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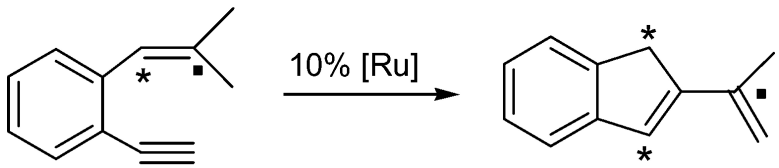

*C and ▪C = ^{13}C-labeled carbon

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Ruthenium-Catalyzed Cycloisomerization of *o*-(Ethynyl)phenylalkenes to Diene Derivatives via Skeletal Rearrangement

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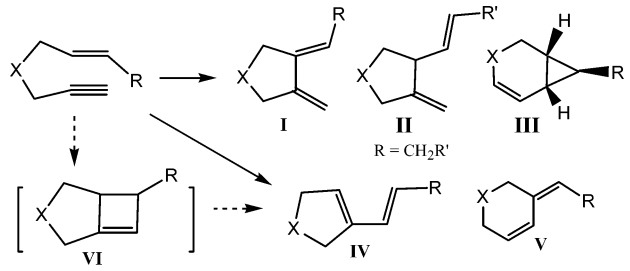
Abstract: Treatment of a series of 2′,2′-disubstituted (*o*-ethynyl)styrenes with $TpRu(PPh_3)(CH_3CN)_2PF_6$ (10 mol %) in benzene (80 °C, 12−18 h) efficiently gave 2-alkenyl-1*H*-indene derivatives. This catalytic reaction represents an atypical enyne cycloisomerization with skeletal rearrangement of starting enyne, where the C═C bond is completely cleaved and inserted by the terminal alkynyl carbon. The reaction mechanism was elucidated by a series of deuterium and ^{13}C labeling experiments, as well as by changing the substituents at the phenyl moieties. The mechanism is proposed to involve the following key steps: 5-*endo-dig* cyclization of ruthenium-vinylidene intermediate, a nonclassical ion formation, and the "methylenecyclopropane-trimethylenemethane" rearrangement.

Introduction

Metal-catalyzed cycloisomerization of organic enynes can be implemented by electrophilic metal species to give various carbo- and heterocyclic compounds **I**−**V** (Scheme 1).[1] Among these cyclic products, metathesis-type product **IV** is particularly interesting in mechanistic considerations because the carbon−carbon double bond of the enyne is completely cleaved.[2] Furthermore, outer diene **IV** is a useful building block for the construction of complex molecules through Diels−Alder cycloaddition. Besides the Grubbs' catalyst $Cl_2RuL(PCy_3)$═CHPh (L = PCy_3, imidazolylidene),[1b,2] $[RuCl_2(CO)_3]_2$,[3] $GaCl_3$,[4] $PtCl_2$,[5] $Pt(dppb)(PhCN)_2^+$,[6] $[Au(PPh_3)^+]$,[7] and palladacyclopentadiene[8] complexes have also been shown to be effective in the catalytic production of outer dienes (**IV**) from α,ω-enynes. In such a metathesis-type reaction, $PtCl_2$,[2] $Pt(dppb)(PhCN)_2^+$,[6] $GaCl_3$,[4] and $[Au(PPh_3)^+]$[7] were proposed to trigger the skeletal rearrangement of α,ω-enynes via the formation of nonclassical carbocations; cyclobutene species (**VI**) were thought to be precursors to the outer dienes (**IV**). Cycloisomerization of enynes to give novel diene skeletons is a fascinating subject with regard to both synthetic and mechanistic aspects.

Scheme 1



To emphasize the electrophilic nature of metal salts, we selected $TpRu(PPh_3)(CH_3CN)_2PF_6$ (**1**) as a catalyst[9] for the

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(2) Recent reviews for enyne metathesis using Grubbs' catalysts, see: ref 1b and (a) Mori, M. *Top. Organomet. Chem.* **1998**, *1*, 133. (b) Poulsen, C. S.; Madsen, R. *Synthesis* **2003**, 1. (c) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413.
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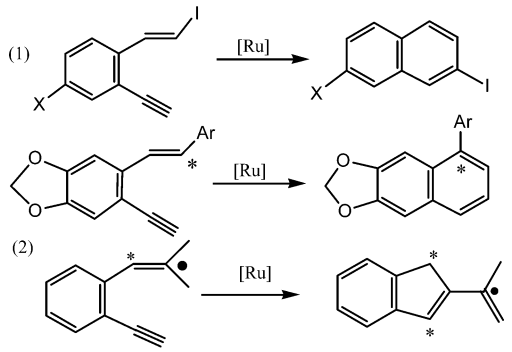
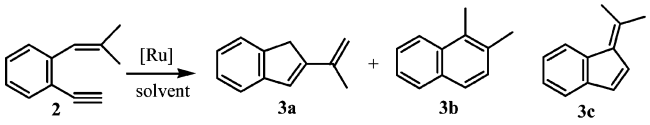
Scheme 2 [a]



[a] *C and •C = ^{13}C-labeling carbon.

