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Ruthenium-Catalyzed Cyclization of 2-Alkyl-1-ethynylbenzenes via a 1,5-Hydrogen Shift of Ruthenium−Vinylidene Intermediates

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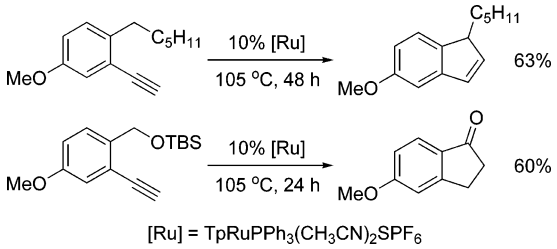
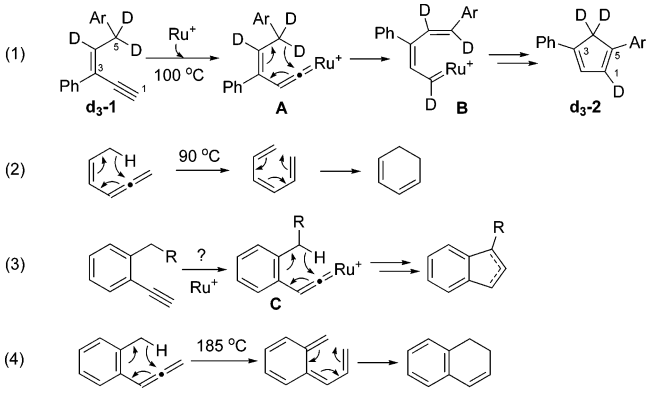
Received December 15, 2006



Catalytic cyclization of 2-alkyl-1-ethynylbenzene derivatives was implemented by $TpRuPPh_3(CH_3CN)_2PF_6$ (10 mol %) in hot toluene (105 °C, 36−100 h) to form 1-substituted-1*H*-indene and 1-indanone products; such cyclizations proceeded more efficiently for substrates bearing electron-rich benzenes. We propose that the cyclization mechanism involves a 1,5-hydrogen shift of initial metal−vinylidene intermediate.

Electrocyclization of polyenes across a benzene group occurs less readily than for an alkene group because the former leads to dearomatization of a benzene group.[1] For instance, 6-π-electrocyclization of *cis*-1,3,5-trienes normally occurs at 60−100 °C[2] whereas the same cyclization of 1,2-divinylbenzenes requires severe conditions[1] (300−350 °C). Although a 1,5-hydrogen shift is well documented for *cis*-1,3-dienes,[3,4] this process remains virtually unknown for *cis*-3-en-1-ynes before our report that $TpRuPPh_3(CH_3CN)_2PF_6$ (Tp = tris(1-pyrazoly)-borate) was an active catalyst for this cyclization to yield cyclopentadiene derivatives.[5] The mechanism of this cyclization is confirmed to involve a 1,5-sigmatropic hydrogen shift of ruthenium vinylidene intermediate **A** according to deuterium labeling studies, as depicted in Scheme 1 (eq 1). This unique

SCHEME 1



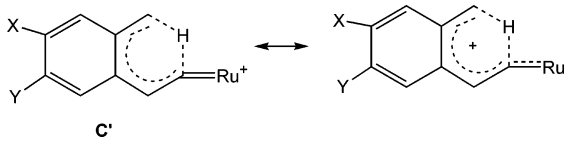
deuterium distribution of cyclopentadiene product **d_3-2** derived from 3-en-1-yne **d_3-1** cannot be rationalized according to a reaction mechanism of the Murai-type.[6] The success of this ruthenium-catalyzed cyclization actually mimics thermal cyclization of *cis*-1,2,4-hexatriene, which occurs at 90 °C (eq 2) close to the conditions (100 °C, toluene, 8−10 h) of ruthenium catalysis.

