Use of Rhodium N-Heterocyclic Carbene Complexes in Catalytic Cyclization and Hydrosilylation of 1,6-Enynes to 2-Methyl-1-silylmethylidene-2-cyclopentane

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Keywords: N-Heterocyclic carbene / Cyclization / Hydrosilylation / Rhodium

The neutral rhodium complexes [RhCl(NHC)(cod)] (NHC = N-heterocyclic carbene) catalyzed the hydrosilylation/cyclization of 1,6-enynes and $HSiR_3$ (R_3 = Et_3 and $PhMe_2$) to form 2-methyl-1-silylmethylidene-2-cyclopentanes in high yields.

Introduction

Development of effective cyclization reactions for the synthesis of carbocycles and heterocycles has been the subject of extensive study because of their relevance to medicine and functional materials.[1] Among the numerous methods available, the transition-metal-promoted cyclization reaction has attracted much attention and has become one of the most popular.[2] However, considerable effort is still being devoted to developing more efficient and practical methods for the synthesis of polycyclic organic compounds from readily available starting materials. Recently, transition-metal-catalyzed hydrosilylation/cyclization reactions have become well developed. Examples are the palladium-catalyzed hydrosilylation/cyclization of dienes, diynes, and enynes,[3] the rhodium-catalyzed hydrosilylation/cyclization of enynes, triynes, and endiynes,[4] the platinum-catalyzed hydrosilylation/cyclization of diynes,[5] the nickel(0)-catalyzed hydrosilylation/cyclization of 1,7-diynes,[6] and the yttrocene-catalyzed hydrosilylation/cyclization of enynes.[7] Hydrosilylation/cyclization processes are of particular use because of the reactivity of the silylated carbocycles formed in these transformations.

N-Heterocyclic carbenes (NHC), such as 1,3-imidazoylidene, represent a class of ligands with a considerable stabilizing effect in organometallic systems compared to the widely utilized tertiary phosphanes. Their donating properties are comparable or superior to those of the most basic phosphanes. The ability of NHCs to coordinate metal centers strongly makes them excellent candidates for the design of well-defined catalysts. Moreover, the significant steric demand brought about by the presence of bulky substituents on the NHC can be used in exploring new catalysts. Recently, the chemistry of transition-metal NHC complexes has been rapidly developed and their deployment has widened to include many catalytic reactions, including the Diels−Alder reaction, the Heck reaction, Suzuki coupling, Sonogashira coupling, and enyne metathesis, etc.[8] However, reports of the use of transition metal NHC complexes in cyclization other than in metathesis are still rare. Thus, we began to study the use of transition metal NHC complexes in cyclization and found that in the presence of silane, rhodium NHC complexes catalyze the hydrosilylation/cyclization of enynes to carbocyclic compounds. Here we report the synthesis of carbocyclic compounds by rhodium NHC-catalyzed cylization/hydrosilylation. This is the first example of the use of NHC complexes as catalysts in the cylization/hydrosilylation of enynes and this methodology has several advantages, such as reusablility, mild reaction conditions, the need for neither additives nor CO, and the use of a neutral complex.

Results and Discussion

The catalysts were prepared as depicted in Equation (1). The X-ray crystal structure of **1** (R = Bu) is depicted in Figure 1. Except for R = Bu, the mono-NHC rhodium complex was obtained as the sole product in high yield (71−83%). When R was a butyl group, a mixture of mono- and bis-NHC rhodium compounds was obtained in 66% yield with a ratio of 1:4. However, the mixture was easily separated by column chromatography. Each rhodium compound was fully characterized by ^{1}H and ^{13}C NMR spectroscopy, high-resolution mass spectrometry, and elemental analysis. Some of the compounds were confirmed by an X-ray diffraction study. We first tested the hydrosilylation/