Table 1. Catalytic Cyclization of *o*-(Ethynyl)styrenes in Various Solvents



entry	solvent[a]	temp (h)	3a[b]	3b	3c
1	toluene	80 °C (12 h)	41%	36%	10%
2	DMSO	80 °C (24 h)	21%	45%	3%
3	DMF	80 °C (24 h)	40%	46%	4%
4	DCE	80 °C (24 h)	47%	45%	
5	3-pentanone	80 °C (18 h)	50%	34%	
6	1,4-dioxane	80 °C (18 h)	57%	28%	
7	DME	80 °C (18 h)	61%	24%	
8	benzene	80 °C (12 h)	68%	22%	
9	benzene	70 °C (30 h)	76%	11%	

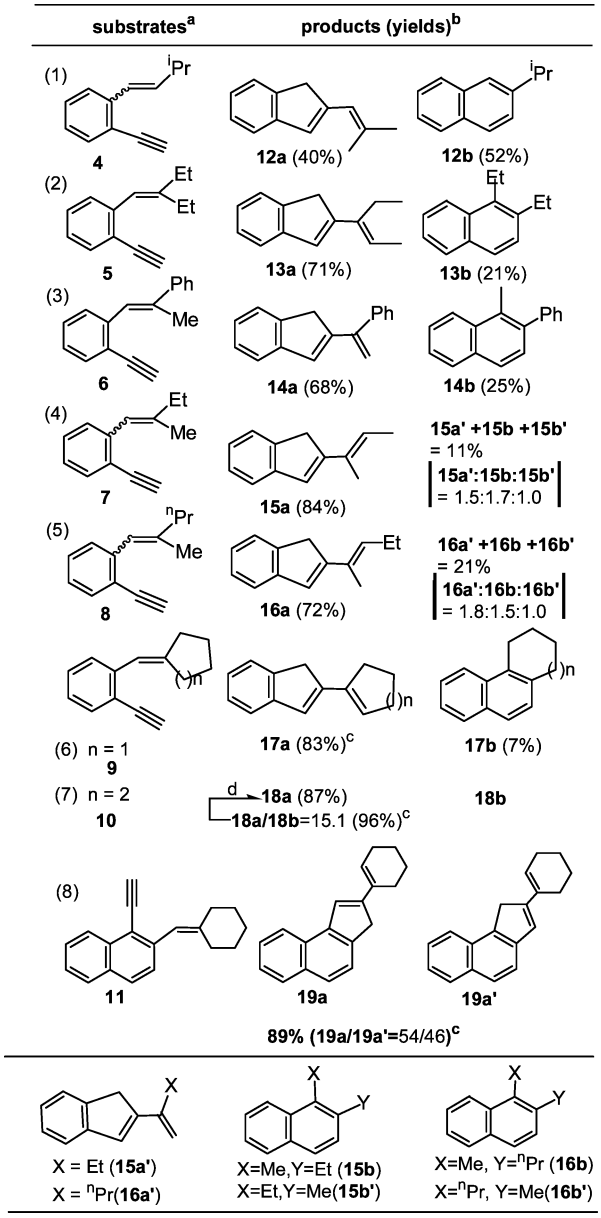
[a] 10 mol % catalyst, [substrate] = 0.65 M. [b] Yields were reported after separation from the silica column.

cycloisomerization reaction. We envision that the cationic nature and two labile CH_3CN groups of this catalyst may generate a reactive carbocation to induce the migration of C−H and C−C σ bonds. Recently, we reported the aromatization of *o*-(ethynyl)-styrenes with a 1,2-shift of iodo and aryl substituent (Scheme 2, eq 1) with the use of catalyst **1**.[9c] In this study, we report new findings with *o*-(ethynyl)styrenes that undergo ruthenium-catalyzed 5-*endo-dig* cyclization to give 2-alkenyl-1*H*-indenes as depicted in Scheme 2 (eq 2). This catalytic reaction involves new skeletal rearrangement of the starting enynes with cleavage of the olefin C−C double bond according to the ^{13}C-labeling experiments.

Results and Discussion

To avoid the formation of naphthalene species, we studied the cycloisomerization of 2′,2′-disubstituted *o*-(ethynyl)styrenes (**2**) to circumvent the undesired 6-*endo-dig* cyclization through increased steric hindrance. As shown in Table 1, treatment of enyne **2** with ruthenium catalyst (10 mol %) in hot toluene (80 °C, 24 h) gave 2-alkenylindene derivative **3a** in 41% yield in addition to naphthalene **3b** (36%) and isopropylidene-1*H*-indene **3c** (10%). The ^{1}H NMR spectra of compound **3a** show a singlet at δ 6.75 ppm, indicative of the indenyl-C(3) proton resonance. The structure of **3a** was also supported by the ^{1}H NMR NOE spectra (see Experimental Section). In this skeletal rearrangement, the carbon−carbon double bond of enyne **2** seemed to be cleaved and inserted by the terminal alkyne carbon. The yields of desired diene **3a** strongly depended on the reaction solvents. As shown in Table 1, DMSO showed an adverse effect, whereas other solvents, including DMF, dichloroethane (DCE), 3-pentanone, and 1,4-dioxane, gave desired diene **3a** with yields increasing from 40% to 68%. The yields of **3a** were as high as 61−68% for dimethoxyethane (DME) and benzene, and up to 76% in benzene at 70 °C (30 h).

