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W(CO)$_5$·THF-Catalyzed Electrocyclizations of Aromatic Enynes via Vinylidene Intermediates

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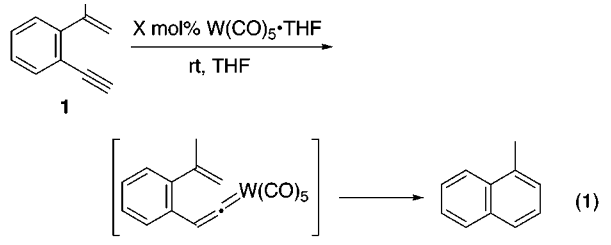
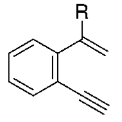
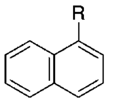
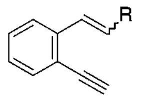
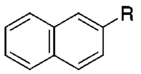
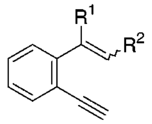
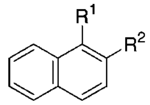
We previously reported a W(CO)$_5$·THF-catalyzed endo-selective cyclization of ω-acetylenic silyl enol ethers.[1] In this reaction, tungsten vinylidene intermediates are believed to be involved as reactive species. Recently, Merlic et al. reported the first example of the transition-metal-catalyzed electrocyclization of dienynes via ruthenium vinylidene intermediates.[2] As another way of utilizing the tungsten vinylidene intermediates,[3−5] we report a highly efficient synthesis of polyaromatics by the electrocyclization of aromatic enynes and related compounds promoted by a catalytic amount of W(CO)$_5$·THF.

As initial substrate, we chose the aromatic enyne **1**, a benzene ortho-substituted with an isopropenyl group and a terminal acetylene. When this was treated with a stoichiometric amount of preformed W(CO)$_5$·THF at room temperature, **1** disappeared within 1 day to give the expected α-methylnaphthalene (**2**) in 83% yield. The amount of W(CO)$_5$·THF could be reduced to 5 mol %, while still giving the cyclized product **2** and without lowering the yield. Although the reaction became slower, W(CO)$_5$(NMe$_3$) also promoted the cyclization.[6] However, when other group 6 metal carbonyl complexes were used for this reaction, it did not proceed smoothly, giving only a trace amount of the cyclized product **2** along with recovered starting material **1**.



2
100 mol%, 1 day, 83%
5 mol%, 4 days, 81%

Table 1. Synthesis of Naphthalene Derivatives

Substrates	Product(%)
 1 R=Me 3 R=COOMe 5 R=OTBS	 2 81% 4 84% 6 100%
 7 R=H^a 9 R=Me 10 R=COOEt^b	 8 68% No reaction No reaction
 7 11*Z* R^1=Me, R^2=COOEt (*Z*) 11*E* R^1=Me, R^2=COOEt (*E*) 13 R^1=OTBS, R^2=Me (*Z*) 15 R^1=Me, R^2=Me^b	 12 100% 12 88% 14 90% 16 31%

Conditions: A preformed 5 mol% amount of W(CO)$_5$•THF in THF (0.1 M) was added to the substrate. The mixture was stirred for 3-5 days. a) 30 mol% amount of the catalyst was used. b) 100 mol% amount of the catalyst was used.

As the electrocyclization of the aromatic enyne **1** was found to proceed in high yield using only a catalytic amount of W(CO)$_5$·THF, we next examined the generality of the reaction.

First, the effect of the electronic nature of a substituent at the α-position of the olefin was examined. The reactions of both α-methoxycarbonyl derivative **3** and α-siloxy derivative **5** proceeded at room temperature even with 5 mol % W(CO)$_5$·THF to give the corresponding naphthalene derivatives **4** and **6** in high yields.[7,8] This demonstrates that both electron-rich and electron-deficient olefins can be employed in this reaction and suggests that the reaction proceeds via 6π electrocyclization of the vinylidene intermediate.

We next examined the reaction of vinyl derivative **7** and those substrates with a substituent at β-position of the olefin (see Table 1). The reaction of the vinyl derivative **7** proceeded slowly and naphthalene **8** was obtained in 68% yield only by increasing the amount of the catalyst to 30 mol %. On the other hand, the reaction of β-methyl derivative **9** or β-ethoxycarbonyl derivative **10** resulted in recovery of the starting material even when a stoichiometric amount of W(CO)$_5$·THF was employed.

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[1] Maeyama, K.; Iwasawa, N. *J. Am. Chem. Soc.* **1998**, *120*, 1928.

[2] Merlic, C. A.; Pauly, M. E. *J. Am. Chem. Soc.* **1996**, *118*, 11319.

