

Rhodium-Mediated Silylative Cyclization of 1,6-Heptadiynes

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Abstract: RhCl(PPh₃)₃ readily reacts with an equivalent mole of a hydrosilane to form the Si-Rh-H species that plays an important role in the silylative cyclization of 1,6-heptadiynes to construct 1,2-dialkylidenecyclopentane derivatives. © 1998 Elsevier Science Ltd. All rights reserved.

Intramolecular carbometalation has become a popular strategy for the construction of carbocycles.¹ In particular, the cyclization of diynes is quite useful for the formation of 1,2-dialkylidenecycloalkanes which are capable of successive cycloadditions.² It is achieved by the stoichiometric participation of titanium³ or zirconium⁴ or by the catalysis of palladium⁵ or nickel⁶ complexes. Of these reactions, the cyclization reported by Tamao *et al.*⁶ is the sole example in which both parts, the hydride and the trialkylsilyl group in a hydrosilane, are used efficiently via oxidative addition of the hydrosilane to zero-valent nickel. This method is successfully applicable to (n, n+6)-diynes as shown in eq 1, whereas it is ineffective in the reaction of (n, n+5)-diynes.

On the other hand, we and Ojima *et al.* found independently rhodium-catalyzed silylative bicyclocarbonylation to give a bicyclo[3.3.0]octenone framework as a result of the coupling of three components, a 1, 6-heptadiyne derivative, a hydrosilane, and CO (eq 2).⁷ In the catalytic cycle of this reaction, the following successive steps are required before incorporation of CO: i) oxidative addition of trialkylsilane to low-valent rhodium, ii) insertion of an acetylenic triple bond into the Rh–Si bond, and iii) the subsequent insertion of the second acetylenic triple bond contained in the same molecule into the resulting Rh–carbon(vinyl) bond. The analogy in the starting materials and in the cyclization pattern between eq 1 and 2 prompted us immediately to turn our attention to the construction of a 1, 2-dialkylidenecyclopentane framework. We report herein a successful rhodium-catalyzed silylative cyclization of 1, 6-heptadiyne derivatives.

First of all, 4,4-di(methoxycarbonyl)-1,6-heptadiyne (1) was subjected to the reaction with Me_2PhSiH in the presence of $Rh_4(CO)_{12}$ under Ar atmosphere, however, the desired product Z- $2a^8$ was isolated in only 29 % yield with the concomitant formation of unexpected 3a (17 %) and 4 (20%). An indane derivative (3a) was

also formed as a major product (63 %) when RhCl(PPh₃)₃ was used as a catalyst under Ar atmosphere. After some groping trials, it was found that the yield of 2a remarkably increased in contrast to the decreasing of the concomitant formation of 3a (8 %) and 4 (9 %) when a mixture of 1 and Me₂PhSiH was added in one portion to a solution of RhCl(PPh₃)₃. The geometrical chemistry of the silylmethylene unit of 2a is E-selective⁸ in the reaction catalyzed by RhCl(PPh₃)₃. This is in reverse to the result observed in the Rh₄(CO)₁₂-catalyzed reaction. The contrastive results are elucidated as shown in Scheme 1. The intermediate Z-5a deduced from the analogy with silylative bicyclocarbonylation⁷ suffers from serious steric hindrance between the silyl group and the rhodium moiety. Such strain results either a rapid reductive elimination of the Z-2a {Rh₄(CO)₁₂ catalyst} or isomerization to E-5a which is intervened by the zwitterionic carbene complex 6 as proposed by Ojima⁹ {RhCl(PPh₃)₃ catalyst}.

$$Z-2\mathbf{a} \leftarrow Z \longrightarrow SiR_3 \longrightarrow Z \longrightarrow SiR_3 \longrightarrow Z \longrightarrow SiR_3 \longrightarrow Z \longrightarrow SiR_3 \longrightarrow E-2\mathbf{a}$$

$$Z = CO_2Me \longrightarrow Z \longrightarrow SiR_3 \longrightarrow Z \longrightarrow SiR_3 \longrightarrow E-2\mathbf{a}$$

Scheme 1

A similar silylative cyclization was observed in reactions of some other 1,6-diynes with Me₂PhSiH by the assist of RhCl(PPh₃)₃, however, there remains much room for improvement in the yields of **2a**, **8a**, **10a**, and **12a**. The results are summarized in Table 1 (entries, 1, 6, 8, and 10).

