ORGANIC LETTERS

2001
Vol. 3, No. 3
385−388

Cyclization/Hydrosilylation of Functionalized Diynes Catalyzed by a Cationic Platinum Phenanthroline Complex

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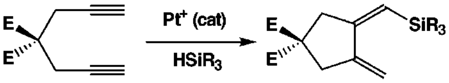
Received November 20, 2000

ABSTRACT



A 1:1 mixture of the platinum phenanthroline complex (phen)PtMe$_2$ and B(C$_6$F$_5$)$_3$ catalyzed the cyclization/hydrosilylation of functionalized 1,6- and 1,7-diynes to form silylated 1,2-dialkylidenecycloalkanes in good yield and with high *Z*-selectivity.

The cyclization/hydrosilylation of dienes, catalyzed by both cationic palladium[1] and neutral yttrocene[2] complexes, has emerged as a useful method for the synthesis of silylated cycloalkanes. Similarly, both yttrocene[3] and low-valent rhodium complexes[4] catalyze the cyclization/hydrosilylation of enynes to form silylated alkylidenecycloalkanes. In addition, several cyclization/addition protocols employing diynes are known.[5] In contrast, the cyclization/hydrosilylation of diynes, particularly 1,6-diynes, to form 1,2-dialkylidenecycloalkanes remains problematic. For example, Ni(0) complexes catalyze the cyclization/hydrosilylation of 1,7-diynes to form silylated (*Z*)-1,2-dialkylidenecyclohexanes but do not cyclize 1,6-diynes.[6] Rhodium phosphine[7] and carbonyl[8] complexes catalyze the cyclization/hydrosilylation of 1,6-diynes but these procedures suffer from several key limitations.[9] The absence of a selective and general catalyst system for the cyclization/hydrosilylation of diynes is unfortunate as the 1,2-dialkylidenecycloalkanes formed in these transformations are useful synthetic intermediates.[10] For this reason, we have been working toward the development of an efficient and general catalyst system for the cyclization/hydrosilylation of diynes. Here we report the platinum-catalyzed cyclization/hydrosilylation of functionalized 1,6-

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[4] Ojima, I.; Donovan, R. J.; Shay, W. R. *J. Am. Chem. Soc.* **1992**, *114*, 6580.

[5] (a) Trost, B. M.; Lee, D. C. *J. Am. Chem. Soc.* **1988**, *110*, 7255. (b) Onozawa, S.; Hatanaka, Y.; Tanaka, M. *Chem. Commun.* **1997**, 1229. (c) Matsuda, I.; Eshibashi, H.; Ii, N. *Tetrahedron Lett.* **1995**, *36*, 241. (d) Onozawa, S.; Hatanaka, Y.; Choi, N.; Tanaka, M. *Organometallics* **1997**, *16*, 5389. (e) Lautens, M.; Smith, N. D.; Ostrovsky, D. *J. Org. Chem.* **1997**, *62*, 8970.

[6] (a) Tamao, K.; Kobayashi, K.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 6478. (b) Tamao, K.; Kobayashi, K.; Ito, Y. Synlett **1992**, 539.

[7] Muraoka, T.; Matsuda, I.; Itoh, K. *Tetrahedron Lett.* **1998**, *39*, 7325.

[8] (a) Ojima, I.; Zhu, J.; Vidal, E. S.; Kass, D. F. *J. Am. Chem. Soc.* **1998**, *120*, 6690. (b) Ojima, I.; Donovan, R. J.; Banerji, P. *J. Org. Chem.* **1994**, *59*, 7594. (c) Ojima, I.; Kass, D. F.; Zhu, J. *Organometallics* **1996**, *15*, 5191.