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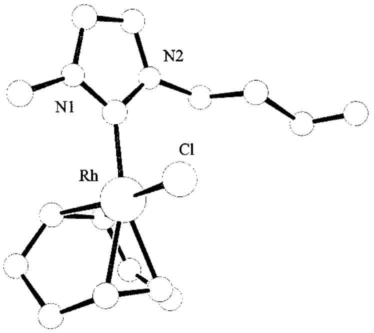
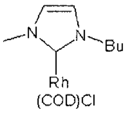
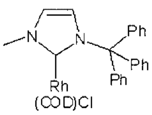
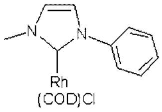
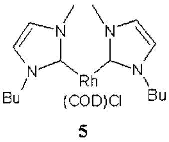
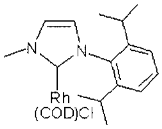
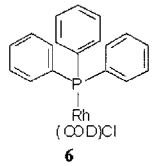


Figure 1. X-ray structure of **1** (30% probability for thermal ellipsoids)

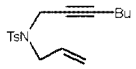
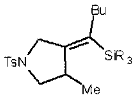
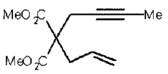
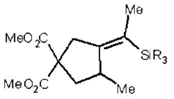
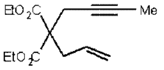
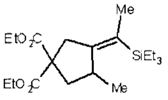
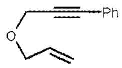
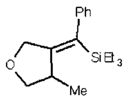
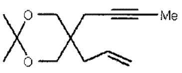
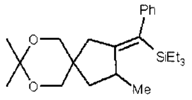
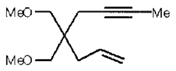
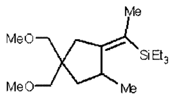
cyclization of nitrogen-bridged enynes by using the prepared rhodium complex as a catalyst (Table 1). As the steric bulkiness of the substituent on the imidazole ring increased, the yield decreased. The yield was the lowest (26%) for the case of bis-NHC rhodium complex. The best result (89%) was obtained when R was a butyl group. The catalytic systems were stable enough for the catalyst to be recovered in 70% yield after the reaction, which is a highly useful experimental result. It is well-known[9] that NHCs can be used as substitutes for phosphanes. Thus, we tested the in situ generated phosphane-substituted rhodium complex (entry 6) as a catalyst to compare its catalytic activity with those of NHC rhodium complexes. We observed the formation of a trace amount of the product. In our hydrosilylation/cyclization reaction, the NHC-rhodium complexes show special activity. We examined the scope of this reaction in terms of functional group tolerance (Table 2). The corresponding products were obtained, but the yields were rather sensitive to the substrate and the hydrosilane source. Initially, triethylsilane was used as a hydrosilane source. The use of Me_2PhSiH instead of Et_3SiH increased the yield. The reaction tolerates various functional groups including ester, ether, and sulfonamide. Enynes bearing an internal acetylene moiety were good substrates. However, the attempted reactions of enynes bearing a terminal acetylene moiety were unsuccessful. Ojima et al. have reported[9] the hydrosilylation/cyclization of enynes catalyzed by rhodium and Rh-Co complexes such as $[Rh(acac)(CO)_2]$, $[(t\text{BuNC})_4RhCo(CO)_4]$, $[Rh_2Co_2(CO)_{12}]$, and $[RhCl(PPh_3)_3]$, for which they proposed a plausible reaction mechanism. Recently, hydrosilylation/cyclization of 1,6-enynes catalyzed by a cationic rhodium bis(phosphane) complex was reported by Widenhoefer et al.[4a] They also proposed a working reaction mechanism that was almost the same as that proposed by Ojima et al. We expect that a plausible reaction mechanism will follow the same lines as those of these other studies (Scheme 1). The reaction should begin with the formation of silyl-[Rh](H) species through the oxidative addition of H-Si to a Rh^I species, followed by insertion of the acetylene moiety of the enyne to generate a silylvinyl-[Rh] complex. Coordination of the olefin moiety, followed by intramolecular carbometallation and hydrosilane-promoted reductive elimination, leads to the formation of 2-methyl-1-silylmethylidene-2-cyclopentane.