Table 2. Cyclization of Various *o*-(Ethynyl)styrenes

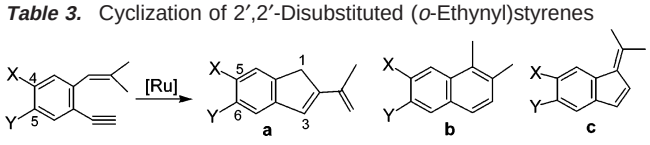


[a] 10 mol % catalyst, [substrate] = 0.65 M, benzene, 80 °C, 18 h. [b] Yields were reported after separation from the silica column. [c] The reaction was performed at 75 °C, 30 h. [d] Recrystallization from hexane.

Table 2 shows the effects of alkenyl substituents on product selectivity. The catalytic reactions were performed with 10% catalyst **1** in hot benzene (80 °C, 18 h). The monosubstituted isopropyl derivative **4** led to the production of 2-alkenyl-1*H*-indene **12a**, which was obtained in 40% yield. The desired indenes **13a** and **14a** were obtained in yields of 68−71% through the cyclization of 2′-ethylbut-1′-enyl **5** and 2′-methylstilbyl **6**. The structures of indenes **12a**, **13a**, and naphthalene **14b** were confirmed by ^{1}H NOE spectra.[10] The catalytic reactions of

(10) ^{1}H NMR NOE maps of compounds **12a**−**13a**, **13b**, **27a**−**29a**, and **32a** were shown in the Supporting Information.

Table 3. Cyclization of 2′,2′-Disubstituted (*o*-Ethynyl)styrenes



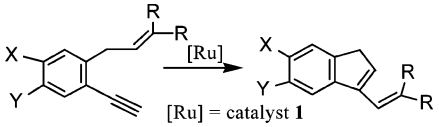
substrates[a]	products[b] (yields)
(1) X = F, Y = H (**20**)	**27a** (91%)[c]
(2) X = Cl, Y = H (**21**)	**28a** (85%)[c]
(3) X = OMe, Y = H (**22**)	**29a** (75%), **29b** (21%)
(4) X = NO_2, Y = H (**23**)	**30a** (3%),[c] **30b** (74%), **30c** (6%)
(5) X = H, Y = F (**24**)	**27a** (X = F, Y = H, 43%)[c] **31b** (50%), **31c** (2%)
(6) X = H, Y = ^{t}Bu (**25**)	**32a** (X = ^{t}Bu, Y = H; 73%) **32b** (X = H, Y = ^{t}Bu; 21%)
(7) X = H, Y = OMe (**26**)	**33b** (89%)

[a] 10 mol % catalyst **1**, [substrate] = 0.65 M, benzene, 80 °C, 18 h. [b] Yields were reported after separation from the silica column. [c] There structures represent the major regioisomers; isomeric ratio 5:1 for **27a** and 4.8:1 for **28a**, 4:1 for **30a**.

substrates **7** and **8** bearing 2′-methylbut-1′-enyl and 2′-methylpent-1′-enyl substituents, respectively, gave indenes **15a** and **16a** in respective isolated yields of up to 84% and 72% (entries 4, 5). A mixture of indenes **15a′** (or **16a′**) and naphthalene species **15b** (or **16b**) and **15b′** (or **16b′**) was produced in small proportions (11−21%) that were not separable on a silica column. The 2′,2′-cyclopentylidene species **9** gave indene **17a** and naphthalene **17b** in respective yields of 83% and 7% at 75 °C (30 h). The cyclohexylstyrene analogue **10** afforded a combined 96% yield of **18a**/**18b** with high selectivity (**18a**/**18b** = 15.1) and gave pure indene **18a** in 87% yield after crystallization from hexane. The naphthalene species **11** was very selective for indenes and gave an 89% yield of products **19a** and **19a′** (**19a**/**19a′** = 54/46) with a negligible amount of naphthalene byproduct.