1*H*-Indene is an important building block for complex bioactive molecules.[7] To enhance the synthetic utility, in this full account, we sought to achieve catalytic cyclization of 2-alkyl-1-ethynylbenzene derivatives to form 1*H*-indene products as depicted in eq 3. This cyclization appears to be more

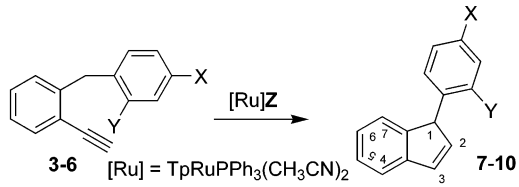
(1) Lamberts, J. J. M.; Laarhoven, W. H. *J. Org. Chem.* **1984**, *49*, 100.
(2) Okamura, W. H.; Delera, A. R. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, UK, 1991; Vol. 5, Part 6.2, p 699.
(3) (a) Robin, M. J.; Guo, Z. O.; Samano, M. C.; Wnuk, S. F. *J. Am. Chem. Soc.* **1999**, *121*, 1425. (b) Okamura, W. H.; Aurrecoechea, J. M.; Gibbs, R. A.; Norman, A. W. *J. Org. Chem.* **1989**, *54*, 4072. (c) Chandraratna, R. A. S.; Bayerque, A. L.; Okamura, W. A. *J. Am. Chem. Soc.* **1983**, *105*, 3588.
(4) (a) Alabugin, I. V.; Manoharan, M.; Breiner, B.; Lewis, F. D. *J. Am. Chem. Soc.* **2003**, *125*, 9329. (b) Kless, A.; Nendel, M.; Willsey, S.; Houk, K. N. *J. Am. Chem. Soc.* **1999**, *121*, 4524. (c) Loncharich, R. J.; Houk, K. N. *J. Am. Chem. Soc.* **1988**, *110*, 2089. (d) Hess, B. A., Jr.; Baldwin, J. E. *J. Org. Chem.* **2002**, *67*, 6025. (e) Replogle, K. S.; Carpenter, B. K. *J. Am. Chem. Soc.* **1984**, *106*, 5751.
(5) For the communication of this paper, see: Datta, S.; Odedra, A.; Liu, R.-S. *J. Am. Chem. Soc.* **2005**, *127*, 11606. The content of that work will not be repeatedly reported in this full account.
(6) Kakiuchi, F.; Murai, S. *Acc. Chem. Res.* **2002**, *35*, 826.

10.1021/jo062573l CCC: $37.00
Published on Web 04/03/2007

SCHEME 2



SCHEME 3[a,b]



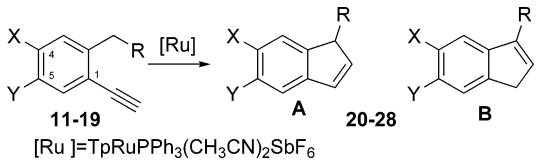
entry	benzene	catalyst	time	product (yields)
1	X = Y = H (**3**)	Z = PF_6	48 h	**7** (11%)
2	(**3**)	Z = SbF_6	36 h	**7** (64%)
3	X = CF_3, Y = H (**4**)	Z = SbF_6	36 h	**8** (46%)
4	X = OMe, Y = H (**5**)	Z = SbF_6	36 h	**9** (69%)
5	X = H, Y = OMe (**6**)	Z = SbF_6	36 h	**10** (81%)

[a] Toluene, 105 °C, 10% catalyst, [substrate] = 0.15 M. [b] Products were given after separation from a silica column.

challenging because the intermediate **A** in the preceding mechanism involves an electrocyclization across a benzene group, which will retard a 1,5-sigmatropic shift (eq 3).[8,9] Thermal cyclization of 2-alkyl-1-allenylbenzenes actually proceeds at 185 °C (eq 4),[9] at which terminal alkynes are prone to oligomerization in the presence of $TpRuPPh_3(CH_3CN)_2PF_6$.[10] One approach to facilitate this ruthenium-catalyzed cyclization is to place electron-donating groups X, Y at the benzene group to stabilize transition state geometry **C′** (Scheme 2). We envisage that the pentadienyl fragment of this transition state should have positive character because of its conjugation with the $[Ru{=}CH_2]^+$ fragment.