[3] For reviews on vinylidene complexes, see: Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. Bruce, M. I. *Adv. Organomet. Chem.* **1983**, *22*, 59.

[4] For the synthetic use of vinylidene intermediates of group 6 metals, see: (a) Quayle, P.; Rahman, S.; Herbert, J. *Tetrahedron Lett.* **1995**, *36*, 8087. (b) McDonald, F. E.; Schultz, C. C. *J. Am. Chem. Soc.* **1994**, *116*, 9363. (c) McDonald, F. E.; Zhu, H. Y. H. *Tetrahedron* **1997**, *53*, 11061. (d) McDonald, F. E.; Olson, T. C. *Tetrahedron Lett.* **1997**, *38*, 7691, and references therein.

[5] For the synthetic use of vinylidene intermediates of other transition metals, see for examples: (a) Trost, B. M. *Chem. Ber.* **1996**, *129*, 1313. (b) Bruneau, C.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1997**, 507. (c) Ohe, K.; Kojima, M.; Yonehara, K.; Uemura, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1823. (d) Tokunaga, M.; Wakatsuki, Y. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2867.

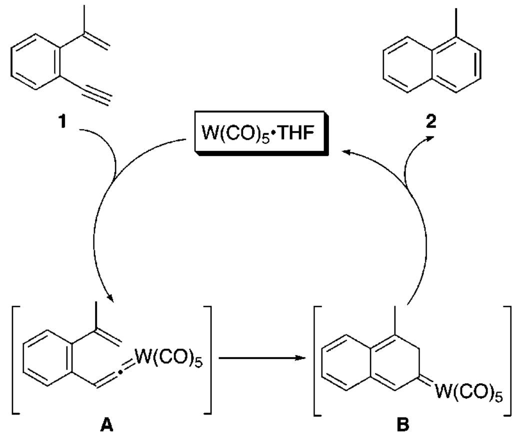
[6] The reaction of **1** with a stoichiometric amount of W(CO)$_5$(NMe$_3$) at room temperature for 2 days gave the product **2** in 55% yield along with recovered **1** in 33% yield.

[7] On the basis of the TLC analysis, the reaction of siloxy derivative **5** is a little faster than that of methoxycarbonyl derivative **3**.

[8] Merlic et al.[2] have reported that in their RuCl$_2$(*p*-cymene)PPh$_3$ catalyzed electrocyclization the reactions proceed smoothly when the electron density at the β-position of the olefin is high.

10.1021/jo981361o CCC: $18.00

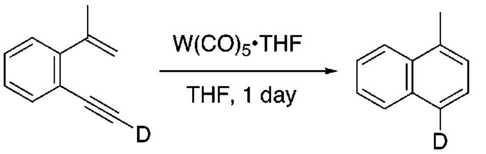
Scheme 1



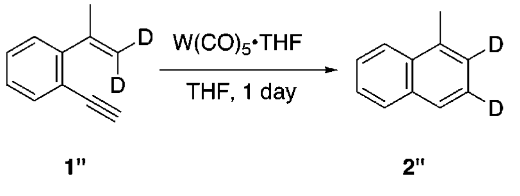
The difference in reactivity between α-substituted derivatives **1**, **3**, and **5** and β-substituted ones **9** and **11** suggests that a substituent at the α-position of the olefinic part is beneficial in this reaction. This α-substituent on the olefinic part would favor the conformation in which the olefinic double bond faces the acetylenic part due to steric repulsion between it and the latter. Additionally, the presence of a β-substituent would make the cyclization difficult due to steric repulsion between it and the approaching tungsten vinylidene moiety.

Finally, the reaction of α,β-disubstituted derivatives **11**, **13**, and **15** was examined. In these cases, the reaction mostly proceeded. For example, the reactions of α-methyl-β-ethoxycarbonyl derivatives **11*Z*** and **11*E*** and α-siloxy-β-methyl derivative **13** proceeded smoothly at room temperature with 5 mol % of W(CO)$_5$•THF. However, the reaction of α,β-dimethyl derivative **15** proceeded sluggishly to give the product in only 31% yield even with a stoichiometric amount of W(CO)$_5$•THF. Probably, the α-methyl group is not sufficiently bulky to counteract the steric hindrance due to the β-methyl group.