Table 3 shows the effects of the 4,5-phenyl substituents on the yields of the desired 2-alkenyl-1*H*-indenes **27a**−**32a**. The desired indene derivatives **27a** and **28a** were obtained in excellent yields (85−91%) with the 4-fluoro and 4-chloro substituents **20** and **21** (entries 1,2) without the formation of naphthalenes. Two regioisomers were detectable for **27a** (5:1), **28a** (4.8:1), and **30a** (4:1); the structures of the major (or sole) regioisomers are shown in Table 3. No adverse effect was observed for 4-methoxy substituent **22**, which gave indene **29a** in 75% yield. Styrene **23** bearing a nitro group exclusively gave naphthalene **30b** (74%), along with a small amount of desired indene **30a** (3%) and isopropylidene derivative **30c** (6%). A less pronounced effect was seen when 5-phenyl substituents were replaced with fluoro, *tert*-butyl, and methoxy groups (entries 5−7). Only the *tert*-butyl derivative **25** (entry 6) gave indene **32a** in a reasonable yield (73%), whereas the methoxy derivative **26** produced only naphthalene **33b** (89%). Notably, the product obtained with 5-fluoro derivative **24** (entry 5) was identical to that produced from its 4-substituted analogue **20** (entry 1). The *tert*-butyl group of indene product **32a** was situated at the indenyl C(5)-carbon rather than the expected C(6)-carbon. The ^{1}H-NOE spectra of compounds **27a**, **28a**, **29a**, and **32a** were examined to identify the 2-alkenylindene structures.[10] The results in Table 3 reveal that the formation of desired 2-vinylindenes is favored by π-donor substituents at the phenyl C4 carbon but disfavored by the same substituents at the C5-carbon.

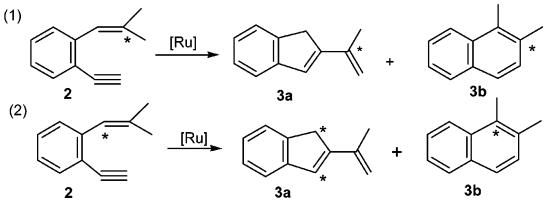
Table 4. Cyclization of Various 1-(*o*-Ethynyl)phenyl-prop-2-enes



substrates[a]	products[b] (yields)	substrates	products (yields)
(1) X = Y = H, R = Me (**34**)	**41** (81%)	(5) X = H, Y = F, R = Me (**38**)	**44** (88%)
(2) X = Y = H, R = Et (**35**)	**42** (83%)	(6) X = H, Y = Cl, R = Me (**39**)	**45** (84%)
(3) X = Y = H, *cis*-R = H, *trans*-R = ^{n}Bu (**36**)	N.R.	(7) X = H, Y = OMe, R = Me (**40**)	**46** (65%)
(4) X = Me, Y = H, R = Me (**37**)	**43** (75%)		

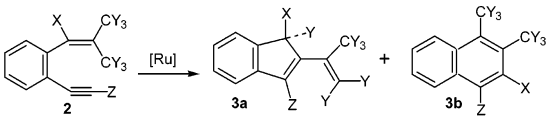
[a] 10 mol % catalyst **1**, [substrate] = 0.65 M, DMF, 100 °C, 12 h. [b] Yields were reported after separation from the silica column.

Scheme 3 [a]



[a] *C = ^{13}C-enriched carbon. [Ru] = 10 mol % catalyst **1**.

Scheme 4 [a]



2	3a	3b
(1) X = Y = 1.0 H, Z = 1.0 D	X = 0.40D, Y = 1.0H, Z = 0.44 D	X = Y = 1.0H, Z = 0.71D
(2) X = Y = 1.0 H, Z = 1.0 H	X = 0.45D, Y = 1.0D, Z = 0.55 D	—

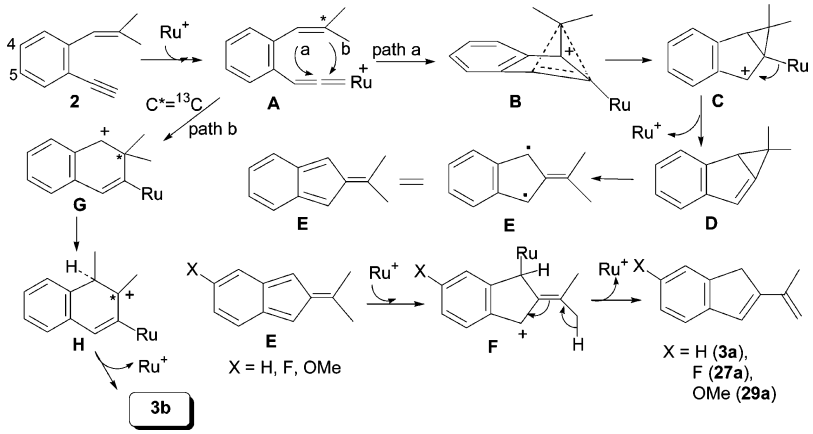
[a] [Ru] = 10 mol % catalyst **1**.

We prepared various 1-(*o*-ethynyl)phenylprop-2-enes **34**−**40** to examine the activity of catalyst **1** (10 mol %). The results are shown in Table 4. Cyclization of enyne **34** in hot DMF (100 °C, 12 h) gave the metathesis-type product **41** in 81% yield. Treatment of enyne **34** with 5 mol % Grubbs' catalyst Cl_2RuL-(PCy_3)=CHPh (L = imidazolylidene) gave the same compound (benzene, 80 °C, 10 h) in 93% yield. The metathesis reaction worked well with 2,2-dimethyl-1-propene species **35**, but failed to proceed with 1,2-disubstituted alkene derivative **36**. The catalytic reaction tolerated a change in the X and Y substituents of the 4- and 5-phenyl carbons of substrates **37**−**40** and gave 3-alkenyl-1*H*-indene products **43**−**46** in good yields.