[9] Rhodium phosphine complexes catalyze the cyclization/hydrosilylation of 1,6-diynes to form (*E*)-1,2-dialkylidenecyclopentanes but suffer from limited substrate scope and low yield. In addition, the *E*/*Z*-selectivity of these cyclizations was not reported.[7] Rhodium carbonyl complexes also catalyze the cyclization/hydrosilylation of 1,6-diynes but form primarily disilylated mono alkylidenecyclopentanes and silylbicyclization products.[8]

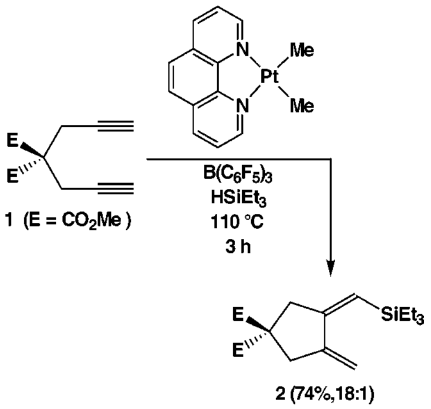
[10] Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (b) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. (c) Trost, B. M.; Hipskind, P. A.; Chung, J. Y. L.; Chan, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1502.

10.1021/ol006901u CCC: $20.00

and 1,7-diynes to form silylated 1,2-alkylidenecycloalkanes in good yield with high *Z*-selectivity.

Cationic platinum complexes containing bidentate nitrogen ligands have attracted recent interest as model compounds for the study of the platinum-catalyzed oxidation of alkanes.[11] These cationic platinum complexes are structurally and electronically similar to the cationic palladium complexes which we have employed as catalysts for the cyclization/hydrosilylation of functionalized dienes.[1] Because of this, we considered that cationic platinum complexes might also serve as active cyclization/hydrosilylation catalysts. To this end, a solution of dimethyl dipropargylmalonate (**1**), $HSiEt_3$, and a catalytic 1:1 mixture of the platinum phenanthroline complex (phen)Pt(Me)$_2$ and the Lewis acid $B(C_6F_5)_3$ in toluene was heated at 110 °C and monitored periodically by GC analysis.[12−14] Diyne **1** reacted over the course of 1.5 h to form a 20:1 mixture of (*Z*)- and (*E*)-1,1-dicarbomethoxy-3-methylene-4-(triethylsilylmethylene)cyclopentane (**2**) which together accounted for ~95% of the products.[15] Evaporation of solvent and flash chromatography of the residue on neutral alumina gave silylated cyclopentane **2** in 74% yield as an 18:1 mixture of *Z*:*E* isomers (Scheme 1).[16]

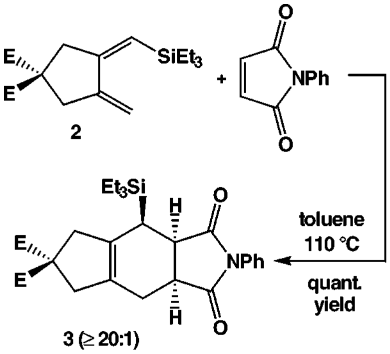
Scheme 1



A number of tertiary silanes reacted with diene **1** under platinum catalysis to give the corresponding 1,2-dialkylidenecyclopentanes in good yield and with good stereoselectivity (≥12:1) (Table 1, entries 1−3). The procedure tolerated a range of functional groups including esters, benzyl and silyl ethers, acetals, sulfonates, and amides (Table 1, entries 4−10). The procedure also tolerated propargyl substitution to give products resulting from silyl transfer to the less hindered alkyne as a mixture of *Z*/*E* isomers (Table 1, entry 11). Mixtures of (phen)Pt(Me)$_2$ and $B(C_6F_5)_3$ also catalyzed the cyclization/hydrosilylation of a 1,7-diyne to form a 1,2-dialkylidenecyclohexane in good yield and with high (26:1) *Z*-selectivity (Table 1, entry 12).

The 1,2-dialkylidenecycloalkanes formed via platinum-catalyzed diyne cyclization/hydrosilylation are active substrates for Diels−Alder cyclization.[17] For example, cyclopentane **2** (20:1, *Z*/*E*) reacted with *N*-phenylmaleimide in refluxing toluene overnight to form the tricyclic compound **3** in quantitative yield (102 ± 2%) as a single diastereomer by ^1H and ^{13}C NMR spectroscopy (≥20:1) (Scheme 2).