The mechanism of the reaction is thought to be as follows (see Scheme 1): treatment of **1** with W(CO)$_5$•THF would give an alkyne-W(CO)$_5$ π-complex, which gradually isomerizes to the vinylidene intermediate **A**; then 6π electrocyclization proceeds to give a carbene intermediate **B**, which gives **2** by 1,2-hydrogen migration with regeneration of W(CO)$_5$•THF. To confirm the mechanism, we carried out deuterium-labeling experiments.[2] When **1′** having a deuterium at the alkyne terminus was treated with W(CO)$_5$•THF, **2′** deuterated at the C4 position was obtained. This fact supports that the vinylidene intermediate **A** is produced by 1,2-migration of acetylenic hydrogen. When **1″** deuterated at both positions of the alkene terminus was treated with W(CO)$_5$•THF, **2″** deuterated at both C2 and C3 positions was obtained. This result suggests that intramolecular 1,2-hydrogen migration occurs from the carbene complex **B** to give the product.

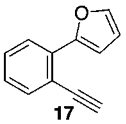
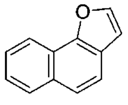
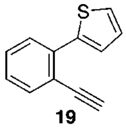
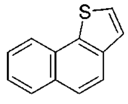
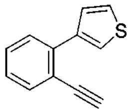
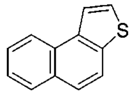
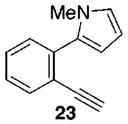
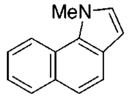


1'   2'   (2)



1"   2"   (3)

Table 2. Synthesis of Polyaromatic Compounds

Substrates	Product(%)	
 **17**	 **18**	82%[a)]
 **19**	 **20**	82%
 **21**	 **22**	99%
 **23**	 **24**	89%

Procedure: The reaction was carried out in the same manner as shown in Table 1. a) 100 mol% amount of W(CO)$_5$•THF was used.

We further applied this reaction to the synthesis of hetero-polyaromatic compounds (see Table 2). Substrates **17**, **19**, **21**, and **23**, benzenes ortho-substituted with an ethynyl and a heteroaromatic group such as furan, thiophene, and pyrrole, were treated with a 5 mol % amount of W(CO)$_5$•THF. In most cases, the desired cyclization proceeded smoothly to give the corresponding hetero-polyaromatics in good yields. Only in the case of furan derivative **17** was it necessary to employ a stoichiometric amount of W(CO)$_5$•THF to obtain the desired product **18** in good yield. It should be noted that such heterocyclic compounds, which sometimes suppress transition-metal-catalyzed reactions through coordination, can be tolerated in this reaction without problem.

In summary, we have developed an efficient method for the preparation of polyaromatic compounds by the W(CO)$_5$•THF-catalyzed 6π electrocyclization of aromatic enynes. This reaction should be of practical use due to the simple procedure and its wide generality.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM500 (500 MHz) or a Bruker DRX500 (500 MHz) spectrometer using CHCl$_3$ (^{1}H, δ 7.24) and CDCl$_3$ (^{13}C, δ 77.0) as internal standards. IR spectra were recorded on a Horiba FT-300S spectrometer. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-SX102A mass spectrometer operating at 70 eV. Flash column chromatography was conducted on silica gel (Merck Kieselgel 60 art. 7734), and preparative thin-layer chromatography (TLC) was carried out on silica gel (Wako gel B-5F). Tetrahydrofuran was distilled from sodium benzophenone ketyl.

Standard Procedure for Electrocyclization. A 0.1 M THF solution of W(CO)$_5$•THF was prepared by irradiation of a slurry of tungsten hexacarbonyl (141 mg, 0.4 mmol) in freshly distilled THF (4 mL) for 4 h with a high-pressure Hg lamp. A 5% molar amount of the above freshly prepared $W(CO)_5{\cdot}THF$ (0.1 M in THF solution) was added to a substrate, and the mixture was stirred for 3−5 days at room temperature under an Ar atmosphere. The reaction was quenched with pH 7 phosphate buffer, and the organic materials were extracted with ethyl acetate three times. The combined extracts were dried over $MgSO_4$. After removal of the solvent, the residue was purified by preparative TLC to give the corresponding cyclized product. Spectral data of the products **2**, **4**, **8**, and **16** coincided with those of the commercially available materials.

1-(*tert*-Butyldimethylsiloxy)naphthalene (6): IR (neat) 3302, 2931, 2858, 1626, 1473, 1306 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.32 (6H, s), 1.13 (9H, s), 6.89 (1H, d, $J = 7.6$ Hz), 7.34 (1H, t, $J = 7.8$ Hz), 7.46−7.49 (3H, m), 7.81−7.83 (1H, m), 8.21−8.23 (1H, m); ^{13}C NMR ($CDCl_3$) −4.2, 18.5, 25.9, 112.6, 120.9, 122.6, 125.1, 125.9, 126.1, 127.6, 128.0, 135.1, 151.7; HRMS calcd for $C_{16}H_{22}OSi$ 258.1419, found 258.1425.