As shown in Scheme 3, we first examined cyclization of ethynylbenzene **3** with $TpRuPPh_3(CH_3CN)_2PF_6$ catalyst (10 mol %) in hot toluene (105 °C, 48 h), giving products in a messy mixture, from which the desired indene derivative **7** was only isolated in 11% yield. The low yield of indene **7** over a protracted period reflects the difficulty of a 1,5-hydrogen shift; we observed a serious polymerization in this case. We thought that the PF_6 salt was likely hydrolyzed by residual water to form a phosphate species during prolonged heating of the reaction solution.[11] The use of SbF_6 salt greatly enhanced the cyclization efficiency, presumably via stabilization of the catalyst; this salt led to a 64% yield of indene **7**. The SbF_6 salt also effected cyclization of ethynylbenzenes **4**−**5** bearing a trifluoromethyl and a methoxy group, respectively; the cyclized indenes **8** and **9** were obtained in respective yields of 46% and 69%. Benzene derivative **6** bearing an *o*-methoxy is very suitable for this cyclization to give the corresponding indene **10** in 81% yield.

TABLE 1. Ruthenium-Catalyzed Cyclization of 2-Alkyl-1-ethynylbenzenes



entry	benzene[a]	time, h	product (yields)[b]
1	X = H, Y = OMe R = Ph (**11**)	36	**20A** (85%)
2	X = OMe, Y = H R = Ph (**12**)	36	**21A** (75%)
3	X = H, Y = F R = Ph (**13**)	48	**22A** (55%)
4	X = F, Y = H R = Ph (**14**)	40	**23A** (66%)
5	X, Y = −OCH_2O− R = Ph (**15**)	32	**24** (**A**/**B** = 3.1, 85%)
6	X = Y = H R = *n*-C_5H_{11} (**16**)	100	**25A** (38%)
7	X = H, Y = OMe R = *n*-C_5H_{11} (**17**)	36	**26A** (63%)
8	X, Y = −OCH_2O− R = *n*-C_5H_{11} (**18**)	30	**27A** (87%)
9	X = Y = OMe R = *n*-C_3H_7 (**19**)	30	**28A** (61%)

[a] Toluene, 105 °C, 10% catalyst, [substrate] = 0.02 M. [b] Products were given after separation from a silica column.

To study the scope of this catalytic cyclization, we prepared various 2-alkyl-1-ethynylbenzenes **11**−**19** via variation of the X, Y, and R substituents of substrates; the results are depicted in Table 1. The resulting indene products **20**−**28** were exclusively obtained in 1-substituted-1*H*-indene regioisomer except species **24** containing a 3-phenyl isomer **24B**. Relative to the preceding ethynylbenzene **3**, the phenyl C(4) and C(5) methoxy groups of substrates **11** and **12** worked as an activating group, and increased the cyclized yields of indene products **21A** and **22A** in 85% and 75%, respectively. In contrast, benzene substrates **13** and **14** bearing a fluoro substituent at the same carbon showed no enhancement of the cyclization efficiency. Benzene derivative **15** bearing a methylenedioxy group was cyclized efficiently to give the desired indene **24** as a mixture of two regioisomer isomers. We further examined this cyclization on benzene species **16**−**19** bearing an *n*-pentyl or *n*-propyl group. For species **16**, completion of the cyclization required a prolonged period (100 h) in hot toluene (105 °C); the yield was only 38%. With an activating methoxy group at the phenyl C(4) and C(5) carbons, the cyclization efficiency of benzene substrates **17**−**19** was significantly improved, and the corresponding indene products **26A**−**28A** were obtained in 61−87% yields.

(7) For selected examples, see: (a) Xi, Z.; Guo, R.; Mito, S.; Yan, H.; Kanno, K.-i.; Nakajima, K.; Takahashi, T. *J. Org. Chem.* **2003**, *68*, 1252. (b) O'Brien, X. M.; Parker, J. A.; Lessard, P. A.; Sinskey, A. J. *Appl. Microbiol. Biotechnol.* **2002**, *59*, 389.

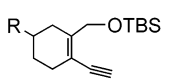
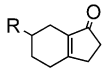
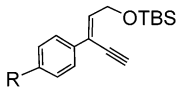
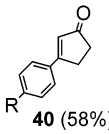
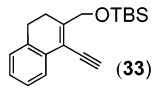
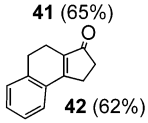
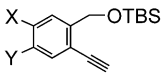
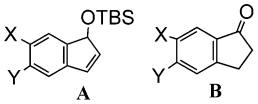
(8) For example, the 1,5-hydrogen shift proceeds rapidly for cyclopentadiene framework at ambient temperatures, but it becomes very difficult in an indene structure. See the following review: Spangler C. W. *Chem. Rev.* **1976**, *76*, 187.