The formation of 2-alkenyl-1*H*-indenes in Tables 1−3 shows an interesting skeletal rearrangement that may be caused by two different reorganizations: the cleavage of an ethenyl carbon−carbon double bond or an ethynyl triple bond. We performed ^{13}C-labeling experiments to elucidate the rearrangement mechanism. We prepared[11] a ^{13}C-enriched sample **2** in which the isopropylidene carbon contains a 10% ^{13}C-content (Scheme 3, eq 1). The resulting product **3a** shows a ^{13}C NMR signal only at the C(1′)-ethenyl tertiary carbon, whereas the naphthalene

(11) The synthetic procedures for the ^{13}C- and ^{2}H-labeled **2**, and ^{1}H, ^{13}C NMR and HMBC spectra of the ^{13}C- and ^{2}H-labeled **3a** and **3b**, were described in the Supporting Information.

Scheme 5

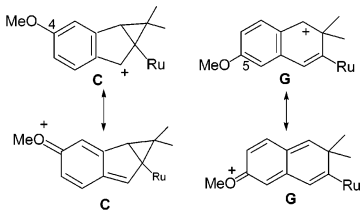


product **3b** has a ^{13}C-carbon only at the C(2)-position according to the HMBC spectra.[11] We also sought to find a method[11] for the synthesis of another ^{13}C-labeled sample **2** (eq 2) containing a 14% ^{13}C-content at the ethenyl C(1′)-carbon. This compound gave 2-vinyl-1*H*-indene species **3a** with equal ^{13}C contents (ca. 7.0%) at the indenyl C(1) and C(3) carbons, whereas naphthalene **3b** showed a ^{13}C-enriched NMR signal only at the C(1) carbon.[12] These ^{13}C NMR results not only indicate that the skeletal rearrangement is caused by cleavage of a carbon−carbon double bond, but also reveal an equal ^{13}C-content for the indenyl C(1) and C(3) carbons of species **3a**.

We also performed deuterium-labeling experiments to better understand the reaction mechanism. As shown in Scheme 4 (entry 1), the alkynyl deuterium of compound **2** is transferred equally to the C(1) and C(3) hydrogens of indene product **3a**, and exclusively to the C4-hydrogen of naphthalene **3b**. One of the six methyl deuterium atoms of enyne **2** migrates evenly to the C(1) and C(3) carbons of indene **3a** (entry 2). Notably, the C(1)H/C(3)H proton ratio of indene **3a** is ca. 2.85 and significantly higher than the equilibrium value 2.35 determined by a separate experiment.[13] Similarly, the C(1)D/C(3)D deuterium ratio of indene **3a** is ca. 2.63, higher than the equilibrium value 1.72.[13] These results suggest that the 1,3-hydrogen (or proton) shift of species **3a** alone is not responsible for the equal ^{13}C-contents at its indenyl C(1) and C(3) carbons shown in Scheme 3 (eq 2).

Scheme 5 shows a plausible mechanism to account for the formation of 2-vinyl-1*H*-indene **3a**. On the basis of the 1,2-shift of the alkynyl deuterium of species **2**, we propose that a ruthenium species readily reacts with alkyne **2** to form a ruthenium-vinylidenium intermediate **A**,[14,15] which undergoes 5-*endo-dig* cyclization (path a) to give tertiary carbocation **B** (Scheme 3). A through-space carbon−carbon bond formation[16,17] of species **B** gives cyclopropylbenzyl cation **C**, which is subsequently transformed into a fulvene species **E** according to the "methylenecyclopropane-trimethylenemethane" rearrangement.[18,19] Further transformation of fulvene species **E** to observed indene products **3a**, **27a**, and **29a** (X = H, F, and OMe) can be achieved by this cationic ruthenium species via the generation of benzyl cation **F**. According to this mechanism, the benzyl cation is preferbably located in a *para*-position relative to electron-donating group X, and ultimately gives the observed major (or sole) regiosiomer **27a** and **29a** (X = F, OMe). The formation of the nonclassical carbocation **C** is likely to occur because the empty π-orbital of species **B** overlaps well with the π-orbital of the indenyl double bond.[16,17]

Scheme 6



According to the ^{13}C-labeling results (Scheme 3, eq 1), we propose that naphthalene product **3b** is derived from the 6-*endo-dig* cyclization[15] (path b) of species **A** via generation of the benzyl cation **G**. The corresponding 5-*endo-dig* cyclization will give the naphthalene product **3b** with the ^{13}C-labeled NMR signal at the naphthyl C(1) carbon[9c] rather than at the observed C(2) carbon. A subsequent 1,2-methyl shift of intermediate **G** generates 1,2-dimethylnaphthalenium **H**, and finally gives the observed product **3b**.