Table 1. Hydrosilylation/cyclization of *N*-allyl-*N*-hept-2-ynylbenzenesulfone amide by various rhodium complexes as catalysts[a]

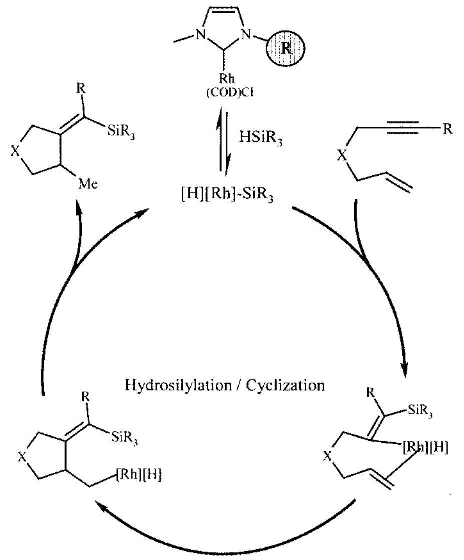
entry	catalyst	yield(%)[b]	entry	catalyst	yield(%)[b]
1	 **1**	89	4	 **4**	43
2	 **2**	67	5	 **5**	26
3	 **3**	63	6	 **6**	trace[c]

[a] Reaction conditions: CH_2Cl_2, reflux, 12 h. [b] Isolated yields. [c] In situ generated phosphane-substituted rhodium complex.

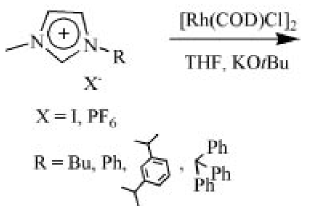
Table 2. Hydrosilylation/cyclization of 1,6-enynes catalyzed by catalyst **1**[a]

entry	substrate	product	yield (%)[b]
			
1		$R_3 = Et_3$	89
2		$R_3 = Me_2Ph$	90[c]
			
3		$R_3 = Et_3$	46
4		$R_3 = Me_2Ph$	77[c]
5			34
6			86
7			65
8			73

[a] Reaction conditions: CH_2Cl_2, reflux, 12 h. [b] Isolated yields. [c] $HSiMe_2Ph$.



Scheme 1. A plausible reaction mechanism

 (1)

Conclusion

In conclusion, we have demonstrated the first NHC-rhodium-catalyzed hydrosilylation/cyclization of enynes. The catalyst tolerates a wide range of functional groups. Moreover, this reaction has several advantages over other reactions such as facile recovery of the catalyst and the use of a neutral complex.

Experimental Section

General Remarks: All reactions were conducted under nitrogen using standard Schlenk-type flasks. Workup procedures were done in air. All solvents were dried and distilled according to standard methods before use. Reagents were purchased from Aldrich Chemical Co. and Strem Chemical Co. and were used as received. ^{1}H NMR spectra were obtained with a Bruker 300 or 500 spectrometer. Elemental analyses were done at the National Center for Inter-University Research Facilities, Seoul National University. High-resolution mass spectra were done at the Korea Basic Science Institute (Daegu).

A Typical Procedure for the Synthesis of Rhodium-NHC Complex (R = Ph): Imidazolium salt (0.30 g, 1.05 mmol) and $[RhCl(cod)]_2$ (0.26 g, 0.53 mmol) were dissolved in 20 mL of THF and KO*t*Bu (0.14 g, 1.25 mmol) was added. The resulting solution was stirred at room temperature for 5 h.

Compound 1: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.80 (d, *J* = 1.8 Hz, 2 H), 5.02 (br. s, 2 H), 4.49 (t, *J* = 2.6 Hz, 2 H), 4.07 (s, 3 H), 3.33 (m, 1 H), 3.23 (m, 1 H), 2.39 (m, 4 H), 1.91 (m, 6 H), 1.48 (q, *J* = 7.4 Hz, 2 H), 1.04 (t, *J* = 7.3 Hz, 3 H) ppm. $C_{16}H_{26}ClN_2Rh$ (384.8): calcd. C 49.99, H 6.82, N 7.29; found C 49.89, H 6.74, N 7.53.

Compound 2: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.20 (d, *J* = 7.9 Hz, 2 H), 7.53 (t, *J* = 7.3 Hz, 2 H), 7.45 (d, *J* = 7.4 Hz, 1 H), 7.17 (d, *J* = 1.8 Hz, 1 H), 7.02 (d, *J* = 1.8 Hz, 1 H), 5.26 (m, 1 H), 5.13 (m, 1 H), 4.13 (s, 3 H), 3.44 (m, 1 H), 2.70 (m, 1 H), 2.28 (m, 2 H), 2.06 (m, 1 H), 1.80 (m, 3 H), 1.42 (m, 2 H) ppm. $C_{18}H_{22}ClN_2Rh$ (404.7): calcd. C 53.46, H 5.49, N 6.93; found C 53.27, H 5.54, N 6.75.