(9) Heimgartner, H.; Zsindely, J.; Hansen, H.-J.; Schmid, H. *Helv. Chim. Acta* **1973**, *56*, 305.

(10) Examples for generation of catalytic vinylidene intermediates using $TpRuPPh_3(CH_3CN)_2PF_6$, see selected examples: (a) Lian, J.-J.; Odedra, A. Wu, C.-J.; Liu, R.-S. *J. Am. Chem. Soc.* **2005**, *127*, 4186. (b) Madhushaw, R. J.; Lo, C.-Y.; Su, M. D.; Shen, H.-C.; Pal, S.; Shaikh, I. R.; Liu, R.-S. *J. Am. Chem. Soc.* **2004**, *126*, 15560. (c) Shen, H.-C.; Pal, S.; Lian J.-J.; Liu, R.-S. *J. Am. Chem. Soc.* **2003**, *125*, 15762. (d) Datta, S.; Chang, C.-L.; Yeh, K.-L.; Liu, R.-S. *J. Am. Chem. Soc.* **2003**, *125*, 9294.

(11) For BF_4^-, PF_6^-, and SbF_6^- anions, these salts may undergo dissociation at elevated temperatures, $MF_{n+1}^- \rightarrow MF_n + F^-$. In this catalytic system, BF_4^- and PF_6^- are more prone to this dissociation than SbF_6^-, and residual water will cause hydrolysis of the resulting BF_3 and PF_5 species to form borate and phosphate. See: (a) Krossing, I.; Raabe, I. *Chem. Eur. J.* **2004**, *10*, 5017. (b) Krossing, I.; Raabe, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2066.

TABLE 2. Ruthenium-Catalyzed Cyclization of Siloxy-Containing 3-En-1-ynes and Ethynylbenzenes

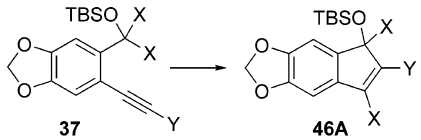
entry	substrates	time	product (yields)
			
1	R = H (**29**)	20 h	**38** (63%)
2	R = *tert*-Bu (**30**)	20 h	**39** (65%)
			
3	R = H (**31**)	24 h	**40** (58%)
4	R = OMe (**32**)	24 h	**41** (65%)
5	 (**33**)	24 h	 **42** (62%)
			 **A** **B**
6	X = Y = H (**34**)	48 h	**43B** (38%)
7	X = H, Y = OMe (**35**)	24 h	**44B** (55%)
8	X = OMe, Y = H (**36**)	24 h	**45A** (78%)
9	X , Y = -OCH_2O- (**37**)	24 h	**46A** (31%), **46B** (39%)
10	**37**	48 h	**46A** (8%), **46B** (61%),

[a] 105 °C, toluene, 10% catalyst, [substrate] = 0.02 M. [b] Products were given after separation from a silica column.

The scope of our previous ruthenium-catalyzed cyclization of *cis*-en-1-ynes is restricted to unfunctionalized substrates.[5] Table 2 manifests the synthetic values of this new cyclization, which provides cyclopentenones, 1*H*-1-indanones, or 1*H*-1-indenols from *cis*-en-1-ynes **29**−**33** and 2-alkyl-1-ethynylbenzenes **34**−**37** bearing a siloxy group. In these reactions, a dilute solution of substrate (0.02 M) was used to reduce polymerization of alkyne substrates. The cyclization of 3-en-1-ynes **29**−**33** was completed in short periods (20 h) in hot toluene (105 °C), and gave cyclopentenone derivatives **38**−**42** in reasonable yields (58−65%, entries 1−5). In the absence of a methoxy group, cyclization efficiency of ethynylbenzene **34** was low over a 48-h period to give its cyclized 1-indanone **43B** in 38% yield. For electron-rich benzenes **35**−**37**, their phenyl methoxy groups facilitate the cyclization, and gave 1-indanones **44B** and **45A** and 1-siloxyindenes **46A** and **46B** with better yields (entries 7−9). The results in entry 10 suggest that 1-indanone **46B** seems to arise from 1-siloxyindene **46A** catalyzed by $TpRuPPh_3(CH_3CN)_2SbF_6$. In a separate experiment, we confirmed that treatment of 1-siloxyindene **46A** with this ruthenium catalyst (10 mol %) in hot toluene (105 °C, 24 h) produced 1-indanone **46B** in 53% yield in addition to unreacted indene **46A**(35%), whereas 1-siloxyindene **46A** remained unreacted if it was heated alone in toluene (105 °C, 24 h).