The chemoselectivity of 3-alkenyl-1*H*-indenes and naphthalenes relies on the stability of intermediate **C** and **G**. π-Donor substituents at the 4-phenyl carbon of *o*-(ethynyl)styrenes help to stabilize the benzyl cation species **C** via electron conjugation in its resonance structure as depicted in Scheme 6, while the same groups at the 5-phenyl carbon of *o*-(ethynyl)styrenes preferably stabilize the naphthyl cation **G**. This hypothesis is

(12) In the ^{2}H and ^{13}C-labeling experiments in Schemes 3 (eq 2) and 4, we purified the crude sample through flash chromatography on a short silica column and obtained a mixture of indene **3a** and naphthalene **3b**. This sample allowed a precise measurement of the deuterium contents of compounds **3a** and **3b** because their NMR peaks were well separated. We found a loss of deuterium content of indene **3a** while we were trying to separate this compound from naphthalene **3b** on a long silica column.

(13) For indene **3a**, the equilibrium ratio 2.35 of the C(1)H/C(3)H content is estimated by treatment of this sample containing C(1)H/C(3)H = 2.85 with Et_3N catalyst (10 mol %) in dry THF. The theoretic value is 2.39 calculated for the sp^3- and sp^2-hybridized C−H vibration frequencies (T = 80 °C). The equilibrium C(1)D/C(3)D value 1.72 was determined in a similar experiment.

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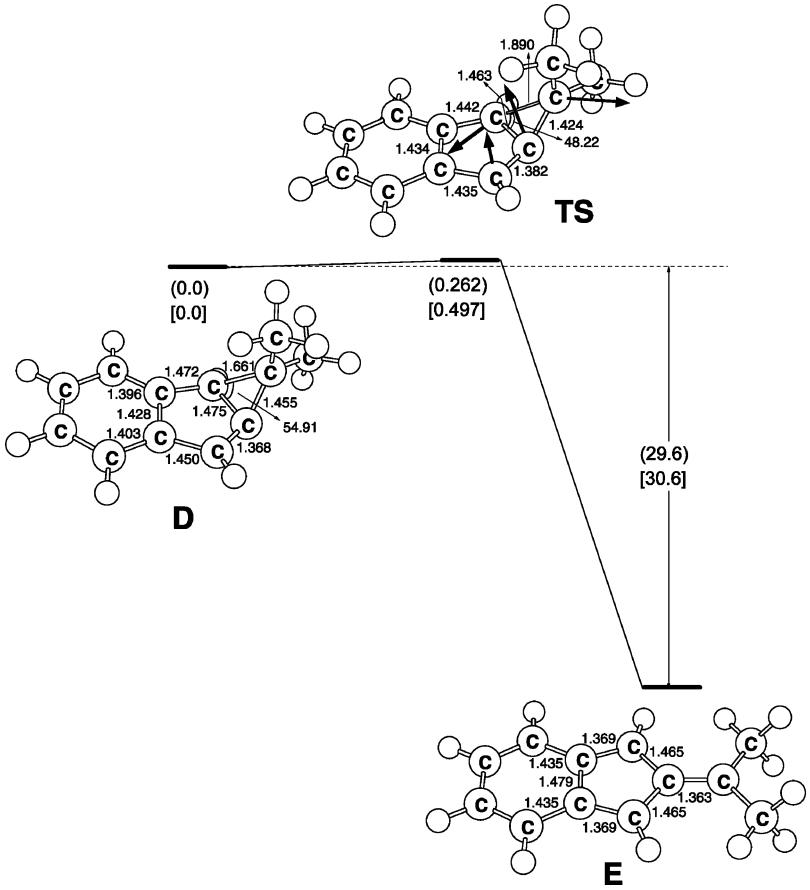
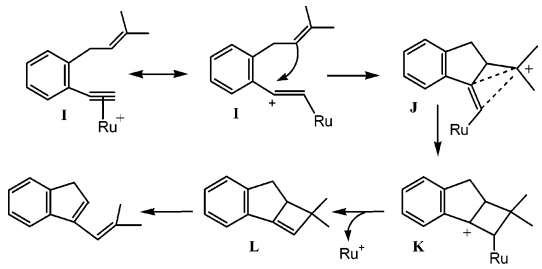


Figure 1. The B3LYP/6-311G** geometries (in Å and deg) for the stationary points in the rearrangement of species **D**. The heavy arrows indicate the main atomic motions in the transition state. The relative energies were obtained at 0 K (round bracket) and 298 K [square braket].

Scheme 7



consistent with our observations in Table 3. The ^{13}C and ^{2}H-labeling experiments (Schemes 3,4) reveal that the alkynyl deuterium and the ethenyl $^{13}C(1')$ carbon of *o*-(ethynyl)styrenes **2** are located equally at C(1) and C(3) carbons of indene **3a**. This character can be attributed to the two resonance forms **E**, which make their C1 and C3 carbons indistinguishable.