Scheme 2



Noteworthy is that Diels−Alder adducts such as **3** possess an allylic silyl group and are therefore potentially reactive toward a range of electrophiles.[18]

We propose a working mechanism for platinum-catalyzed diyne cyclization/hydrosilylation involving *β*-migratory insertion of an alkyne into the Pt−Si bond of platinum silyl alkyne complex **I** to form platinum alkenyl alkyne complex **II** (Scheme 3). *β*-Migratory insertion of the coordinated alkyne into the Pt−C bond of **II** could form the platinum dienyl species **III** which could oxidatively add silane to form the platinum silyl hydride intermediate **IV**.[19] C−H reductive elimination from **IV** coupled with alkyne coordination would then form diene **2** with regeneration of palladium silyl alkyne

Scheme 3

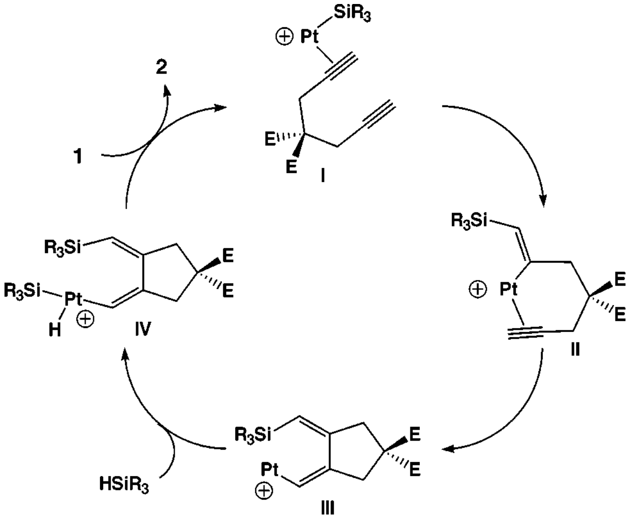


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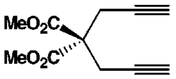
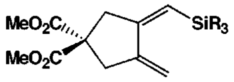
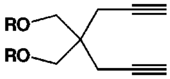
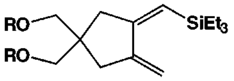
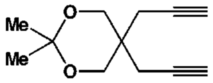
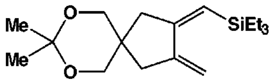
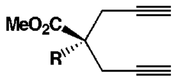
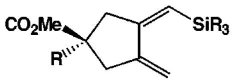
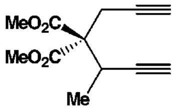
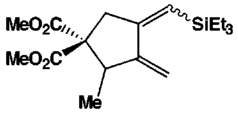
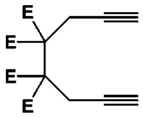
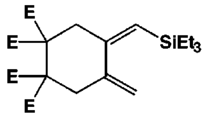
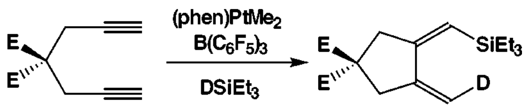
Table 1. Cyclization/Hydrosilylation of Functionalized Diynes Catalyzed by a 1:1 Mixture of (phen)PtMe$_2$ and B(C$_6$F$_5$)$_3$ in Toluene at 110 °C

entry	diene	silane	carbocycle	yield (%)[a]	E/Z[b]
					