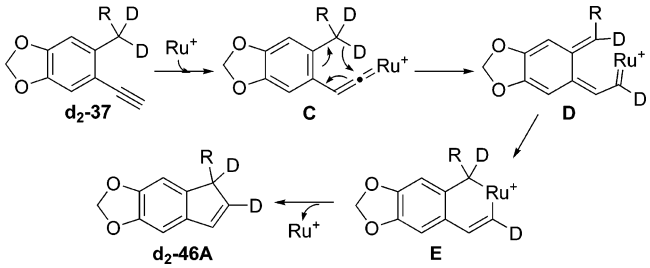
We performed deuterium-labeling experiments to characterize the mechanism of cyclization. As depicted in Scheme 4, ethynylbenzene **37** bearing an alkynyl deuterium produced its cyclized 1*H*-indene **46A** with deuterium content 65% at its indenyl C(3) carbon (entry 1), indicative of a 1,2-hydrogen shift.[12] The loss of deuterium contents in this case is caused by the exchange of residual water with alkynylmetal hydride species, which was a preceding intermediate for metal vinylidene intermediates.[12] For compound **37** bearing a deuterated benzyl group, its resulting indene **46A** has full deuterium content each at the C(1) and C(2) carbons, respectively. In entry (2), we did not obtain indanone **46B** from ruthenium-catalyzed isomerization of indene **46A,** likely due to the kinetic isotopic effect.[13]

SCHEME 4



37	**46A**
(1) X = H. Y = 0.95D	X = Y = H Z = 0.65D
(2) X = 1.0D, Y = 1.0 H	X = 1.0D, Y = 1.0D Z = 1.0 H

SCHEME 5

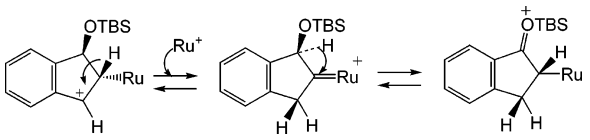


Scheme 5 shows a plausible mechanism to rationalize deuterium-labeling experiments as well as the results in Tables 1 and 2. The distribution of cyclized product **d_2-46A** has a distinct deuterium distribution from those of **d_2-2** because of different structural frameworks. The deuterium labeling experiment in Scheme 4 (entry 1) indicates the involvement of ruthenium−vinylidene species **C**, which undergoes a 1,5-hydrogen shift to give ruthenium-containing 1,3,5-hexatriene **D**. A subsequent 6-π-electrocyclization[2] of species **D** is expected to generate ruthenium-containing cyclohexadiene **E**, which undergoes reductive elimination to produce the observed 1-substituted-1*H*-indene **46A** rather than their 3-substituted-indene isomers. This proposed mechanism rationalizes not only the preceding deuterium-labeling experiments but also the observed indene regioselectivity depicted in Table 1.

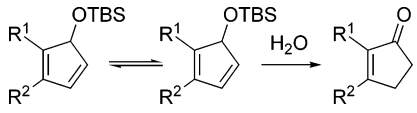
According to this proposed mechanism, the presence of an electron-donating group at the phenyl X and Y of substrates is expected to enhance the cyclization efficiency because of their stabilization effect on transition state structure **C′** during the hydrogen shift. This speculation is consistent with our observation that methoxy derivatives **11**, **12**, **15**, and **17**−**19** are much more efficient in the cyclization than their unsubstituted benzene analogues **3** and **16**, and a similar trend was observed in Table

(12) Bustelo, E.; Carbo, J. J.; Lledos, A.; Mereiter, K.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **2003**, *125*, 3311.

