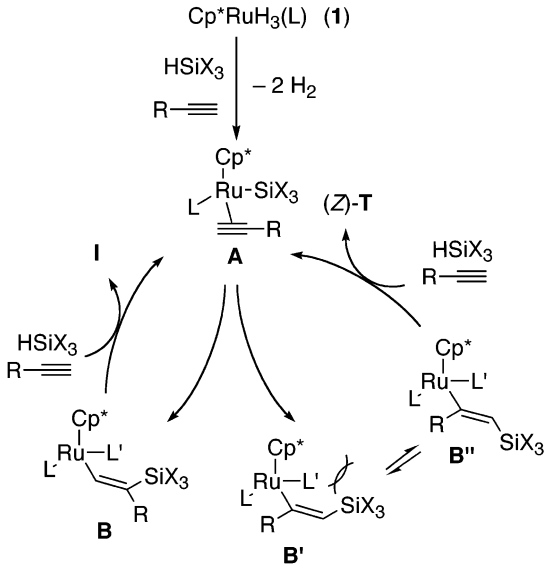


**Figure 1.** Plausible silylruthenation pathway for the hydrosilylation of 1-alkynes.

a key step may involve the silylruthenation, probably in a manner syn to the coordinated alkyne to form either $\beta$-silylated alkenylruthenium **B** or **B′**. This step is akin to that of dehydrogenative silylation of alkynes mediated by iridium complexes[13] but different from the conventional catalytic pathway proposed by Chalk and Harrod.[14] The intermediate **B** would be sterically less demanding and constitutes the major loop, while **B′** may be more congested due to an additional steric repulsion between the ruthenium center and the substituent R, becoming the minor one. Subsequently, the presence of a bulky Cp* ligand and, at the same time, bulkier $PCy_3$ than $PPh_3$ as a supporting ligand on the ruthenium center in **A** would help silylruthenation proceed highly regioselectively in favor of **B** rather than **B′**. Thus, formal $\sigma$-bond metathesis between the hydrosilane and **B** would follow to preferentially give the internal adduct **I** and regenerate the key intermediate **A**. These arguments are consistent with the fact that the ruthenium catalysts bearing no Cp* ligand exhibited an inferior and even opposite regioselectivity in the products, probably due to the diminished steric requirements around the ruthenium center in both **B** and **B′**.

The fact that the minor terminal adduct **T** forms mainly with the (*Z*)-configuration may well be understood as follows. An existing steric repulsion between the ruthenium center and a silyl substituent across the carbon−carbon double bond in **B′** would be released once **B′** undergoes geometrical isomerization into **B″** by way of a possible metal carbene zwitterionic complex, which has been proposed to explain an apparent anti addition of a hydrosilane to phenylacetylene catalyzed by rhodium[3] and iridium complexes.[15] Again, formal $\sigma$-bond metathesis between the hydrosilane and **B″** would result in a terminal adduct **T** with a preferential (*Z*)-configuration and regenerate the key intermediate **A**. Such an isomerization in **B** as well as in **B′** might take place, resulting in the internal adduct **I**, which is indistinguishable from that formed directly from **B**. To test this possibility, the reaction of 1-heptyne-$d_1$ with $HSiMeCl_2$ using the complex **1** as an catalyst was examined to give mainly the internal adduct **I**, an NOE measurement of which is indicative of the formal anti addition of the hydrosilane across the triple bond.[16]

In conclusion, we have shown that Cp*Ru(II) complex-catalyzed hydrosilylation of 1-alkynes proceeds with novel regioselectivity to afford predominantly internal adducts **I**.

**Acknowledgment.** Financial support by the "Grant-in-Aid for Encouragement of Young Scientists" (11750753) from Japan Society for the Promotion of Science is gratefully acknowledged.

**Supporting Information Available:** Representative procedure for the hydrosilylation and spectral data of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) This sort of geometrical isomerization has also been suggested by Crabtree for the iridium-catalyzed hydrosilylation via the $\eta^2$-vinylmetal tautomers (ref. 13), the so-called Ojima−Crabtree mechanism.

(16) By an NOE effect (2%) observed between allylic protons and one of vinylidene protons (cis to each other), another vinylidene proton in the ordinary internal adduct **2** obtained from 1-heptyne could easily be assigned, while the product from 1-heptyne-$d_1$ was found to lack the latter vinylidene proton, indicating clearly (*Z*)-1-deuterio-2-(diethoxymethylsilyl)-1-heptene.