1		HSiMe$_2$*t*-Bu		73	14:1
2		HSiMe$_2$Bn		77	12:1
3		HSi(*n*-Bu)$_3$		79	14:1
					
4	R = Pv	HSiEt$_3$		83	18:1
5	R = Bn			82	12:1
6	R = TBMS			72[c]	8:1[d]
7		HSiEt$_3$		81	13:1
					
8	R = Ph	HSi(*n*-Bu)$_3$		89	8:1
9	R = SO$_2$Me	HSiEt$_3$		71	12:1
10	R = CONMe$_2$	HSi(*n*-Bu)$_3$		68	12:1
11		HSiEt$_3$		75	1.2:1
12	 E = CO$_2$Et	HSiEt$_3$		74	26:1

[a] Yields refer to isolated material of ≥95% purity. [b] *E*/*Z* ratio determined by GC analysis of the purified material. [c] Refers to isolated yield of the Diels−Alder adduct with 4-phenyl[1,2,4]triazole-3,5-dione. [d] *E*/*Z* ratio determined by GC analysis of the crude reaction mixture.

intermediate **I**.[20] Consistent with the proposed mechanism, platinum-catalyzed reaction of **1** and DSiEt$_3$ led to the isolation of **2**-d_1 with exclusive incorporation of deuterium into the *Z* position of the exocyclic methylene group (Scheme 4).[21]

Scheme 4



1 (E = CO$_2$Me)

2-d_1 (67%, 12:1)

In summary, cationic platinum complexes generated in situ from mixtures of (phen)PtMe$_2$ and B(C$_6$F$_5$)$_3$ catalyzed the cyclization/hydrosilylation of both 1,6- and 1,7-diynes to form silylated 1,2-dialkylidenecyclopentanes and 1,2-dialkylidenecyclohexanes, respectively, in good yield and with high *Z*-selectivity. These 1,2-dialkylidenecycloalkanes are reactive

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(12) The mixture of (phen)Pt(Me)$_2$ and B(C$_6$F$_5$)$_3$ forms the active cationic catalyst in situ.[13] Comparable results were observed when the preformed cationic complex [(phen)Pt(Me)CH$_3$CN]$^+$ [MeB(C$_6$F$_5$)$_3$]$^-$ was employed as the catalyst. The individual precatalysts employed separately gave no cyclization under reaction conditions.

(13) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1996**, 1809.

(14) These catalysts were inactive toward both dienes and enynes.

(15) Addition of toluene to the precatalyst mixture prior to the diyne led to immediate darkening of the solution and low subsequent conversion. This observation suggests that the cationic platinum complex formed via methyl abstraction is unstable in the absence of a coordinating ligand such as an alkyne.

(16) The stereochemistry of both *E*-**2** and *Z*-**2** was determined by ^{1}H NOE. The remainder of the products consisted of disilylated compounds.

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(18) (a) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207. (b) Masse, C. E.; Panek, J. S. *Chem. Rev.* **1995**, *95*, 1293.

substrates for subsequent Diels–Alder cyclizations to form fused polycyclic compounds which possess an allylic silyl group.

Acknowledgment is made to the National Institutes of Health (GM59830-01) for support of this research. R.W. thanks the Camille and Henry Dreyfus Foundation and DuPont for young faculty awards and the Alfred P. Sloan Foundation for a Research Fellowship. We thank Ms. H. Annita Zhong for helpful discussions.

Supporting Information Available: Experimental procedures and spectroscopic and analytical data for relevant compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Oxidative addition of hydrosilanes to both neutral Pt(II) diphosphine[19a] and cationic Pt(II) diimine[19b] complexes has been demonstrated. (a) Pfeiffer, J.; Kickelbick, G.; Schubert, U. *Organometallics* **2000**, *19*, 62. (b) Fang, X.; Scott, B. L.; Watkins, J. G.; Kubas, G. J. *Organometallics* **2000**, *19*, 4193.

(20) Diyne **1** could also enter the catalytic cycle in the conversion of **II** to **III**. Initial formation of **I** presumably occurs via H–Si oxidative addition to a cationic Pt–Me complex followed by C–H reductive elimination.

(21) Determined by ^{1}H and ^{13}C NMR spectroscopy. Chromatographic purification of **2**-d_1 on SiO_2 led to diminished yield.