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Ruthenium-Catalyzed Aromatization of Aromatic Enynes via the 1,2-Migration of Halo and Aryl Groups: A New Process Involving Electrocyclization and Skeletal Rearrangement

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Electrocyclization of aromatic enynes can be achieved by a metal-catalyzed reaction via the generation of a metal vinylidene intermediate (Scheme 1, eq 1).[1,2] Merlic and Pauly first reported[1] the aromatization of dienyl alkynes using a $RuCl_2$(*p*-cymenes)PPh_3 catalyst. Iwasawa and co-workers[2a] achieved similar results with $W(CO)_5$(THF) catalyst. This tungsten catalyst also effected the electrocyclization of *o*-(iodoethynyl)styrenes to give iodo-substituted naphthalene,[2b] and the mechanism is thought to involve tungsten-iodinated vinylidene intermediates. On the basis of this principle, the metal-catalyzed aromatization of *o*-(ethynyl)phenyl ketones[3] and aldehyde[4] has recently been developed to give useful oxygen-containing compounds. Surprisingly, none of these catalytic reactions is accomplished by cationic metal complexes, which may lead to a novel skeletal rearrangement in electrocyclization via the generation of reactive carbocation intermediates.[5] In this report, we describe the cleavage of carbon−carbon and carbon−halide bonds in the aromatization of *o*-(ethynyl)styrenes using a cationic ruthenium complex. Notably, the regiochemistries for the 1,2-shifts of aryl and halo substituents are completely different (Scheme 1, eq 2).

We first examined the catalytic transformations of various *o*-(ethynyl)styrenes with $TpRu(PPh_3)(CH_3CN)_2PF_6$ (10 mol %) catalyst[6] to study the structural effects of the substrates. The results are summarized in Table 1. As shown in entries 1−3, this catalyst effected the aromatization of monosubstituted, 1′,2′- or 1′,1′-disubstituted, and 1′,1′,2′-trisubstituted styrene derivatives **1**−**4** to naphthalene derivatives **6**−**9** (>88% yields) without migration of the styryl substituent. This method is also applicable to the cyclization of 2′-iodovinyl derivative **5** (*E*/*Z* =1.1),[7] but with a remarkable 1,2-shift of the iodo-substituent to the terminal alkyne carbon, based on the results with a deuterated sample *d*-**5a**. A similar phenomenon is observed for the 1,2-bromo shift based on the cyclization of a deuterated sample *d*-**5b**, but the yield of 3-bromonaphthalene *d*-**10b** is low (30%).

We prepared various 2-(2′-iodoethenyl)ethynylbenzenes to examine the generality of this cycloisomerization. The halide species **11a**−**17** contain a mixture of *Z* and *E* (*E*/*Z* = 1.5−1.0) isomers.[7] Most of the samples were prepared in deuterated form to confirm the 1,2-shift. Entries 1−4 show the suitability of this reaction with a change in the *para*-phenyl substituents (R = OMe, ^{t}Bu, Me, F), with the methoxy group being the most effective. The relative positions of the deuterium, iodo, and methoxy groups of product **18a** were confirmed by ^{1}H NOE spectra.[8] Such an iodo shift works well not only for *meta*-methoxy, 3,4-(methylenedioxy), and 3,4-dimethoxyphenyl groups **12**, **13**, **14b** (entries 5, 6, and 8), but also for dienyl alkyne derivatives **15** and **16** (entries 9, 10). A low yield (40%) of naphthalene **21a** was obtained for the bromo shift (entry 7). For 1-ethyl-2-iodovinyl species **17**, two naphthalenes **24a** and **24b** were obtained in equal proportions, resulting from nonmigration and 1,2-migrations pathways, respectively.

Scheme 1

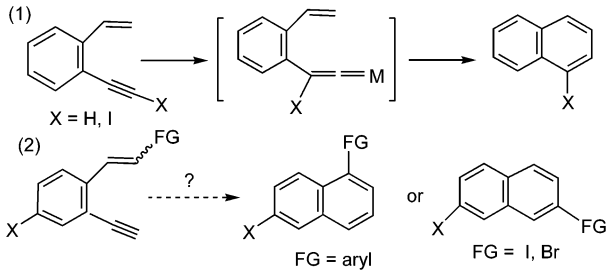

Table 1. Aromatization of Various *O*-(Ethynyl)styrenes

substrates	products a,b	substrates	products
(1) **1**	**6** (95%)	(3) **3** R = H, **4** R = Bu	**8** R = H (92%), **9** R = Bu (87%)
(2) **2** X = H, **d-2** X = D	**7** X = H (88%), **d-7**, X = D (91%)	(4) **5a** X = H, Y = I[c], **d-5a** X = D, Y = I, **d-5b** X =D, Y = Br	**10a** X = H, Y = I (80%), **d-10a** X = D, Y = I (83%), **d-10b** X =D, Y = Br (30%)

[a] 10 mol % catalyst, [substrate] = 0.05 M in toluene, 110 °C, 6−8 h. [b] Yields were reported after separation from the silica column. [c] A mixture of *Z*/*E* isomers was present for **5a**, *d*-**5a**, and **5b**.