RhCl(PPh₃)₃ readily reacted with an equivalent mole of Me₂PhSiH to give a new species the formation of which was detected by the appearance of a signal (δ -15.07) assigned to Rh–H in the ¹H NMR spectrum, whereas Rh₄(CO)₁₂ did not show any clear evidence of interacting with Me₂PhSiH under Ar atmosphere. The sole indication observed was the disappearance of the spin-spin coupling between the proton bound to Si and the silylmethyl protons. It is well established that R_{3-n}Cl_nSiH reacts readily with RhCl(PPh₃)₃ to give Rh(SiCl_nR_{3-n})HCl(PPh₃)₂ as the result of oxidative addition. The structure is regarded as a trigonal bipyramid with trans phosphines at the apices by analogy with Rh(SiCl₃)HCl(PPh₃)₂ of which geometry was determined unambiguously by X-ray analysis. ¹⁰ The ¹H NMR signal assigned to the Rh–H in five-coordinate complexes, Rh(SiCl_nR_{3-n})HCl(PPh₃)₂, appears around δ -15 with the splitting pattern, a doublet of triplet, resulted by the coupling with ¹⁰³Rh ($J_{Rh-H} \approx 21 - 27$ Hz) and two equivalent ³¹P ($J_{H-Rh-P} \approx 13 - 15$ Hz). On the basis of these diagnostic points, the species derived from the interaction of RhCl(PPh₃)₃ with Me₂PhSiH could be deduced as Rh(SiMe₂Ph)HCl(PPh₃)₂ (**13a**; δ_{Rh-H} -15.27, J = 22.8 and 15.5 Hz).

Table 1. Silylative Cyclization of 1,6-Heptadiynes Induced by RhCl(PPh₃)₃

					Yield (%)	
Entry	Diyne	R ₃ SiH	Method ^a	Product	Catalytic reactions ^b	Stoichiometric reactions ^c
1	, "	Me₂PhSiH	Α	2a	61	-
2	$MeO_2C\sqrt{}$	Me ₂ PhSiH	В	2 a	61	94
3	MeO_2C	MePh ₂ SiH	В	2 b	15	80
4	1	Et ₂ MeSiH	В	2 c	40	77
5		EtMe ₂ SiH	В	2 d	46	83
6	_=	Me ₂ PhSiH	Α	8a	27	-
7	7	Me ₂ PhSiH	В	8a	53	78
8	Ph∕N =	Me ₂ PhSiH	Α	10a	23	-
9	9	Me ₂ PhSiH	В	10a	32	90
	¹BuMe ₂ SiO					
10		Me ₂ PhSiH	Α	12a	42	-
11	11	Me ₂ PhSiH	В	12a	55	94

^a Method A: A mixture of a diyne and a hydrosilane was added in one portion into a CH₂Cl₂ solution of RhCl(PPh₃)₃ (3 mol %). Then, the resulting mixture was refluxed for 2 hours. Method B: A mixture of a diyne and a hydrosilane was added in one portion into the CH₂Cl₂ solution provided by mixing a catalytic amount (3 mol %) of RhCl(PPh₃)₃ and an equivalent mole of the corresponding hydrosilane at 25 °C for 25 min prior to use. Then, the mixture was refluxed for 2 hours. ^b Isolated yield. ^c Reactions proceeded at 25 °C.

Though the preliminarily formed 13a did not react with 1 to give any single product, steady formation of 2a was observed over a period of 2 h in the 1 H NMR spectrum of a mixture containing 0.038 mmole each of 1, Me₂PhSiH, and 13a at 25 °C. About 2 h later, the starting 1 and Me₂PhSiH were almost consumed to give 2a in selectivity of 94 %. This fact strongly suggests that the present silylative cyclization proceeds through the intermediacy of R₃Si–Rh–H species. In addition, a preformed species 13a catalyzed a reaction of 1 with Me₂PhSiH to give 2a in 61% yield with the concomitant formation of 3a (10 %), 4 (5 %), and the product derived from simple hydrosilylation (7 %) (entry 2 in Table 1). Other hydrosilanes also readily reacted with RhCl(PPh₃)₃ to form the corresponding complex within 30 min; MeEt₂SiH (13b; δ_{Rh-H} -15.34, J = 23.4 and 14.7 Hz), Me₂EtSiH (13c; δ_{Rh-H} -15.36, J = 23.7 and 14.9 Hz), and MePh₂SiH (13d; δ_{Rh-H} -15.07, J = 22.2

and 16.0 Hz). All of these species 13a-13d reacted smoothly with a mixture of a stoichiometric amount of 1 and the corresponding hydrosilane in good to excellent selectivity (entries 3, 4, and 5 in Table 1), and were efficient as a catalyst for silylative cyclization. The alkyl substituents on the silicon atom exerted an appreciable effect on the yield of 2a-2d in the catalytic reactions. The results summarized in Table 1 (entries 2, 3, 4, and 5) show that Me₂PhSiH is apparently the hydrosilane of choice. Although the selectivity of the silylative cyclization induced by preformed 13a-13d was lower in catalytic reactions than that in stoichiometric reactions, the isolated yields of 8a, 10a, and 12a were remarkably improved (entries 7, 9. and 11 in Table 1) in contrast to the results of the RhCl(PPh₃)₃ catalyst (entries 6, 8, and 10 in Table 1). The present approach catalyzed by RhCl(PPh₃)₃ was not efficient with 1,7-octadiyne, in which the major reaction course was a simple hydrosilylation of two acetylenic units.

In conclusion, we have accomplished the silylative cyclization of 1,6-diynes which is promoted by the Si-Rh-H complex resulted in the interaction of RhCl(PPh₃)₃ and R₃SiH. The present reaction provides a new route to construct 1,2-dialkylidenecyclopentanes which are useful as building blocks for polycycles.

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- 8. The geometrical chemistry of the silylmethylene unit was deduced by NOE analysis as exemplified by the following data.

 $Z = CO_2Me$

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