Scheme 7 shows the formation mechanism of 3-alkenyl-1*H*-indene with ruthenium-π-alkyne **I** as a reactive species. The proposed mechanism is analogous to those proposed by Fürstner on the $GaCl_3$[4] and $PtCl_2$[5] catalytic systems. 5-*Exo*-*dig* cyclization of intermediate **I** gives alkenylruthenium species **J**, and ultimately generates cyclobutene derivative **L** via nonclassical ion formation of benzyl cation **K**. The catalytic activity relies on the stability of tertiary carbocation **J**.

We have used density functional theory (DFT) to investigate the potential energy surface of the **D** → **E** (i.e., **D** → **TS** → **E**) transformation shown in Scheme 5. Figure 1 shows the relative energies of the stationary points for this process on the basis of the B3LYP/6-311G** level. The transition state (TS) along with the calculated transition vectors are also shown schematically. Our DFT results suggest that the activation energy for the **D** → **E** transformation is predicted to be only 0.50 kcal/mol with an exothermic enthalpy of −31 kcal/mol at 298 K. In contrast, the activation energy of the "6,6-dimethylbicyclo[3.1.0]hex-1-ene to 5-isopropylidenebicyclo[2.1.0]pentane" rearrangement had been calculated[18,19] to be 16.8 kcal/mol.[20] These results prove that the proposed "methylenecyclopropane-trimethylenemethane" arrangement **D** → **E** should be very feasible in both kinetic and thermodynamic aspects.

Conclusions

In summary, we have reported an atypical cycloisomerization of 2′,2′-disubstituted (*o*-ethynyl)styrenes to 2-alkenyl-1*H*-indenes. In this skeletal rearrangement, the C═C bonds of the starting enynes are completely cleaved and inserted by the terminal alkynyl carbon. On the basis of ^{13}C- and ^{2}H-labeling experiments, the mechanism is proposed to proceed through the following key steps: 5-*endo*-*dig* cyclization of ruthenium-vinylidene species, formation of a nonclassical carbocation, and the methylenecyclopropane-trimethylenemethane rearrangement.

Experimental Section

(1) General Sections. Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere in oven-dried glassware using standard syringe, cannula, and septa apparatus. Benzene, diethyl ether,

(20) For this rearrangement, we obtained a value of 15.0 kcal/mol with the same procedure, slightly smaller than that (16.8 kcal/mol) reported by Berson and co-workers.[19,20]

tetrahydrofuran, and hexane were dried with sodium benzophenone and distilled before use. $TpRuPPh_3(CH_3CN)_2PF_6$ (**1**) catalyst was prepared by heating $TpRu(PPh_3)_2Cl$ with $LiPF_6$ in CH_3CN.[21] 2-Bromobenzaldehyde and 2-bromo-1-iodobenzene were obtained commercially and used without purification. *o*-(2′-Trimethylsilylethynyl)benzaldehyde and *o*-(2′-trimethylsilylethynyl)bromobenzene were obtained by the Sonogashira coupling reaction of 2-bromobenzaldehyde and 2-bromo-1-iodobenzene with trimethylsilylacetylene, respectively.[22]

(2) Theoretic Calculation. The geometries and energetics of the stationary points on the potential energy surfaces of the migration reactions (**D** → **TS** → **E**) have been calculated with the DFT (B3LYP) method[23] in conjunction with the 6-311G** basis set.[24] All of the stationary points have been positively identified as equilibrium structures (the number of imaginary frequency (NIMAG = 0) or transition states (NIMAG = 1). All calculations were performed using the Gaussian 94/DFT package.[25]

(3) Typical Procedure for the Synthesis of 2′,2′-Disubstituted (*o*-Ethynyl)styrenes (2). To a THF solution (20 mL) of isopropyltriphenylphosphonium bromide (4.00 g, 10.4 mmol) at 0 °C was added *n*-BuLi (6.5 mL, 1.6 M, 10.4 mmol), and the mixture was stirred at 0 °C for 0.5 h. To this solution was added *o*-(2′-trimethylsilylethynyl)-benzaldehyde (2.02 g, 10.4 mmol), and the mixture was stirred at room temperature for 4 h. The solution was quenched with water and concentrated in vacuo. The organic layer was extracted with diethyl ether, dried over $MgSO_4$, and chromatographed (hexane, $R_f = 0.71$) over a silica column to give the olefination product as a colorless oil (1.47 g, 6.42 mmol, 63%). This silyl compound was then dissolved in THF (10 mL), added with Bu_4NF (1.0 M THF, 6.5 mL, 6.50 mmol), and the mixture was stirred at 26 °C for 8 h before the addition of water (10 mL). The solution was concentrated, extracted with diethyl ether, and chromatographed on a silica column (hexane, $R_f = 0.84$) to give enyne **2** (951 mg, 6.10 mmol, 95%) as a colorless oil.

