

Rhodium-Mediated Silylative Cyclization of 1,6-Heptadiynes

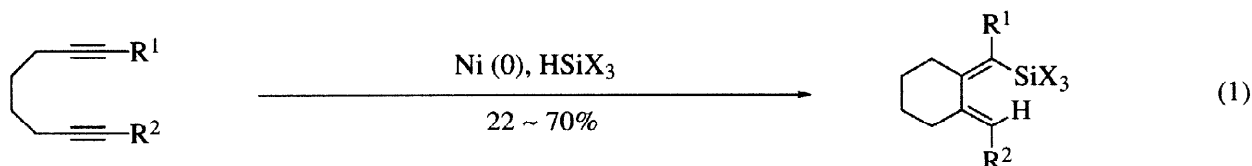
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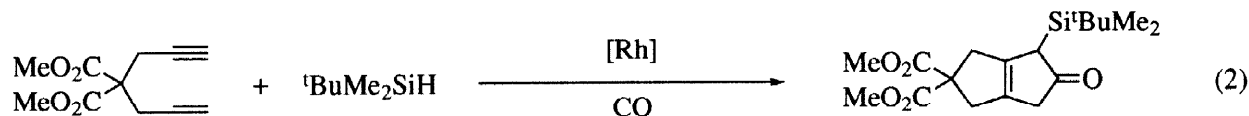
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Abstract: $\text{RhCl}(\text{PPh}_3)_3$ readily reacts with an equivalent mole of a hydrosilane to form the Si–Rh–H species that plays an important role in the silylative cyclization of 1,6-heptadiynes to construct 1,2-dialkylidenecyclopentane derivatives. © 1998 Elsevier Science Ltd. All rights reserved.

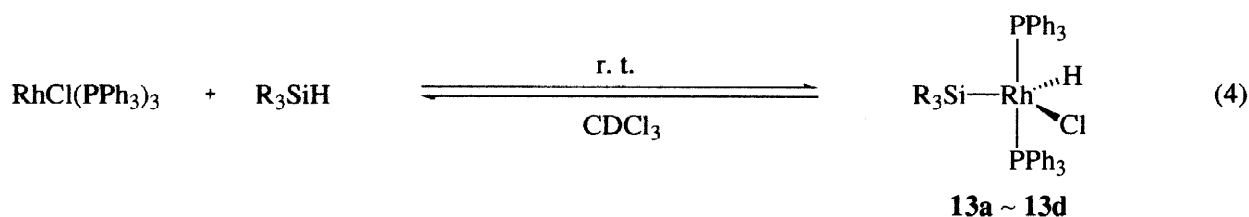
Intramolecular carbometalation has become a popular strategy for the construction of carbocycles.¹ In particular, the cyclization of diynes is quite useful for the formation of 1,2-dialkylidenecycloalkanes which are capable of successive cycloadditions.² It is achieved by the stoichiometric participation 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 $\text{Rh}_4(\text{CO})_{12}$ 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

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

Entry	Diyne	R ₃ SiH	Method ^a	Product	Yield (%)	
					Catalytic reactions ^b	Stoichiometric reactions ^c
1		Me ₂ PhSiH	A	2a	61	-
2		Me ₂ PhSiH	B	2a	61	94
3		MePh ₂ SiH	B	2b	15	80
4		Et ₂ MeSiH	B	2c	40	77
5		EtMe ₂ SiH	B	2d	46	83
6		Me ₂ PhSiH	A	8a	27	-
7		Me ₂ PhSiH	B	8a	53	78
8		Me ₂ PhSiH	A	10a	23	-
9		Me ₂ PhSiH	B	10a	32	90
10		Me ₂ PhSiH	A	12a	42	-
11		Me ₂ PhSiH	B	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 ¹H 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

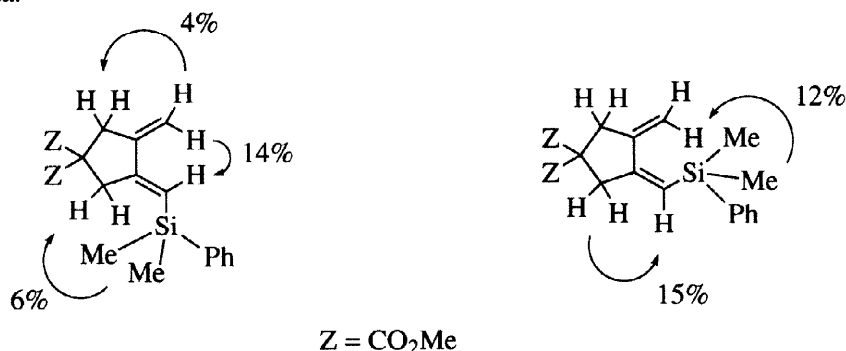
and 16.0 Hz). All of these species **13a-13d** reacted smoothly with a mixture of a stoichiometric amount of **1** and the corresponding hydrosilane in good to excellent selectivity (entries 3, 4, and 5 in Table 1), and were efficient as a catalyst for silylative cyclization. The alkyl substituents on 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 Me_2PhSiH 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 $\text{RhCl}(\text{PPh}_3)_3$ catalyst (entries 6, 8, and 10 in Table 1). The present approach catalyzed by $\text{RhCl}(\text{PPh}_3)_3$ 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 $\text{RhCl}(\text{PPh}_3)_3$ and R_3SiH . The present reaction provides a new route to construct 1,2-dialkylidenecyclopentanes which are useful as building blocks for polycycles.

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