(13) We propose that the ruthenium-catalyzed transformation of 1-siloxy-1*H*-indenes into 1-indanones presumably proceeds via a sequential 1,2-hydride shift of intermediate. The discussion of this mechanism is provided in the Supporting Information.



SCHEME 6

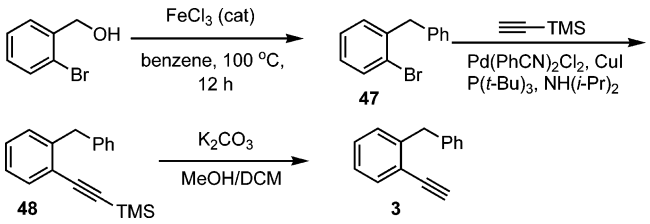


2. The formation of cyclopentenones from 5-siloxy-3-en-1-ynes **29**−**33** is not surprising because a 1,5-sigmatropic shift occurs rapidly on a cyclopentadiene framework[3,4] at ambient temperatures as depicted in Scheme 6. This shift should be very difficult for indene structure at 100 °C but we observed a transformation of 1-siloxy-1*H*-indene **46A** into 1-indanone **46B** catalyzed by $TpRuPPh_3(CH_3CN)_2SbF_6$ (vide infra). We tentatively proposed that this isomerization is caused by a sequential 1,2-hydride shift of carbocationic intermediate **H**,[14] and the speculated mechanism is provided in the Supporting Information.

In summary, we report from this investigation the feasibility of a through-benzene 1,5-hydrogen shift activated by a cationic ruthenium−vinylidene intermediate. This new key step allows catalytic cyclization of 2-alkyl-1-ethynylbenzene derivatives to form 1-substituted-1*H*-indene products. This proposed mechanism rationalizes not only key deuterium-labeling experiments but also the observed indene regioselectivity. The synthetic value of this new cyclization is manifested by its efficient synthesis of cyclopentenones, 1*H*-1-indanones, and 1*H*-1-indenols. Further use of this new method to construct the complex carbocyclic framework is under current investigation.

Experimental Section

(1) Representative Procedure for Preparation of 2-Alkyl-1-Ethynylbenzenes: (A) Synthesis of 1-Benzyl-2-ethynylbenzene (3).



(a) Synthesis of 1-Benzyl-2-bromobenzene (47). In a pressure tube, 2-bromobenzyl alcohol (1.87 g, 10.0 mmol) and $FeCl_3$ (10 mol %, 0.05 mmol) were dissolved in benzene (20 mL). After being stirred for 12 h at 100 °C the reaction mixture was passed though short silica pad with ether as eluent. Solvent was removed under reduced pressure and residue was subjected to column to afford **47** (1.61 g, 6.5 mmol) in 65% yield.

(b) Synthesis of ((2-Benzylphenyl)ethynyl)trimethylsilane (48). To a dry toluene (20 mL) solution of $Pd(PhCN)_2Cl_2$ (36 mg, 0.11 mmol) and CuI (21 mg, 0.11 mmol) was added P(*t*-Bu)$_3$ (44 mg 0.22 mmol), HN(*i*-Pr)$_2$ (0.47 g, 4.69 mmol), bromo compound **47** (0.89 g, 3.61 mmol), and trimethylsilyl acetylene (0.42 g, 4.33 mmol), and this mixture was stirred at room temperature for 10 h. The reaction mixture was diluted with hexane (40 mL), filtered through a small silica pad, concentrated, and purified by flash chromatography, to yield the desired product **48** (0.81 g, 85%) as a colorless oil.

(c) Synthesis of 1-Benzyl-2-ethynylbenzene (3). To a methanol/dichloromethane solution (20 mL, 2:1, v/v) of **48** (0.81 g, 3.06 mmol) was added K_2CO_3 (0.507 g, 3.67 mmol), and resulting mixture was stirred at 25 °C for 2 h. The mixture was quenched with water, and the organic layer was extracted with ether (3 × 20 mL), washed with saturated NaCl solution, dried over $MgSO_4$, and concentrated under reduced pressure. The residues were chromatographed on a silica column to afford pure **3** (0.54 g, 2.81 mmol) in 92% yields. IR (neat, cm^{-1}): 2952 (s), 2103 (w), 1599 (s). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 (d, 1 H, J = 7.8 Hz), 7.33−7.16 (m, 8 H), 4.23 (s, 2 H), 3.29 (s, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 143.6, 140.4, 132.8, 129.3, 128.9, 128.3, 126.0, 121.7, 82.5, 81.1, 39.9. HRMS calcd for $C_{15}H_{12}$ 192.0939, found 192.0939.