Ethyl 1-Methyl-2-naphthalenecarboxylate (12): IR (neat) 3062, 2933, 1716, 1624, 1466, 1277, 1238 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.43 (3H, t, $J = 7.1$ Hz), 2.93 (3H, s), 4.42 (2H, q, $J = 7.1$ Hz), 7.52−7.57 (2H, m), 7.69−7.71(1H, m), 7.80−7.84 (2H, m), 8.17−8.18 (1H, m); ^{13}C NMR ($CDCl_3$) 14.4, 15.8, 61.1, 125.3, 125.8, 126.1, 126.5, 127.2, 128.3, 128.5, 132.9, 134.6, 136.8, 168.9; HRMS calcd for $C_{14}H_{14}O_2$ 214.0994, found 214.0993.

1-(*tert*-Butyldimethylsiloxy)-2-methylnaphthalene (14): IR (neat) 2960, 2931, 1599, 1385, 1255 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.06 (6H, s), 0.96 (9H, s), 2.41 (3H, s), 7.25−7.29 (1H, m), 7.39−7.49 (3H, m), 7.76−7.78 (1H, m), 8.07−8.08 (1H, m); ^{13}C NMR ($CDCl_3$) −3.1, 17.5, 18.7, 26.1, 121.3, 122.7, 123.0, 124.7, 124.9, 127.5, 128.2, 129.6, 133.6, 148.4; HRMS calcd for $C_{13}H_{15}OSi$ 215.0892 (M-*t*-Bu), found 215.0891.

Naphtho[1,2-*b*]furan (18):[9] IR (neat) 1510, 1392, 1321, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.90 (1H, d, $J = 2.0$ Hz), 7.47−7.49 (1H, m), 7.57−7.60 (1H, m), 7.65 (2H, s), 7.76 (1H, d, $J = 2.0$ Hz), 7.93 (1H, d, $J = 8.2$ Hz), 8.31 (1H, d, $J = 8.2$ Hz); ^{13}C NMR ($CDCl_3$) 107.6, 119.7, 120.0, 121.5, 122.9, 123.4, 125.0, 126.3, 128.3, 131.4, 144.1, 150.5.

Naphtho[1,2-*b*]thiophene (20):[10] IR (KBr disk) 3051, 1323, 1259, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.48 (1H, d, $J = 5.3$ Hz), 7.52 (1H, d, $J = 5.3$ Hz), 7.52−7.54 (1H, m), 7.58−7.61 (1H, m), 7.75 (1H, d, $J = 8.6$ Hz), 7.84 (1H, d, $J = 8.6$ Hz), 7.95 (1H, d, $J = 8.1$ Hz), 8.17 (1H, d, $J = 8.1$ Hz); ^{13}C NMR ($CDCl_3$) 122.0, 123.6, 125.0, 125.0, 125.2, 125.2, 125.5, 125.6, 126.6, 128.8, 129.0, 130.7, 137.3.

Naphtho[2,1-*b*]thiophene (22):[11] IR (KBr disk) 3067, 1263, 1113, 806 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.51−7.54 (1H, m), 7.58−7.62 (2H, m), 7.74 (1H, d, $J = 8.7$ Hz), 7.88 (1H, d, $J = 8.7$ Hz), 7.94 (1H, d, $J = 8.4$ Hz), 7.99 (1H, d, $J = 5.3$ Hz), 8.33 (1H, d, $J = 8.4$ Hz); ^{13}C NMR ($CDCl_3$) 120.6, 122.0, 123.6, 125.0, 125.2, 125.8, 126.4, 128.5, 129.3, 130.9, 135.9, 137.3.

Naphtho[1,2-*b*]-1-methylpyrrole (24): IR (KBr disk) 3057, 2971, 2916, 1504, 1354 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.29 (3H, s), 6.63 (1H, d, $J = 2.9$ Hz), 7.07 (1H, d, $J = 2.9$ Hz), 7.44−7.46 (1H, m), 7.52−7.56 (2H, m), 7.72−7.74 (1H, m), 7.97−7.98 (1H, m), 8.48−8.50 (1H, m); ^{13}C NMR ($CDCl_3$) 38.5, 102.1, 120.6, 120.9, 121.1, 123.3, 123.4, 125.1, 125.8, 129.0, 129.2, 129.9, 131.3. Anal. Calcd for $C_{13}H_{11}N$: C, 86.15; H, 6.12; N, 7.73. Found: C, 85.86; H, 6.19; N, 7.82.

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Supporting Information Available: Procedures for the preparation of the precursors of the cyclization. This material is available free of charge via the Internet at http://pubs.acs.org.

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