We also observed a 1,2-aryl shift for the aromatization of various 2-(2′-aryl-vinyl)ethynylbenzenes even though the parent compound *d*-**2** failed to show such a phenomenon (Table 1, entry 2). As shown in Table 3 (entries 1,2), the 2′-aryl group preferably underwent a 1,2-shift to the 1′-vinyl carbon rather than the terminal alkyne carbon. The NMR spectral data of naphthalene derivatives **32A** and **32B** are identical to those of authentic samples prepared from independent routes.[9] This shift is favored by electron-donating groups mainly on the migrating aryl R group and less on the *para*-phenyl substituent X according to the results in entries 1−7.

We prepared deuterated samples *d*-**14b** and *d*-**31** to better understand the mechanism of migration. As shown in Scheme 2, the 1′-vinyl proton of compound **14b** remains unshifted, whereas the alkynyl proton undergoes 1,2-migration to the internal alkynyl carbon (entries 1−2). In contrast, the 1′-vinyl proton of compound **31** undergoes 1,2-migration to its 2′-carbon (entry 3), whereas the alkynyl proton migrates to the internal carbon (entry 4). We finally prepared a ^{13}C-containing sample **31** which has 10 atom % enrichment at the =*C*HPh carbon. Notably, the ^{13}C NMR spectrum of the resulting product **38A** shows the enrichment at δ 140.0 that is assigned to be the quarternary *C*Ph carbon according to ^{13}C−^{1}H HMBC spectra.

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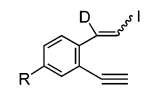
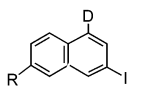
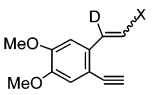
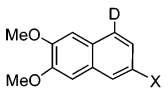
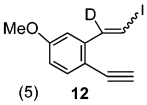
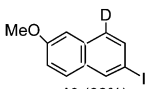
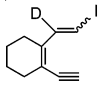
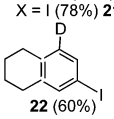
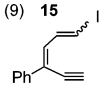
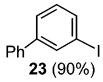
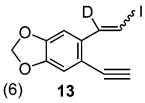
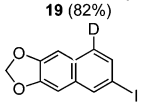
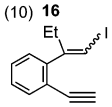
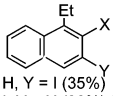
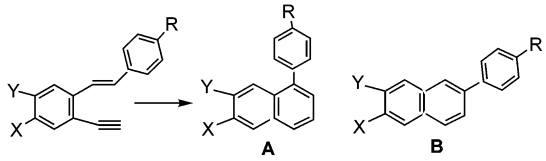
Table 2. Aromatization of 2-(2′-Iodovinyl)ethynylbenzene

substrates	products[a,b]	substrates	products
 (1) R = OMe **11a** (2) R = ^{t}Bu **11b** (3) R = Me **11c** (4) R = F **11d**	 R = OMe **18a** (82%) R = ^{t}Bu **18b** (72%) R = Me **18c** (68%) R = F **18d** (65%)	 (7) X = Br **14a** (8) X = I **14b**	 X = Br (40%) **21a** X = I (78%) **21b**
 (5) **12**	 **19** (82%)	 (9) **15**	 **22** (60%)
 (10) **16**	 **23** (90%)		
 (6) **13**	 **20** (80%)	 (11) **17**	 X = H, Y = I (35%) **24a** X = I, Y = H (38%) **24b**

[a] 10 mol % catalyst, [substrate] = 0.05 M in toluene, 110 °C, 6−8 h. [b] Yields were reported after separation from the silica column.

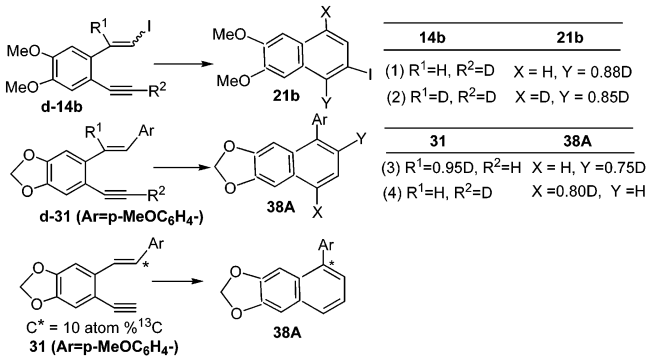
Table 3. 1,2-Aryl Shift for 2-(2′-Arylvinyl)ethynylbenzene



substrates	products (yields)[a,b]
(1) X = Y = H, R = Me (**25**)	**32A** (35%), **32B** (35%)
(2) X = Y = H, R = OMe (**26**)	**33A** (60%), **33B** (15%)
(3) X = OMe, Y = H, R = Me (**27**)	**34A** (54%), **34B** (18%)
(4) X = OMe, Y = H, R = OMe (**28**)	**35A** (64%), **35B** (6%)
(5) X = Y = O−CH_2−O, R = H (**29**)	**36A** (18%), **36B** (56%)
(6) X = Y = O−CH_2−O, R = Me (**30**)	**37A** (61%), **37B** (15%)
(7) X = Y = O−CH_2−O, R = OMe (**31**)	**38A** (73%), **38B** (trace)

[a] 8 mol % catalyst, [substrate] = 0.05 M in toluene, 110 °C, 6−8 h. [b] Yields were reported after separation from the silica column.