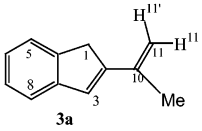
(4) Typical Procedure for the Synthesis of 1-(*o*-Ethynyl)-phenylprop-2-enes (34). A THF solution (20 mL) of *o*-(2′-trimethylsilylethynyl)bromobenzene (2.00 g, 7.90 mmol) was treated with BuLi (1.6 M, mL) at −78 °C for 30 min before addition of tetramethylethylenediamine (0.93 g, 8.0 mmol), and the mixture was stirred for an additional 20 min. To this solution was added 1-chloro-3-methylbute-2-ene (0.84 g, 8.0 mmol), and the mixture was stirred at −78 °C for 1 h before the temperature was slowly brought to 25 °C. The solution was concentrated, extracted with diethyl ether, and chromatographed on a silica column (hexane, $R_f = 0.88$) to give (trimethylsilylethynyl)-benzene (1.16 g, 4.81 mmol, 61%) as a colorless oil. This silyl compound was then dissolved in THF (10 mL), added with Bu_4NF (1.0 M THF, 4.9 mL, 4.9 mmol), and the mixture was stirred at 26 °C for 8 h before the addition of water (10 mL). The solution was concentrated, extracted with diethyl ether, and chromatographed on a silica column (hexane, $R_f = 0.86$) to give enyne **34** (0.79 g, 4.66 mmol, 97%) as a colorless oil.

(5) Experimental Procedure for Catalytic Cyclization. A long tube containing $TpRu(PPh_3)(CH_3CN)_2PF_6$ (**1**) (45.5 mg, 0.060 mmol) was dried in vacuo for 2 h before it was charged with enyne **2** (94 mg, 0.60 mmol) and benzene (1.0 mL). The mixture was heated at 80 °C for 18 h before cooling to room temperature. The solution was concentrated and eluted through a long silica column (hexane) to afford **3a** (63 mg, 0.41 mmol, 68%) and naphthalene **3b** (20.6 mg, 0.13 mmol), respectively; both were present as a yellow oil.

(6) Spectral Data for 1-Ethynyl-2-(2′-methyl-propenyl)benzene (2). IR (Nujol, cm^{-1}): 3311(s), 3008(s), 2119(s), 2239(m), 1650(w), 630(w). ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, $J = 7.2$ Hz, 1H), 7.16−7.34 (m, 3H), 6.53 (s, 1H), 3.29 (s, 1H), 1.97 (s, 3H), 1.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.0, 136.9, 132.7, 129.0, 128.2, 125.7, 123.5, 121.3, 82.6, 81.0, 26.6, 19.5. HRMS calcd. for $C_{12}H_{12}$, 156.0939; found, 156.0943.

(7) Spectral Data for Isopropenyl-1*H*-indene (3a). IR (Nujol, cm^{-1}): 3068(s), 2950(m), 1640(w), 1598(s), 1457(s), 1397(w), 946-(m), 768(m). ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, $J = 7.6$ Hz, 1H), 7.30 (t, $J = 7.6$ Hz, 1H), 7.23 (t, $J = 7.6$ Hz, 1H), 7.14 (d, $J = 7.6$ Hz, 1H), 6.75 (s, 1H), 5.23 (s, 1H), 4.99 (s, 1H), 3.57 (s, 2H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 145.2, 143.0, 139.5, 128.9, 126.4, 124.9, 123.5, 120.9, 112.9, 38.2, 20.4. HRMS calcd. for $C_{12}H_{12}$, 156.0939; found, 156.0933.

NOE-map of compound **3a**



3a

irradiation	enhancement (%)
H^1 (δ 3.57)	$H^{11'}$ (δ 5.23, 0.74%); H^5 (δ 7.37, 0.25 %)
	H^3 (δ 6.75, 0%)
H^3 (δ 6.75)	H^8 (δ 7.30, 0.23 %), Me (δ 2.05, 0.96 %)
	H^1 (0 %)

(8) Spectra Data for 1,2-Dimethylnaphthalene (3b). IR (Nujol, cm^{-1}): 3050(m), 1598(s), 1511(s), 1500(s), 1383(m), 1179(s), 771-(m), 530(s). ^1H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, $J = 8.0$ Hz, 1H), 7.84 (d, $J = 8.0$ Hz, 1H), 7.58 (d, $J = 8.0$ Hz, 1H), 7.49 (t, $J = 8.0$ Hz, 1H), 7.40 (t, $J = 8.0$ Hz, 1H), 7.24 (d, $J = 8.0$ Hz, 1H), 2.58 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.1, 132.7, 129.1, 128.9, 128.3, 127.7, 127.1, 126.4, 125.5, 124.4, 20.7, 14.4. HRMS calcd. for $C_{12}H_{12}$, 156.0939; found, 156.0931.

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Supporting Information Available: Synthetic procedure for ^2H- and ^{13}C-labeled samples of enyne **2**, NMR spectra and spectral data of compounds **2**−**46**, ^1H-NOE map of compounds **12a**−**13a**, **14b**, **27a**−**28a**, and **32a**, and ^1H, ^{13}C NMR and HMBC spectra of the ^{13}C- and ^2H-labeled **3a** and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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