(2) Representative Procedures for Catalytic Reaction: (A) Ruthenium-Catalyzed Synthesis of Indene 7. To a toluene solution (0.15 M) of ethynyl benzene **3** (100 mg, 0.52 mmol) was added $TpRuPPh_3(CH_3CN)_2SbF_6$ (46 mg, 0.052 mmol), and the mixture was heated at 105 °C for 36 h. The reaction mixture was passed through a short silica pad with hexane as eluent to remove catalyst. The solvent was removed under reduced pressure and the residue was chromatographed on a silica column to afford indene **7** (62 mg, 32 mmol, 62%) as a colorless oil. IR (neat, cm^{-1}): 3068 (s), 2885 (w), 1610 (s). ^{1}H NMR (600 MHz, CD_2Cl_2): δ 7.38 (d, 1 H, J = 7.2 Hz), 7.26−7.19 (m, 3 H), 7.13−7.08 (m, 2 H), 6.90 (s, 1 H), 6.58 (s, 1 H), 4.61 (s, 1 H). ^{13}C NMR (150 MHz, CD_2Cl_2): 148.7, 144.5, 140.1, 139.9, 131.9, 129.1, 128.1, 127.2, 125.6, 124.2, 121.6, 56.9. HRMS calcd for $C_{15}H_{12}$ 192.0939, found 192.0939.

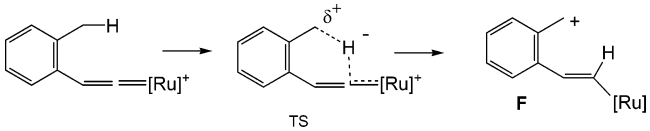
(B) Ruthenium-Catalyzed Cycloisomerization of Siloxy-Contanining 3-En-1-ynes: Synthesis of Cyclopentenone 38. To a toluene solution (0.02 M) of enyne **29** (100 mg, 0.40 mmol) was added $TpRuPPh_3(CH_3CN)_2SbF_6$ (36 mg, 0.04 mmol), and the mixture was heated at 105 °C for 20 h. The solution was passed through a short silica column (ether) to remove catalyst. Solvent was removed under reduced pressure and column chromatography on silica gel (hexane:EtOAc, 10:1) afforded pure cyclopentenone **38** (34 mg, 0.25 mmol, 63%). IR (neat, cm^{-1}): 2930 (w), 2850 (w), 1695 (s), 1645 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.46−2.40 (m, 2 H), 2.31 (t, 2 H, J = 4.4 Hz), 2.29−2.25 (m, 2 H), 2.08−2.03 (m, 2 H), 1.69−1.63 (m, 2 H), 1.61−1.56 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.0, 173.6, 138.6, 34.4, 30.0, 28.5, 22.0, 21.6, 19.9. HRMS calcd for $C_9H_{12}O$ 136.0888, found 136.0890.

Acknowledgment. The authors wish to thank National Science Council, Taiwan, for support of this work.

Supporting Information Available: Mechanistic discussion of the isomerization between species **46A** and **46B**,[14] experimental procedures for the synthesis of 2-alkyl-1-ethynylbenzene substrates, NMR spectra, and spectral data for compounds **4**-**46B**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO062573L

(14) Sames et al. recently reported a unique Lewis acid-catalyzed hydroalkylation of electron-deficient alkenes,[15] indicating the feasibility of a through-space 1,5-hydride shift. We cannot exclude this mechanism because our experimental results in this work are also compatible with a through-space 1,5-hydride shift. We prefer the classical 1,5-hydrogen shift because it was reported for 2-alkyl-1-allenylbenzenes at 185 °C.[9]



(15) Pastine, S. J.; McQuaid, K. V.; Sames, D. *J. Am. Chem. Soc.* **2005**, *127*, 12180.