Scheme 2

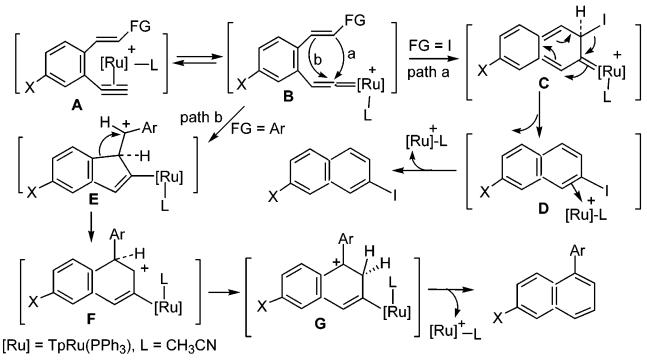


14b	21b
(1) R^1=H, R^2=D	X = H, Y = 0.88D
(2) R^1=D, R^2=D	X =D, Y = 0.85D

31	38A
(3) R^1=0.95D, R^2=H	X = H, Y =0.75D
(4) R^1=H, R^2=D	X =0.80D, Y =H

A plausible mechanism (Scheme 3) involves an equilibrium[3,10] between ruthenium−alkyne complexes **A** and ruthenium−vinylidene species **B**. Electrocyclization of species **B** via a 6-*endo-dig* pathway (a) gives ruthenium naphthylidene species **C** which subsequently undergoes a 1,2-iodo shift to give ruthenium-η^2-naphthalene **D**, ultimately producing the expected product and active ruthenium species. The mechanism in the transformation of species **C** to **D** is analogous to the classical conversion of a methyl substituted carbene to a metal-olefin species.[11] On the basis of ^{2}H- and ^{13}C-labeling results, we propose that a 1,2-aryl shift arises from the 5-*endo-dig* electrocyclization (pathway b) of species **B** to give ruthenium fluorenyl species **E** which bears a benzyl cation to induce

Scheme 3



a 1,2-shift of a carbon−carbon bond to generate intermediate **F**. Notably, a loss of deuterium content of naphthalene **38A** (75%) was observed as compared to its starting compound *d*-**31** (95%). This information suggests that species **F** undergoes a 1,2-hydride shift to give the more stable diphenyl methyl cation **G**. Dissociation of a proton from species **G**, followed by cleavage of the ruthenium−naphthyl bond, produces active ruthenium species and naphthalene product.

In summary, we have reported unusual 1,2-iodo and aryl shifts in the electrocyclization of *o*-(ethynyl)styrenes.[12] Isotopic labeling experiments were performed to elucidate the reaction mechanism, and the results indicate that the 1,2-aryl shift arises from 5-*endo-dig* electrocyclization of a ruthenium−vinylidene species, whereas the 1,2-iodo shift follows a 6-*endo-dig* pathway.

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

Supporting Information Available: Experimental procedures, synthetic schemes and spectral data of compounds **1**−**38**, and ^{13}C NMR and ^{13}C−^{1}H HMBC spectra of ^{13}C-enriched sample **38A** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) The *E*/*Z* ratios of iodovinyl species in Table 2 are provided in the Supporting Information.
(8) ^{1}H-NOE map of compounds **18a** and ^{13}C−^{1}H HMBC and ^{13}C NMR spectra of ^{13}C-enriched **38A** are provided in the Supporting Information.
(9) The authentic samples **32A** and **32B** are prepared from Suzuki coupling of 4-methylphenyl boric acid with 1- and 2-naphthyl bromides, respectively.
(10) (a) Trost, B. M. *Acc. Chem. Res.* **2002**, *35*, 695. (b) Bruneau, C.; Dixneuf, P. *Acc. Chem. Res.* **1999**, *32*, 311. (c) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (d) Bustelo, E.; Carbo, J. J.; Lledos, A.; Mereiter, K.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **2003**, *125*, 3311. (e) Iwasawa, N.; Maeyama, K.; Kusama, H. *Org. Lett.* **2001**, *3*, 3871.
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(12) Our results indicate that the 1,2-iodo and phenyl shifts are not applicable to *o*-(ethynyl)styrenes bearing internal alkynes.

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