Compound 3: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.45 (d, *J* = 7.7 Hz, 1 H), 7.36 (dd, *J* = 1.5 Hz, 6.3 Hz, 1 H), 7.18 (dd, *J* = 1.5 Hz, 6.3 Hz, 1 H), 7.01 (d, *J* = 1.8 Hz, 1 H), 6.85 (d, *J* = 1.8 Hz, 1 H), 5.10 (m, 2 H), 4.22 (s, 3 H), 3.79 (m, 1 H), 3.68 (m, 1 H), 2.35 (m, 1 H), 2.13−1.86 (m, 4 H), 1.75 (m, 2 H), 1.63 (m, 1 H), 1.43 (d, *J* = 6.7 Hz, 3 H), 1.33 (q, *J* = 2.4 Hz, 2 H), 1.12 (d, *J* = 6.9 Hz, 3 H), 1.11 (d, *J* = 6.9 Hz, 3 H), 0.95 (d, *J* = 6.8 Hz, 3 H) ppm. $C_{24}H_{34}ClN_2Rh$ (488.9): calcd. C 59.00, H 7.02, N 5.74; found C 59.16, H 6.97, N 5.81.

Compound 4: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.14 (d, *J* = 8.6 Hz, 2 H), 7.27 (m, 15 H), 7.17 (d, *J* = 1.9 Hz, 1 H), 7.01 (d, *J* = 1.9 Hz, 1 H), 5.22 (m, 1 H), 5.08 (m, 1 H), 4.11 (s, 3 H), 2.34 (m, 2 H), 1.92 (m, 4 H), 1.40 (m, 2 H) ppm. $C_{31}H_{29}ClN_2Rh$ (567.9): calcd. C 65.21, H 5.65, N 4.91; found C 65.60, H 5.35, N 4.94.

Compound 5: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.02 (d, *J* = 1.8 Hz, 1 H), 6.99 (d, *J* = 1.8 Hz, 1 H), 6.95 (q, *J* = 2.3 Hz, 2 H), 4.63 (m, 1 H), 4.21 (m, 2 H), 4.07 (s, 3 H), 4.01 (s, 3 H), 2.47 (m, 4 H), 2.18 (m, 4 H), 1.88 (m, 2 H), 1.67 (m, 5 H), 1.44 (m, 6 H), 1.02 (m, 6 H) ppm. $C_{24}H_{40}ClN_4Rh$ (523.0): calcd. C 55.15, H 7.72, N 10.73; found C 55.39, H 7.89, N 10.89.

A Catalytic Reaction: An enyne substrate (0.20 g, 0.65 mmol), Et_3SiH (0.52 mL, 3.25 mmol), and catalyst (10 mg, 0.026 mmol) were dissolved in 20 mL of CH_2Cl_2. The resulting solution was heated to reflux for 12 h. Evaporation followed by chromatography on a silica gel column eluting with hexane/diethyl ether (10:1) gave a product and the catalyst.

Triethyl[(4-methyldihydrofuran-3-ylidene)phenylmethyl]silane: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.28−7.08 (m, 5 H), 3.85 (d, *J* = 5.4 Hz, 2 H), 1.56 (d, *J* = 6.8 Hz, 2 H), 1.21 (s, 1 H), 0.86−0.69 (m, 15 H), 0.49 (m, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 141.7, 139.7, 135.4, 129.3, 128.4, 127.4, 116.9, 71.9, 70.1, 30.0, 7.9, 7.6, 4.9, 4.3, 3.9, 3.5, 1.4 ppm. HRMS for ($C_{18}H_{28}OSi$): calcd. 288.1909; found 288.1912.

3-Methyl-1-(toluene-4-sulfonyl)-4-(1-triethylsilanylpentylidene)-pyrrolidine: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.64 (d, *J* = 9.1 Hz, 2 H), 7.28 (d, *J* = 9.1 Hz, 2 H), 3.97 (d, *J* = 5.9 Hz, 2 H), 2.42 (s, 3 H), 2.00 (d, *J* = 6.9 Hz, 2 H), 1.99 (s, 1 H), 1.42 (d, 8.3 Hz, 2 H), 1.31 (m, 5 H), 0.88 (m, 14 H), 0.45 (m, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 143.8, 133.2, 130.0, 127.4, 126.3, 124.9, 124.1, 111.8, 44.0, 31.9, 27.7, 22.8, 22.0, 14.9, 14.4, 7.9, 3.4 ppm. HRMS for ($C_{23}H_{39}O_2NSSi$): calcd. 421.2471; found 421.2467.

3-[1-(Dimethylphenylsilanyl)pentylidene]-4-methyl-1-(toluene-4-sulfonyl)pyrrolidine: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.57−7.24

(m, 9 H), 3.89 (d, $J = 9.2$ Hz, 2 H), 2.41 (s, 3 H), 1.87 (m, 2 H), 1.65 (m, 1 H), 1.53 (s, 1 H), 1.26 (m, 5 H), 0.86 (m, 3 H), 0.43 (d, $J = 5.2$ Hz, 3 H), 0.22 (s, 3 H), 0.16 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 134.2$, 133.5, 133.4, 132.9, 129.5, 129.0, 127.8, 127.4, 127.3, 127.0, 125.9, 59.6, 43.6, 31.4, 30.9, 28.5, 27.1, 21.5, 13.9, 3.5, 3.4, 2.4 ppm. HRMS for ($C_{25}H_{35}O_2NSSi$): calcd. 441.2158; found 441.2159.

X-ray Crystallographic Study: Single crystals of **1** were grown by slow diffusion of hexane into a dichloromethane and ethereal solution of **1** at −15 °C. X-ray data for single crystals were collected on an Enraf−Nonius CCD single-crystal X-ray diffractometer at room temperature using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ A). The structures were solved by direct methods (SHELXS-97), and refined against all F^2 data (SHELXS-97). All non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms were treated as idealized contributions. Crystal data and refinement are given in Table 3, and selected bond lengths and angles are listed in Table 4. CCDC-212324 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 3. Crystal data and structure refinement for **1**

Empirical formula	$C_{16}H_{26}ClN_2Rh$	
Molecular weight	384.75	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, *C*2/*c*	
Unit cell dimensions	$a = 14.9240(10)$ Å	$\alpha = 90$ deg
	$b = 17.2370(10)$ Å	$\beta = 111.826(2)$ deg
	$c = 14.4620(10)$ Å	$\gamma = 90$ deg
Volume	3453.6(4) Å^3	
Z, Calculated density	8, 1.480 Mg/m^3	
Absorption coefficient	1.137 mm^{-1}	
F(000)	1584	
Crystal size	0.80 × 0.40 × 0.40 mm	
Theta range for data collection	1.89 to 27.45 deg	
Limiting indices	$-19 \le h \le 19$, $-20 \le k \le 22$, $-18 \le l \le 18$	
Reflections collected/unique	6906/3936 [*R*(int) = 0.0404]	
Completeness to theta = 27.45	99.5%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8872 and 0.7806	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/params	3936/1/183	
Goodness-of-fit on F^2	1.004	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0452$, $wR2 = 0.1229$	
R indices (all data)	$R1 = 0.0935$, $wR2 = 0.1633$	
Largest diff. peak and hole	1.566 and −1.261 e.A^{-3}	

Table 4. Selected bond lengths (Å) and angles (deg) for **1**

Cl−Rh	2.3866(18)	Rh−C(9)	2.227(6)
Rh−C(4)	2.023(6)	Rh−C(10)	2.198(7)
N(1)−C(4)	1.345(8)	Rh−C(13)	2.104(7)
N(2)−C(4)	1.358(7)	Rh−C(14)	2.114(7)
C(4)−Rh−Cl	87.86(17)	N(1)−C(4)−N(2)	104.3(5)
C(9)−Rh−Cl	93.5(2)	N(2)−C(5)−C(6)	114.5(5)
C(13)−Rh−Cl	162.8(2)	C(13)−C(12)−C(11)	112.9(6)
C(4)−N(1)−C(1)	124.4(5)	C(14)−C(15)−C(16)	113.6(7)

Acknowledgments

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